10 BREAKTHROUGH IDEAS IN ENERGY FOR THE NEXT TEN YEARS
Dear friends!

This is the third annual report of the Association. Here you will find the most advanced innovative energy ideas of the decade.

In the coming years, demand for affordable and reliable energy sources will continue to grow, while the trend for transition to low-carbon systems will remain.

Every country possesses its own margin of natural resources, cultural heritage, regulatory framework, and geopolitical features. Thus, we believe energy strategy for each nation to be individual, as well as the path towards sustainable development. It is essential to consider values, needs, and capabilities of all countries, most particularly of developing ones.

Sustainable development requires balance between the need to use natural resources rationally and providing access to affordable, reliable, and sustainable energy.

That is why the report traditionally highlights technologies that purify and enhance environmental friendliness of existing sources that for a long time will be inalienable for energy mix.

This year's edition included research on "Electric vehicles and supporting infrastructure", "Blockchain-powered micro grids", "Production of hydrogen from coal mine methane", "Zero and low-carbon ammonia shipping fuel", "Closed fuel cycle", "Direct-air-capture (DAC) of CO₂", etc.

Speaking about energy future, we think of those who will take on research and implementation of new energy technologies in the years to come. Thus, the chapter about modern methods and technologies to enhance safety and efficiency of hydrocarbon energy, prepared by the winners of Association's Young Scientist 4.0 programme hold a special place in the report.

I would like to emphasise that ideas and technologies presented in this edition have an enormous potential in energy and can influence our future.

Let your reading be interesting and insightful!

Deputy Prime Minister
of the Russian Federation
A. Novak
Around 90% of traded goods depend on the maritime transport sector as its main transportation mode and the OECD estimates maritime trade may increase three-fold volume-wise by 2050 [1]. In 2019, maritime trade volumes reached 11.08 billion tons according to UNCTAD, and while the COVID-19 pandemic that began in 2020 resulted in a volume decrease of 4.1%, recovery in 2021 should result in a 4.8% expansion in trade volumes, according to their latest report on maritime transport [2].

While maritime transport remains the most energy and cost efficient mode for movement of large volumes of goods all over the world (a breakdown of the types of goods transported in 2019 is presented in Figure 1.), the sheer size of this sector means that its associated emissions are still significant.

The International Maritime Organization (IMO) estimates that maritime transport GHG emissions totaled 1,076 Mt CO$_2$eq, or 2.89% of anthropogenic GHG emissions in 2018, with accompanying energy consumption of 9.1 EJ [3]. Current IMO “business as usual” (BAU) forecasts, taking into consideration future shipping demand, fleet composition and fuel mix indicates that 2050 CO$_2$ emissions could be 90-130% of baseline 2008 values (equivalent to 100-150% of 2018 values). These values agree with IEA BAU scenario estimates, which place 2050 CO$_2$ emissions by the maritime transport sector at 135% of 2018 values [4].

While the aviation sector, another ‘hard-to-decarbonise’ transport sector, has recently announced its goal to achieve industry-wide net-zero carbon emissions by 2050 [5], the maritime sector has yet to make such pledge. Although the maritime shipping industries in individual countries (e.g., Nordic countries, such as Denmark and Norway) have announced their carbon neutrality goals for 2050 [6], current IMO GHG emissions reduction targets still expect positive emissions from the sector in the medium term (i.e., 40% CO$_2$ reduction by 2030 and 70% CO$_2$ reduction by 2050, and up to 50% reduction of total GHG emissions by 2050, from a 2008 baseline), as illustrated in Figure 2.

Accelerating the decarbonisation of the maritime transport sector will require swift action from policymakers, industrial stakeholders, and technology developers, if goals in line with limiting the increase in global average temperature by the end of this century to 1.5°C relative to pre-industrial levels are to be met. Furthermore, if the IMO decides on the adoption of net-zero emissions targets by 2050, as seen in recent sectoral and national pledges [8], a portfolio of solutions is likely to be necessary in order to effectively decarbonise the maritime transport sector.

Among these solutions, adoption of decarbonised fuels (with associated development of fuel production, supply infrastructure and compatible propulsion systems) is the key to reducing direct emissions (Table 1). Currently, multiple decarbonised fuels, such as biofuels, electricity (i.e., e-fuels and battery/fuel cell systems), low-carbon hydrogen (and its derivatives, such as ammonia and methanol), are still under consideration and remain promising options. Among these, hydrogen, and ammonia in particular, has emerged as promising candidates to serve as shipping fuels of the future. We therefore assess decarbonised ammonia as a shipping fuel in greater detail in the following sections.
The use of ammonia as an energy vector is proposed for use cases where energy density (i.e., amount of useful energy per unit mass and/or unit volume) is paramount, and where direct electrification presents a challenge due to the inherent handicaps of current battery technologies. Despite recent advances in battery technology for electrical energy storage, chemical energy storage remains orders of magnitude higher from an energy density perspective and thus represents a more viable option for heavy-duty and long-distance transport needs. Among potential chemical fuels, both carbon-containing and carbon-free molecules are considered for use as renewable fuels with the final classification depending on how they are produced.

According to the IEA Net Zero Emissions Scenario (NZE2050), by 2050 around one-third of hydrogen demand may stem from the production of hydrogen-based fuels such as ammonia, synthetic kerosene and synthetic methane. This transport-specific demand represents an increase from the current value of approximately 20 kt H\(_2\)/yr to more than 100 Mt H\(_2\)/yr by 2050 [10]. The expansion of use cases for ammonia beyond existing applications in the chemicals sector (primarily for fertilisers) is most notable in maritime transport (in particular long-distance shipping), where up to 45% of global shipping fuel demand could be met by ammonia in the NZE2050 scenario.

Ammonia is favoured for shipping applications as its energy density of 23 MJ/kg is comparable to that of fossil fuels, such as LNG (55 MJ/kg) and bunker fuel (i.e., heavy fuel oil, at 30-40 MJ/kg). Even though hydrogen itself has a much higher energy density per unit mass (142 MJ/kg), hydrogen’s volumetric energy density at ambient conditions is only 13 MJ/m\(^3\), which is just a fraction of heavy fuel oil’s volumetric energy density of 41,500 MJ/m\(^3\) [11]. Liquefaction of hydrogen to achieve a volumetric energy density of 10,039 MJ/m\(^3\) requires cooling hydrogen to a temperature of -253°C and this comes at a significant energy cost. Ammonia, on the other hand, can be liquefied by cooling it at atmospheric pressure to -33°C. The resulting liquid has a volumetric energy density of 15,600 MJ/m\(^3\) making ammonia more suitable than hydrogen for applications that require high volumetric energy density, such as shipping fuel [12].

### TECHNOLOGY

<table>
<thead>
<tr>
<th>Fuel candidate</th>
<th>Maximum GHG reduction potential (%)</th>
<th>Current fuel cost ($/GJ)</th>
<th>Carbon cost-effectiveness ($/t_\text{CO}_2)</th>
<th>Compatibility with existing propulsion systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG</td>
<td>10%</td>
<td>7.1</td>
<td>340.1</td>
<td>Requires gas-fed or dual-fuel engine and associated cryogenic storage</td>
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<td>Bio-LNG</td>
<td>169%(^{a})</td>
<td>113</td>
<td>49.5</td>
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<tr>
<td>Methanol</td>
<td>92%</td>
<td>28.7</td>
<td>305.3</td>
<td>Not drop-in, compatible with ICE with retrofits</td>
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<tr>
<td>Ammonia</td>
<td>79%(^{a}) / 100%(^{b})</td>
<td>31.9</td>
<td>400.5</td>
<td>Compatible with ICE (spark ignition coupled with hydrogen, or dual-fuel with pilot diesel)</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>95%(^{a}) / 100%(^{b})</td>
<td>89.2</td>
<td>1,028.7</td>
<td>Compatible with ICE (spark ignition or dual-fuel with pilot diesel), requires compressed or cryogenic storage</td>
</tr>
<tr>
<td>FAME</td>
<td>84%</td>
<td>17.0</td>
<td>174.0</td>
<td>Drop-in (blended &lt;20% FAME into fossil HVO)</td>
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<tr>
<td>Bio-HVO</td>
<td>91%</td>
<td>17.2</td>
<td>163.3</td>
<td>Drop-in (blended or neat)</td>
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</tbody>
</table>

Note: \(^{a}\): negative emissions are possible assuming use of bioenergy with carbon capture and storage (BECCS) during production; 
\(^{b}\): assuming biological pathway is used; 
\(^{c}\): assuming chemical synthesis pathway with renewable or carbon-neutral electricity; 
LNG: liquified natural gas; 
FAME: fatty acid methyl esters; 
HVO: heavy fuel oil; 
ICE: internal combustion engine

Table 1 summarises the main attributes of low-carbon shipping fuel alternatives currently explored for adoption by the maritime transport sector.
Industrial production of ammonia is an established process dating back to the early 20th Century. The most widely adopted and technologically mature production pathway is the Haber-Bosch process, in which pure nitrogen gas (N₂) is combined with hydrogen gas (H₂) in a reactor in the presence of a catalyst under high temperature and pressure conditions. This is an exothermic (i.e., energy producing), thermodynamically favourable reaction, represented by the following net equation:

\[
N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta G = -33 \text{ kJ mol}^{-1}
\]

In reality, the main reactions involved in ammonia production, combustion and fuel cell use are summarised below [18].

**Traditional Haber-Bosch ammonia synthesis:**

\[
6H_2O + 2N_2 \rightarrow 4NH_3 + 3O_2
\]

**Renewable ammonia synthesis:**

\[
4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2
\]

**Ammonia combustion (use in internal combustion engines, ICE):**

\[
4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2
\]

**Ammonia splitting (use in fuel cells):**

\[
2NH_3 \rightarrow 3H_2 + N_2
\]

The focus on ammonia as shipping fuel stems from its lack of CO₂ emissions when combusted as a fuel in propulsion engines. However, it is important to emphasise the need to account for whole value chain emissions in the production of ammonia, as otherwise associated CO₂ emissions are merely moved upstream towards the point of fuel production. The nitrogen gas for ammonia is usually sourced from the atmosphere using an air separation unit (ASU), the hydrogen reactant has traditionally been produced using conventional fossil sources. Around 95% of ammonia production worldwide is reliant on fossil fuels with 72% of global ammonia production originating from hydrogen produced from natural gas via steam methane reforming (SMR) and 22% of global ammonia production originating from hydrogen produced from coal gasification (where China is the major producer via this pathway) [19]. The hydrogen produced from natural gas reforming is often referred to as grey hydrogen whereas the hydrogen produced from coal is referred to as black depending on the source of coal. Lower-carbon, and even zero-carbon, ammonia production may be achieved by adoption of low-carbon and renewable energy sources to supply energy for air separation, heating, filtration and purification and the use of blue hydrogen (i.e., grey, brown or black hydrogen coupled with CCUS), green hydrogen (i.e., water electrolysis using renewable power), turquoise hydrogen (i.e., methane splitting via pyrolysis) or pink hydrogen (i.e., water electrolysis using nuclear power). Low-carbon hydrogen, which in the context of this work includes zero-carbon hydrogen, can also be produced via the organic fraction of municipal solid waste (OF-MSW), from wastewater treatment plants (WWTP), or via bioelectrochemical systems, such as microbial electrochemical cells (MEC). Currently, however, such bio-based ammonia synthesis pathways are not primary contributors to industrial ammonia industrial production.

Thus, the main alternatives for industrial ammonia production tend to be separated by the "colour" of hydrogen used in the Haber-Bosch synthesis: green hydrogen, from renewable energy sources, leads to the so-called "green ammonia", while blue hydrogen from fossil sources coupled with carbon capture, utilisation and storage (CCUS) technologies leads likewise to "blue ammonia".

**TABLE 2. Comparison of main low-carbon fuel alternatives for use in maritime shipping.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hydrogen</th>
<th>Ammonia</th>
<th>Methanol</th>
<th>Biomethane</th>
<th>LNG or Bio-LNG</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content (wt %)</td>
<td>0</td>
<td>0</td>
<td>37.5</td>
<td>74.8</td>
<td>(\approx 75) (90-99% CH₄)</td>
<td>86.9 (Cₕ₋₁₀ range molecules)</td>
</tr>
<tr>
<td>Density at (15^\circ)C (kg/m³)</td>
<td>0.08 (1 bar)</td>
<td>0.72 (1 bar)</td>
<td>794.6</td>
<td>422.5a</td>
<td>431 to 464⁴</td>
<td>833 to 881</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-253</td>
<td>-33</td>
<td>64.5</td>
<td>-161.5</td>
<td>-160</td>
<td>163 to 399</td>
</tr>
<tr>
<td>Net heating value (MJ/kg)</td>
<td>142</td>
<td>23</td>
<td>20</td>
<td>50</td>
<td>55</td>
<td>42.5</td>
</tr>
<tr>
<td>Volumetric energy density (MJ/m³)</td>
<td>13 (ambient⁴)</td>
<td>5,600 (700 bar)</td>
<td>15,600 (liquefied, -33 °C)</td>
<td>16,000 (ambient⁴)</td>
<td>337.8 (ambient⁴)</td>
<td>3,000 (800 bar)</td>
</tr>
<tr>
<td>Propulsion technology</td>
<td>ICE (single-fuel)</td>
<td>Fuel cell (alkaline, alkaline membrane, hydrazine borane, ammonia borane and ammonia-fed solid oxide)</td>
<td>Hydrogen fuel cell (onboard conversion to hydrogen)</td>
<td>ICE (single or dual-fuel engines)</td>
<td>ICE (single fuel, conventional engine drop-in fuel)</td>
<td></td>
</tr>
<tr>
<td>TRL⁸</td>
<td>7 (ICE)</td>
<td>6 (ICE)</td>
<td>5-6 (ICE)</td>
<td>10+ (ICE)</td>
<td>10+ (ICE)</td>
<td>10+ (ICE)</td>
</tr>
</tbody>
</table>

**Note:** a: ambient conditions at standard temperature and pressure equal to 25°C and 1 bar; b: using methane boiling point; PEM: proton exchange membrane; HT-PEM: high-temperature PEM; FC: fuel cell; ICE: internal combustion engine; d: in case of onboard conversion to hydrogen, hydrogen fuel cell technologies are applicable; e: TRL values based on the extended scale by IEA for evaluation of Clean Development Technologies [13]. Adapted from [9-11,14-17]
These two varieties of low-carbon ammonia production are illustrated in Figures 2 and 3, respectively. While blue hydrogen production may utilise CCUS technologies, such as enhanced oil recovery (EOR) and/or synthetic hydrocarbon production (e.g., methanol synthesis) for the generation of other value-added products (Figure 3), the blue ammonia generated from this hydrogen feedstock would not be truly carbon neutral. If zero-carbon ammonia is the desired product, production via green hydrogen is necessary (in line with the “power-to-X” concept, Figure 4).

Both hydrogen and ammonia already have existing infrastructure in place for transmission, storage and distribution, as the former is currently used primarily in oil refining and petrochemical industries while the latter is one of the main products (at around 175 Mt/yr) of the chemical industry sector, particularly for use in fertiliser production [22]. While wider adoption of either energy vector for fuel applications would require further investments in dedicated infrastructure, the potential to convert or repurpose existing liquefied petroleum gas (LPG) propulsion technology and infrastructure for ammonia-based systems tilts the balance in favor of the latter option [23]. In addition, engines capable of combustion of ammonia blended with conventional hydrocarbon fuels (i.e., dual-fuel use engines) provide a transition pathway option where gradual replacement of conventional maritime fuels is possible [24,25].

Low-cost technologies for the production of green hydrogen remain the major obstacle for its widespread adoption, while blue hydrogen faces challenges in the economic feasibility of CCUS, particularly CO₂ storage. Further, the use of ammonia derived from low-carbon hydrogen as a shipping fuel must take into consideration trade-offs between decarbonisation alternatives, as demonstrated in Figure 5. While direct electrification of propulsion systems via renewable electricity coupled with energy storage could provide up to 80% energy conversion efficiency, the energy density of current battery technologies is not sufficient for large, long-haul ships, as cargo capacity would need to be reduced to allow for the substantial battery weight and volume requirements. In comparison to lithium-ion batteries, which have gravimetric energy densities of approximately 1 MJ/kg and volumetric energy densities approximately 2800 MJ/m³, low or zero-carbon ammonia has a gravimetric density of approximately 23 MJ/kg and a volumetric energy density, in the liquid state, of approximately 15,600 MJ/m³. Hence, ammonia would have a much smaller storage requirement and be a more suitable decarbonisation option for heavy fuel oil. Regarding the trade-offs between liquid hydrogen and liquid ammonia for use as shipping fuel, liquid ammonia has about a 55% higher volumetric energy density than hydrogen and can be liquefied at atmospheric pressure by cooling to -33°C whereas hydrogen requires cooling at atmospheric pressure to -233°C to achieve the liquid state. Hence, ammonia is altogether a more cost-effective fuel option.
The production costs of green ammonia remain a barrier for its wider adoption [26], as current estimates put its price at 480$/tNH₃ (around 1,080$/toe), based on a levelised cost of hydrogen of 3.0$/kg [27]. By 2030, the levelised cost of ammonia could fall to 350$/tNH₃ (around 790$/toe), and as low as 310$/tNH₃ (under 700$/toe) in certain geographical locations, such as Oceania [28]. Although bunker fuel commodity prices exceeded 600$/toe in late September 2021 [29] with the recovery of oil prices above 80$/bbl [30], fuel costs per ton and mile of cargo shipped are still higher for green ammonia relative to heavy fuel oil due to the fact that ammonia weighs twice as much and requires three times more space to contain the same amount of energy as heavy fuel oil. On a per unit energy content, the levelised cost of green ammonia would have to fall by more than 65% and approach 60-70$/MWh to match the cost range of maritime fossil fuels, which as seen in Figure 6 is not likely in the near term.

FIGURE 6. Production cost comparison and forecast projection between green ammonia (e-NH₃) and maritime fossil fuels.

ECONOMIC POTENTIAL

In evaluating the potential for zero and low-carbon ammonia for shipping fuel, a number of notable advantages and opportunities are evident:

**Established production of carbon neutral or low-carbon ammonia with broad benefits:** The production of fossil fuel-derived ammonia in the chemicals sector was responsible for around 406 Mt CO₂/yr in CO₂ emissions in 2018, larger than that of methanol production (at 211 Mt CO₂/yr) and of other high-value chemicals production (at 258 Mt CO₂/yr) [22]. The wide adoption of ammonia as a shipping fuel will require extensive deployment of renewable and low-carbon hydrogen production, or the environmental benefits from the adoption of ammonia by the maritime transport sector will not be realised. Nonetheless, such benefits extend beyond decarbonisation as the replacement of heavy fuel oil with ammonia is broadly beneficial to the marine environment (Table 3) [37,38].

### STANDARDS AND REGULATIONS

Industry standard setting bodies, such as the American Bureau of Shipping (ABS), have published in 2021 guidance documents for the design and construction of ammonia-powered vessels [32]. Other relevant documentation published in 2021 includes certification and notation class rule sets, e.g., by Bureau Veritas (“NR671 ammonia-fueled ships - tentative rules”) [33], RINA (“Ammonia as fuel” and class notation “Ammonia Ready”) [34], DNV (new notation covering ammonia as fuel, “Gas fueled ammonia”) [35], and Korean Register (“Guidelines for Ships Using Ammonia as Fuels”) [36].

These guidance documents are in line with safety standards such as the “International Code of Safety for Ships Using Gases or Other Low Flashpoint Fuels” (also known as the IGF Code) by the International Maritime Organization (IMO). It is also in line with other IMO efforts to promote sustainable development, such as the 1973 “International Convention for the Prevention of Pollution from Ships” (“MARPOL Convention”) and the sectoral GHG emissions reduction targets.

### PATH FORWARD

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In order to realise these benefits and opportunities, concerted actions are needed, particularly:

- **Infrastructure and propulsion technology retrofits**: The relative ease of retrofitting existing shipping-associated infrastructure for ammonia is a further opportunity, particularly when compared with the requirements for hydrogen infrastructure. This is due to scale (i.e., ammonia shipping infrastructure is more widely developed than that of hydrogen bulk shipping, in particular liquid hydrogen), technical (e.g., infrastructure for maritime shipping use of liquified petroleum gas, LPG, is similar to that needed for ammonia and may more readily be converted) and regulatory (i.e., although ammonia is considered a toxic chemical, safety regulatory frameworks are already in place for its use in the maritime transport sector, while equivalent regulations for hydrogen use are still being developed) [23,39].

- **Safety, performance and regulatory aspects**: Regarding challenges for use of ammonia as a shipping fuel, use in engines and for power production in general requires attention. Ammonia use in compression ignition engines is hindered by higher compression ratio requirements for ignition than current fuel oil. Overcoming this constraint is possible via use of ammonia with spark ignition engines or use of a pilot fuel with a lower ignition point. While the former is less desirable from a technical perspective due to inherent reliability issues with ammonia flammability characteristics, the latter is technologically achievable via in situ ammonia cracking for hydrogen production (which has a much wider ignition range and thus fits the role of a pilot fuel) [40]. Emerging technologies for use of ammonia to generate power include solid oxide fuel cells (SOFC) and direct combustion in gas/steam turbines, but energy efficiency yields (both work and thermal efficiency) are yet to match those of current combustion engines [41].

- **Continued investments in R&D**: Stakeholders in the shipping industry must commit to an ongoing effort to support R&D efforts on the development of renewable and low-carbon ammonia production systems. This effort is directly aligned with the development of the hydrogen economy, as whether electricity-based ammonia or fossil-based ammonia coupled with CCS are pursued, both pathways share multiple technologies with hydrogen production as an energy vector. In addition, further developments for ammonia-based fuel use can have direct implications in the development of use cases in stationary applications, such as grid-balancing and power systems. Thus, research efforts typically need to bring low- and mid-TRL technologies to market should be targeted, and include topics in the scaling up of technology pathways, design and implementation of transmission, distribution, and storage systems, as well as business models and policy and regulatory drivers to enable ammonia adoption in reasonable timeframes. Furthermore, potential synergistic opportunities with other end-use sectors, such as agriculture, terrestrial transport and chemicals industry must also be investigated, as industrial clusters can provide de-risking opportunities for new investments in ammonia projects [18].

- **Capital requirements for fleet replacements and technology investments**: In order to achieve wider adoption of ammonia use as a shipping fuel, current seagoing vessels will need to undergo retrofits or be replaced by ships powered by propulsion systems capable of dual-fuel use (i.e., blending of fuels for simultaneous combustion) or adapted ammonia use. Recent scenarios investigated by DNV put the total investment in the 250-800 billion dollars range, with peak investment as high as 60 billion $/yr between now and 2050 [17]. Furthermore, upstream investments would be necessary to ensure up to 8 TW of renewable energy production capacity, or 750 Mt CO₂/yr of CCS, for the production of sufficient green and blue ammonia, respectively, by the year 2050. In total, up to 2.4 trillion dollars might be needed to achieve net zero goals by 2050 for complete decarbonisation of the maritime sector, with 0.6 trillion dollars for ship efficiency interventions (e.g., drag reduction, exhaust treatment and power systems not including engine retrofits), 0.1 trillion dollars for operational efficiency interventions (in particular via digitalisation and big data analytics), and 1.7 trillion invested in alternative shipping fuels (mainly hydrogen and ammonia production, storage and transmission infrastructure, bunkering, onboard storage and engines and propulsion systems) [42]. Without increased efforts to develop and implement mechanisms to enable access to capital markets and infrastructure investment opportunities, the transition to ammonia as a decarbonised shipping fuel may not be possible given the large sums required.

- **Policy support and consumer expectations**: Clear and harmonised policy frameworks are necessary to support efforts by shipping companies to pursue emissions reductions via technology investments and adoption of low- and zero-carbon fuels. In particular, the establishment of appropriate carbon pricing mechanisms that avoid leakage across borders is paramount, as economic incentives for decision-makers are often an important nudge factor to overcome organisational inertia and unwillingness to innovate [43]. In addition, international companies whose movement of low-carbon ammonia production that is required to reduce costs for shipping fuel applications. Notable projects from shipbuilding companies are pursuing the use of ammonia-fuelled propulsion systems in Japan (e.g., Mitsubishi Heavy Industries [46], Nihon Shipyards [47] and Nippon Yusen Kaisha [48]) and Korea (e.g., Hyundai Heavy Industries [49] and Samsung Heavy Industries [50]), developed in partnership with major industrial stakeholders in European countries (e.g., A.P. Møller – Maersk, Wärtsilä, MAN Energy Solutions, ECONNECT Energy) and also in the chemicals sector (e.g., Yara International [51]).
The inherent advantages of low-carbon and carbon-free fuels for the decarbonisation of the maritime transport sector will only be achieved if low-carbon production pathways are used and full value-chain emissions are considered. Both hydrogen and ammonia seem poised for adoption as low-carbon fuels as production costs are driven down by technology innovations, wider industrial adoption and captive market demand and policy mechanisms that support harmonised pricing of CO2 emissions are adopted. In the maritime transport sector, ammonia appears to have an advantage over other low-carbon fuel options, as ammonia has good gravimetric and volumetric energy density and is largely compatible with existing shipping infrastructure.

While industrial efforts around the development of ammonia as a shipping fuel have surged in 2021, continued support for the development of ammonia production systems (both blue and green) and technology pathways is required. Alignment of the sector with other industrial activities where ammonia is relevant, as well as applications where it is used as a primary feedstock, may enable faster development of infrastructure while also serving to de-risk project investments. Finally, while regulatory efforts for use of ammonia as a shipping fuel are moving ahead, the maritime transport industry through its international representation and trade bodies, must ensure that its sectoral goals towards climate change mitigation move in tandem with ambitious climate change mitigation global targets towards at the global level.

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PEROVSKITE SOLAR CELLS

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INTRODUCTION

Climate changes make it necessary to search for alternative energy sources, more energy-efficient technologies and environmentally friendly materials. Solar energy is widespread, and meets the need for affordable and clean energy. They convert solar energy directly into electricity through the use of semiconductor materials that effectively absorb photons with energy exceeding their energy gap values and produce charge carriers. Then they pass through the device and are collected in an external circuit by applying reverse bias. Solution-processed organic-inorganic hybrid halide perovskite solar cells (PSCs) have rapidly evolved since the seminal work by Miyasaka et al. [4], who exploited organic-inorganic hybrid halide perovskites as sensitizers for visible-light conversion in dye-sensitised solar cells (DSSCs) achieving, however, a modest power conversion efficiency (PCE) of 3.8%. A great breakthrough was made in 2012 by the Graetzel [5] group that reported solar cells based on methylammonium (MA) lead trihalide perovskites with efficiencies >9%. Similarly to DSSCs, these devices included a mesoporous titanium dioxide (TiO₂) electron transport layer, therefore, termed meso-superstructured solar cells (MSSCs). At the same time, Snaith [6] group introduced the meso-superstructured solar cell architecture employing insulating mesoporous alumina as an inert scaffold for the perovskite film and further increasing the PCE to >12%. In the following years, the planar PSC architecture using a thin and compact perovskite absorber was introduced [7-15]. Advances in thin film deposition methods using either solution-processing [16] or thermal evaporation [17], allowed their PCEs to rapidly increased and reach the outstanding values reported to date. The fundamental understanding of the basic physical and chemical properties of the perovskite thin film and crystal surfaces, including topics such as electronic structure, crystal imperfections, surface termination and surface reactivity, has also enabled progress in materials and device engineering [18]. However, a common attribute of these solar technologies is their lack of sufficient evidence of their long-term stability that hinders their commercial viability. In particular, any new solar cell technology
must pass the IEC 61646 protocol of stability and lifetime before it becomes commercially available. This protocol includes testing standards, including thermal cycling and freeze tests, along with illumination and damp heat tests [19,20]. In addition, there are economic and marketing standards to be met known as ISOS protocols [21]. These include but are not limited to facile fabrication using low-cost materials and processes [22-23]. All these requirements can be met by judicious material design, sophisticated device engineering and suitable device packaging/encapsulation [24-25]. Intensive research efforts have been focused on interface engineering, the dimensionality and compositional optimisation of the perovskite active layer, and thin film deposition process parameters. Also, the developments of all-inorganic compounds for the perovskite absorber and for the interfaces, investigations of passivation materials and approaches that can reduce the surface, interface and bulk defects in perovskites have greatly affected the device performance and stability. These efforts have recently resulted in highly enhanced photovoltaic efficiency and improved long-term stability of PSCs that are now approaching maturity, which will soon enable their impressive market entry.

**DEVICE CONFIGURATIONS: MESOSCOPIC AND PLANAR N-I-P AND P-I-N SOLAR CELLS**

**Mesoscopic structure.** The first reported PSCs had adopted the mesoporous configuration of the dye-sensitised solar cells (DSSC) adapted from solid-state DSSCs in which the dye sensitisers has been replaced by the halide perovskite. These first demonstrations of PSCs were based on the archetypal 3-dimensional (3D) methylammonium lead iodide (MAPbI₃) perovskite and yielded PCEs between 6-10% [26,27], which were significantly improved to over 25% [28].

In a typical mesoscopic device architecture, a thin (~50 nm) compact layer of TiO₂ is coated on the fluorinated tin oxide (FTO) transparent conductive oxide (TCO), which serves as the electron selective contact on a glass substrate[28]. The mesoporous TiO₂ layer is then printed onto the compact layer to serve as the scaffold for the infiltration of the perovskite absorber as well as the electron transport layer (ETL) (also termed as the electron selective layer, ESL). After sintering at a high temperature (about 450°C), the deposition of the 300-600 nm thick perovskite absorber layer using either solution processing or vacuum deposition is accomplished. The device architecture (shown in Figure 1a) is completed by the deposition of a thin hole transport layer (HTL) (or else hole selective layer, HSL) capped with a metal electrode (usually gold (Au) or silver (Ag)). The working principle of these devices is based on the absorption of light by the perovskite absorber, generation of charge carrier pairs within the absorber layer, charge dissociation and separation, and charge transport to respective electrodes (Figure 1b) [29]. For high efficiencies, the perovskite absorber should possess an optimum bandgap of 1.55-1.6 eV and a high absorption coefficient (~10^5 cm⁻¹) so as a maximum portion of the visible light to be absorbed [30]. The transparent TCO and the charge transport layer coated on it should have negligible absorption in order to ensure that most incident light reaches the perovskite absorber where it produces photogenerated electron-hole pairs. These pairs are next dissociated into free charge carriers. The low exciton binding energy of perovskite absorbers (in the range of a few meV [31]) practically results in the generation of free charge carriers. This enables high-efficiency solar cell operation since there is no need for the application of external forces to separate the photogenerated electron-hole pairs [32]. The device performance is also affected by the efficient charge transport within the device layers and extraction towards respective electrodes. Charge selective layers that allow only one type of charge carriers to be extracted at each electrode are hence employed to influence interfacial recombination, charge accumulation and extraction, and consequently to determine the achieved photovoltaic parameters achieved in these devices.

**Planar structure.** In recent years, the regular planar (n-i-p) or inverted planar (p-i-n) PSC architectures have dominated due to its simplicity and high efficiencies already achieved. In these structures, the perovskite planar absorber is deposited directly either on the electron transport (n-i-p) or the hole transport (p-i-n) material (Figure 1c,d), which transport photogenerated charges towards the anode and cathode contact respectively [35,36]. As the mesoporous TiO₂ layer is omitted in these planar devices, they can be processed at a temperature below 150°C and therefore are advantageous for mass production.

The regular (n-i-p) planar architecture consists of a bottom transparent electron extracting contact (also termed as the anode), an n-type thin, compact ETL (or else ESL), the perovskite absorber layer, the p-type HTL (or else HSL) and the top metal cathode (which is the hole extracting contact). The most efficient devices are based on a tin oxide (SnO₂) instead of TiO₂, bottom ETL [37]. PSCs with the inverted p-i-n structure have a revere sequence of the ETL and HTL comparable to the regular n-i-p structure [38]. In these devices, the bottom HTL is either an organic p-type semiconductor or a p-type transition metal oxide such as tungsten, nickel and copper oxides (WOx, NiOx, CuOx); the latter enabled sufficient rise in efficiency but, most importantly, instability to ambient air [39-41]. Notably all these device architectures use metal contacts such as gold (Au) or silver (Ag) as the top electrodes [42,43]. However, carbon composite electrodes can offer an affordable, conductive alternative with abundant sources and blends of carbon black and graphite which are also chemically resistant towards oxidation/reactions, thus acting as protective by drop-casting the precursor solution through the printed carbon (C) layer, which served as the top cathode electrode [33]. Despite the fact that this device was free of hole transport layer, it yielded a PCE of 12.84% and good long-term stability. However, it is challenging to control the perovskite crystallisation in these devices due to the complicated structure of the triple-layer scaffold [34].

**FIGURE 1.** (a) Typical device architecture of mesoscopic perovskite solar cells. (b) Schematic of the working principle of perovskite solar cells. (c) The regular planar (n-i-p) PSC configuration where electrons are collected at the conducting substrate and (d) the inverted planar (p-i-n) architecture where holes are collected at the FTO substrate.
COMPOSITION AND DIMENSIONALITY OF PEROVSKITE MATERIALS

Composition of perovskite materials. Halide perovskites are materials of the general formula ABX₃, where A-site constitutes of monovalent cations such as organic methylammonium (CH₃NH₃, MA) and formamidinium (CH(NH₂)₂, FA) or an inorganic cation such as cesium (Cs) and rubidium (Rb). For B-site occupation, a heavy divalent metal such as lead (Pb) or tin (Sn) is applied and X is a halogen anion (i.e., Cl, Br, I). In this structure, X occupies the vertices in [BX₆] octahedral, which share corners in all three orthogonal directions to generate infinite 3D [BX₆] frameworks. The divalent B²⁺ are placed at the centers of these octahedral [46]. The smallest volume enclosed by neighboring octahedral defines a cuboctahedral cavity and hosts the monovalent cation A⁺. Different possible perovskite structures can be regarded as obtained by rotating or distorting the BX₆ octahedra, displacing the B²⁺ metal cations off-center and rotating the A⁺ cations within the cuboctahedral cavity. More than one structure is usually found for a perovskite material with a given chemical composition, depending on the temperature and preparation methods. For example, the archetypal MAPbI₃ perovskite undergoes phase transformations during cooling from cubic to tetragonal at the temperature of 54°C and from tetragonal to orthorhombic at -111°C (Figure 2a-c) [47]. To predict the crystal structure stability of halide perovskites, V. M. Goldschmidt introduced in 1926 the tolerance factor, α, which describes an estimate of the achieved lattice geometry by taking into account the ionic radii of various ions in the structure. The tolerance factor describes the size mismatches that a perovskite structure can tolerate through the formula:

\[ \alpha = \frac{r_A+r_X}{\sqrt{2}(r_B+r_X)} \]

with \( r_i \) being the radii of i = A, B and X ions in the perovskite ABX₃. It has been found that perovskite materials with a tolerance factor of \( \alpha = 0.9–1.0 \) are capable of forming an ideal cubic structure; those with \( \alpha < 0.6–0.9 \) usually form distorted perovskite structures (usually orthorhombic) consisting of tilted octahedra, while non-perovskite structures are formed when the tolerance factor is above 1 or below 0.8 (Figure 2d) [49]. The ideal cubic perovskite phase is also denoted as the α-phase and the phase with non-perovskite structures as the β-phase. Both the performance and stability of PSCs are highly connected with the formation of the black perovskite α-phase. Based on the above considerations, there are only limited possibilities for the A⁺ cations that enable tolerance factor values between 0.8 and 1 and stabilise perovskite structures, namely Cs⁺, CH₃NH₃⁺ (MA⁺), and HC(NH₂)₂⁺ (FA⁺) [50-52].

Composition plays a crucial role in determining the stabilisation of crystal structure and optoelectronic properties of the resultant material. For example, the archetypal MAPbI₃, although it stabilises to a black quasi-cubic phase upon post-annealing, it decomposes to PbI₂ when exposed to light or moisture; it is also decomposed during annealing at 85°C even in an inert atmosphere.

Finally, incorporation of traces of the small radius rubidium (Rb) (\( f_{\text{Rb}^+} = 152 \text{ pm} \) versus \( f_{\text{Cs}^+} = 167 \text{ pm} \)) has been recently found to stabilise the black phase of FA perovskites at room temperature. Whereas it is clear from the tolerance factor discussion above that Cs⁺ is the only elemental cation that it is large enough to sustain the perovskite structure, Rb⁺, despite not being suitable as a pure cation in perovskite compounds, hence offering the possibility for fully printable large area devices for facile incorporation in substrates of various schemes [44,45].

FIGURE 2. Crystal structures of the three different MAPbI₃ phases: (a) cubic, (b) tetragonal, and (c) orthorhombic phases. The crystal structures of the three phases differ by rotation of the inorganic octahedral cages. The critical temperatures of the phase transitions are marked on the temperature axis. (d) Correlations between tolerance factor and crystal structure of perovskite materials. (e) The calculated energy difference between α-phase and different δ-phases for FA, CsPbI₃, alloys with different Cs ratios.
it can still be integrated in small amounts into the mixed-cation structures [59]. Recent studies implied very small non-radiation recombination losses in mixed-cation perovskites with RB’ traces owing to very low bulk and surface defect density in these materials [60]. Moreover, it was observed that the charge transport within the RbCsMAFA perovskite layer is substantially faster than in CsMAFA, which is already much more defect-free than MAFA.

**Dimensionality of perovskite materials.**

Besides the widely studied three-dimensional (3D) perovskite structures, low dimensional such as two- and zero-dimensional (2D, 1D, 0D) perovskites have been recently synthesised and studied for their intriguing optoelectronic properties. Those with a 2D structure, also known as Ruddlesden–Popper (RP) layered perovskites, can be described by the formula $L_{2}\text{An-1BnX}_3\text{n+1}$. (a) The quantum well structure, formed by alternating mixed-cation structures [59]. Recent studies implied very small non-radiation recombination losses in mixed-cation perovskites with RB’ traces owing to very low bulk and surface defect density in these materials [60]. Moreover, it was observed that the charge transport within the RbCsMAFA perovskite layer is substantially faster than in CsMAFA, which is already much more defect-free than MAFA.

These perovskites generally exhibit superior structural stability arising from the strong van der Waals forces among the organic spacers [63]. Moreover, the large hydrophobic in nature organic ligands serve as buffer layers that protect the perovskite sub-layers from thermal and moisture initiated decomposition [65,67]. Notably, the organic spacers act as large energy gap quantum wells that prohibit migration which is a significant bottleneck in 3D counterparts (Figure 3b) [63,68]. However, this multiple quantum well structure of RP perovskites results in weaker visible absorption and lower charge carrier mobility compared to their 3D counterparts [69–71].

**FIGURE 3.** (a) Illustrative schematic of the crystal structure of different halide perovskite materials. Perovskites with the chemical formula ABX$_3$, RP perovskites with n=1. RP perovskite with n=2. The chemical formula of RP perovskites is $L_{2}\text{An-1BnX}_3\text{n+1}$. (b) The quantum well structure, formed by alternating semiconductor inorganic sheets with organic layers having a wider bandgap. (c) Schematic illustration of the proposed self-assembled 2D-3D perovskite film structure.

Moreover, they present higher exciton binding energies compared to 3D perovskites (in the range of 170–480 meV compared to 40–50 meV), which prohibits direct dissociation of excitons (the excitons in 2D are generally considered as the Wannier-type) to free carriers [72]. Therefore, photogenerated electron-hole pairs are strongly bound with Coulombic attraction in 2D perovskites [73]. This is why the so-called excitonic absorption can be easily observed in these perovskites even at room temperature. It appears as a sharp peak below the bandgap onset. In addition, the low carrier mobility of these perovskites due to the presence of the insulating organic spacers induces charge accumulation and non-radiative recombination at the interface of the conductor/insulator phases and hinders charge transport and extraction.

Because of these unfavorable characteristics, 2D perovskite-based solar cells lag behind in efficiency compared to their 3D counterparts by the interface of the conductor/insulator phases and hinders charge transport and extraction.

**DEPOSITION METHODS: VACUUM DEPOSITION, SOLUTION DEPOSITION AND PRINTING TECHNIQUES**

The structural and optoelectronic properties of perovskite materials are highly related to the procedure adopted for their preparation. This is because only high-quality films can enable the excellent intrinsic perovskite material characteristics to be fully exploited. A variety of deposition methods have been reported, which can be categorised into vacuum deposition and solution processes.

**Vacuum deposition.** With the vacuum deposition, the perovskite films are prepared by co-evaporation of two or more precursors (Figure 4a). The precursors are sublimated and travel freely from the source towards the substrate surface and deposited onto it. This method produces high-quality perovskite films and high efficiency PSCs [81]. It can be used for the deposition of layered thin films for the fabrication of multiple junction solar cells on top of large substrates [82]. However, it also requires the use of expensive vacuum facilities and increases the device fabrication cost.

The easiest way to employ the thermal chemical vapour deposition is by a one-step sublimation of the precursor materials on top of the desired substrate. However, this process requires careful adjustment of the quantities and sublimation rate of each reagent in order to achieve the desired stoichiometry of the perovskite film. Another possibility is to prepare the perovskite powder and use it instead of the precursors for sublimation [83]. This would allow better control over the stoichiometry of the thin film, which would affect its properties. In both cases, this method offers the deposition of extremely uniform and pinhole-free films of adjusted thickness all over the substrate area [84–86]. Besides co-evaporation of different precursors, sequential vaporization by using dual-source thermal evaporators is also
adopted. A major advantage of this sequential method is the full surface coverage and high crystallisation phase purity, as well as the highly smooth surface of the resultant perovskite films [86]. In spite of the exceptionally uniform films and the high reproducibility that this technique offers, the cost of the infrastructure required for the perovskite formation is a bottleneck for use in a larger scale.

Pulse laser deposition (PLD) is another vacuum deposition method in which the precursor material is subjected to a pulsed laser beam of high energy while being inside the high vacuum chamber. In this way, the laser vapourises the target material almost instantly, thus creating a plasma plume which is deposited as a thin layer onto the desired substrate. The substrate can be either perpendicular (on-axis deposition) or parallel to the plasma plume (off-axis deposition) (Figure 4b) [87]. The solid precursors can be kept at room temperature during the deposition and the plasma energy source is placed outside the vacuum chamber, making this method quite simple compared to other vacuum methodologies. At the same time, the superior quality of the crystalline layers could be attributed to the high energy of the impacting ions [88,89]. However, possible disadvantage of PLD could be the different vapourisation rate of each moiety, which in turn affects their deposition and the composition of the formulated film. For example, the organic moiety creates a smoother surface on the film, because of its easy volatisation through plasma, while the inorganic moiety has a different morphology due to a different forming path, thus creating inhomogeneous areas on the substrate. This is why the target material should not stoichiometrically but its organic part is in excess.

**FIGURE 4.** (a) Schematics of a dual-source evaporation for vacuum deposition of perovskite films. (b) On-axis and off-axis fabrication of thin films through PLD. (c) Schematic fabrication of perovskite (i.e., MAPbI₃) thin film through CVD.

In vacuum chemical vapour deposition (CVD), the volatile precursors that form the perovskite film are generated and then injected from the main gas flow into a quartz chamber under vacuum conditions. In the chamber, gas-phase reactions take place, forming intermediate products, which are then deposited on top of the substrates. The precursors are adsorbed onto the substrate surface, followed by diffusion of the reagents, nucleation and crystal growth, with the final result being the formation of the perovskite film. During the film formation, the precursors can either react or decompose. Any volatile byproducts formed during the reaction are desorbed and transferred to the main flow [90]. When the pressure conditions during the reaction are taken into consideration, the CVD techniques can be categorised as atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD) and ultrahigh vacuum CVD (UHVCVD). If the gas phase is taken into consideration, the technique can have as subcategories the metal-organic chemical vapour deposition (MOCVD), aerosol assisted CVD (AACVD), direct liquid injection CVD (DLICVD), and hybrid physical CVD (HPCVD) [91]. The easiest way of categorisation, however, is by one-step and two-step methodology.

During the one-step deposition, the organic and inorganic moieties in the gas phase are simultaneously injected into the vacuum chamber, are co-evaporated and adsorbed on the preheated substrate. This method is quite helpful since no secondary evaporation step is necessary and is a gas-only method. However, this method can also be applied in the case of mixed halide perovskites, producing pinhole-free films [92]. In this case, the differences in vapourisation time should be taken into consideration. In the case of the two-step deposition, each moiety is deposited separately on the preheated substrate. This method is more helpful since, over the final film thickness and stoichiometry [93,94]. The two-step chemical vapour deposition can also be combined with the metal-alloying technique in order to control the film morphology. The engineering of the alloy composition enhances the quality of perovskite films through large-sized grains in the uniform film.

**Solution deposition.** In the early attempts, solution deposition was sufficiently accomplished in a single step using a common solution of PbI₂ and MAI precursors (Figure 5a) [95]. However, the lack of suitable solvents that can dissolve both components and the high perovskite reaction rate resulted in large morphological variations and, therefore, to large deviations in the achieved efficiencies. In 2013, Grätzel and co-workers described a sequential deposition method for the successful infiltration of the perovskite pigment within the porous of TiO₂ film (Figure 4b) [96]. In particular, lead iodide (PbI₂) was first introduced via spin coating from solution into the nanoporous TiO₂ film and subsequently dipped to a solution of methyl ammonium iodide (MAI) to synthesise the resultant MAPbI₃ perovskite film. It was found that the conversion to perovskite occurred within the nanoporous oxide as soon as the two precursors came into contact, hence allowing for better control over the morphology and reproducibility of perovskite films.

The most widely used technique for the fabrication of PS Cs in the laboratory scale is spin-coating. It can be either a one-step or a two-step deposition method that is characterised as a solution-processing based one. The main advantages of this method are its simplicity, as well as its low cost. During the one-step process, the organic halides along with the metal halides are mixed with an appropriate solvent forming the precursor solution. Mostly apotic polar solvents are used, such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ-butyrolactone (GBL), 2-methoxyethanol (2-ME) and acetonitrile (ACN), which exhibit high boiling point and low vapour pressure when at room temperature. The solution formed is subsequently deposited on the substrate surface on top of the ETL in standard architecture solar cells. This substrate is placed on a spin-coater and spun at high rotational speeds for a couple of seconds so that the excess solvent evaporates. During the evaporation, the formation of the perovskite layers takes place, with crystals being formed and grown due to ionic interaction between metal cations and halogen anions. The substrate is then annealed at a temperature between 80 and 150°C for 10 minutes to 2 hours so that the rest of the solvent is removed. A similar technique to this is hot casting, during which the mixture of the organic and inorganic solutes is firstly heated at 70°C and subsequently deposited on an already heated substrate at 180°C (Figure 5c) [97]. The substrate is then put in a spin-coater and finally annealed on a hot plate, which leads to the development of millimetre-scale crystals. Drop casting is another solution-based deposition method for perovskite films [98]. The main advantages of this method is its low cost and ease of execution. During this method, the perovskite solution containing both the organic and the inorganic moieties is deposited into a substrate with the help of a pipette. This allows the substrate to be placed in a hotplate so that the solvent can be evaporated, thus forming the film. Nonetheless, the thickness, morphology and optoelectronic properties of the perovskite film are highly dependent on the concentration of the solution, its viscosity and the rate of evaporation of the solvent while on the substrate since no spinning is performed.
Vacuum and solution processes constitute two dominant fabrication techniques for perovskite films. Nevertheless, although vacuum-based environment processes, where the inorganic and organic components (i.e. PbX₂ and MAX, respectively) serve as the vapour source, provide high-quality films with respectable features, they also lead to time consuming deposition steps and costlier equipment. On the other hand, while the fabrication of a perovskite film via solution process appears as an alternative approach due to the simple concept that both materials can rapidly form from their solution phase reaction after annealing, undesired pinholes may occur across the whole film [98,99]. Thus, a different deposition technique is developed called Vapour Assisted Solution Process (VASP) that combines both processes’ advantageous characteristics [Figure 5d] [95,100], VASP is considered to be a modified two-step sequential solution deposition process in which the second step is replaced by a modified two-step sequential solution deposition process in which the second step is replaced by a gas-phase reaction. According to this technique, the evolution of the film starts with the construction of the inorganic framework of the perovskite material by a solution process and subsequently, an in situ reaction between the inorganic species and the desired organic vapours takes place, forming the perovskite film [101]. A crucial factor to the formation of the film is the source temperature that provides the appropriate vapour pressure so as not to damage or decompose the gaseous halides salts completely. The substrate temperature will also affect the dynamics of the perovskite formation. In other words, VASP exploits the kinetic reactivity of the organic vapour and the thermodynamic stability of perovskite during the growth process. Hence, the advantage this technique holds over pure vacuum and solution processing is the intercalation of the organic components into the inorganic framework through vapour, as it prevents the high growth rate of the perovskite material during the co-deposition of precursors as well as possible degradation of the inorganic framework upon dipping into an organic solution. Summarising, VASP can provide perovskite films with full substrate coverage, small surface roughness and well-defined grain sizes up to microscale.

Hydrothermal synthesis is also applied for perovskite films formation. It has emerged as a green technology for single crystal growth and metal leaching [102,103]. Hydrothermal synthesis is regarded the synthesis of substances by chemical reactions in a sealed, heated aqueous solution at an appropriate temperature (100–1000°C) and pressure (1–100 MPa) [104]. According to reaction temperature, hydrothermal synthesis is classified into two categories: subcritical and supercritical synthesis reaction. A subcritical synthesis reaction is carried out in the temperature range of 100–240°C, while supercritical synthesis reaction occurs for much higher temperatures. In addition, according to the vapour pressure of the main composition in the reaction, either low-pressure or high-pressure conditions can be employed to control the morphological features of the as-made materials. The uniqueness of this technique stems from the fact that any stable precursor used in the process can break at a relatively low temperature, thus preventing the extensive agglomeration that solid-state reactions generally cause under high sintering temperatures. Given the fact that hydrothermal synthesis permits rapid mixing of precursors for homogeneous products with controllable parameters, it has become one of the most preferable and adaptable chemical routes to prepare homogeneous perovskite films. Like hydrothermal synthesis, solvothermal synthesis is a solution reaction-based procedure used for perovskite deposition [105,106]. The difference between the two techniques is that instead of water, in solvothermal synthesis, the primary solvent is usually an organic one. The implementation of solvothermal synthesis, whereby an often homogeneous mixture of liquid and solid precursors are heated in a sealed reaction vessel close or above the boiling point of the main solvent, is particularly well known for the preparation of crystalline materials. Solvothermal synthesis constitutes a versatile alternative to calcinations for developing under milder temperatures metal-organic framework structures such as perovskites. Nevertheless, controlling crystal morphology in terms of particle shape and size is challenging when using solvothermal synthesis.

One of the most effective ways to form better crystals is by temperature tuning. Several approaches of synthetic protocols have been proposed for hybrid perovskites ranging from two-step processes to direct crystallisation. Although perovskites have the merit of being deposited from their precursors into a thin film by solution-based processes, it is rather difficult to gain control over the nucleation and crystallisation of the as-prepared film from a saturated solution. Several approaches of synthetic protocols have been proposed for hybrid perovskites ranging from two-step processes to direct crystallisation. Although perovskites have the merit of being deposited from their precursors into a thin film by solution-based processes, it is rather difficult to gain control over the nucleation and crystallisation of the as-prepared film from a saturated solution. Several approaches of synthetic protocols have been proposed for hybrid perovskites ranging from two-step processes to direct crystallisation. Although perovskites have the merit of being deposited from their precursors into a thin film by solution-based processes, it is rather difficult to gain control over the nucleation and crystallisation of the as-prepared film from a saturated solution. Several approaches of synthetic protocols have been proposed for hybrid perovskites ranging from two-step processes to direct crystallisation. Although perovskites have the merit of being deposited from their precursors into a thin film by solution-based processes, it is rather difficult to gain control over the nucleation and crystallisation of the as-prepared film from a saturated solution.
applied to an engraved printing cylinder and then it is coated onto the surface of the substrate through a precise coating head whereas in spray coating the precursor is moved across in-line with the surface, creating complex 2D patterns. In slot-die, the perovskite precursor is transferred from the surface that needs to be covered; the blade is moved across in-line with the surface, creating an impression roller. Unlike the other printing methods, gravure printing deposits and patterns the desired impression roller. In blade coating, the coating solution is placed for the fabrication of large-area perovskite modules (d) Illustration of the gravure printing technique. Finally, blade coating, slot-die coating, spray coating, and gravure printing can also be applied for the fabrication of large-area perovskite modules [111]. In blade coating, the coating solution is placed in front of a blade which is placed at a fixed distance from the surface that needs to be covered; the blade is moved across in-line with the surface, creating a perovskite film. In slot-die, the perovskite precursor is coated onto the surface of the substrate through a precise coating head whereas in spray coating the precursor is sprayed onto the substrate to deposit the perovskite film. In gravure printing, the ink is applied to an engraved printing cylinder and then it is placed on the substrate (Figure 6d). The printing process goes as follows: The printing cylinder, which has an engraved pattern, is filled with the perovskite ink and then it is placed on the substrate. In order to remove the excess ink from the inactive area of the printing cylinder, a doctor blade is often used. Then, the ink is transferred from the cylinder to the substrate by applying a specific pressure through the impression roller. Unlike the other printing methods, gravure printing deposits and patterns the desired layer at once, with high precision and resolution and in a short time. Also, this technique can also create complex 2D patterns.

Perovskite solar cells have achieved impressive performance due to progress made in the perovskite absorber and the charge transport and interfacial materials used in the device configuration. In fact, the interfaces between the perovskite film and the charge transport layers are among the most important factors that determine both the efficiency and stability of planar and mesoscopic PSCs [112]. The most critical aspects of such materials that govern the performance of the complete device include possible chemical interactions between those materials and perovskite absorber, the energy level alignment at the interfaces, the charge transport properties of the interlayers and charge recombination therein and so on. Various design strategies for the interfaces and the interfacial materials have been proposed and enabled efficient and stable device operation [113].

**Electron transporting materials.** The first PSCs adopted the mesoscopic structure where the perovskite absorber was infiltrated within the TiO2 mesoporous oxide that served as a scaffold as well as the electron transport layer (ETL), while also blocking the photogenerated holes from reaching the electron selective contact [114]. TiO2 exhibits high transparency, good electron mobility, well-matched energy levels with those of perovskite and ease of fabrication which render it an excellent choice for mesoscopic PSCs [115]. It appears in the anatase, brookite and rutile phases, dependent on the fabrication procedure, with the anatase to be the most effective amongst the three phases for application in PSCs [116]. However, the commonly used anatase phase generally possesses lower mobility compared with the rutile one [117], an implication leading to lower short-circuit current (JSC), although with higher open-circuit voltage (VOC), achieved in the anatase based devices. To increase the mobility of TiO2, doping with metal or halogen atoms has been widely adopted. Niobium (Nb), lithium (Li), magnesium (Mg), tin (Sn), zinc (Zn), yttrium (Y), zirconium (Zr), and molybdenum (Mo) have successfully been used as doping elements for the planar and mesoporous TiO2 ETL [118-122]. Moreover, graphene has been successfully used as a dopant for TiO2 due to the excellent electron transport capability of the former, which helps to improve the electron collection efficiency of the corresponding PSC [123]. In addition, surface modification of the ETL has also been applied to passivate surface defects and reduce interface recombination. Ultrathin interlayers of alumina (Al2O3) or titanium nitride (TiN) have been deposited with atomic layer deposition (ALD) and significantly improved the interface properties but also the optical and morphological properties of the perovskite absorber coated on top of it [124,125]. In addition, various organic materials such as amino acids [126], thiols [127], and fullerences [128], have been used as TiO2 modifiers facilitating the perovskite crystal growth and enhancing the device performance and long-term stability. Due to its higher electron mobility compared with TiO2, and low crystallisation temperature, zinc oxide (ZnO) is another widely applied ETL in PSCs [129]. Similarly to TiO2, doping and interfacial modification can further improve its properties to enable fast extraction rates in PSCs. For example, Al-doped (AZO), and nitrogen (N)-doped [131] ZnO nanorods exhibit reduced work function (WF) and improved electron transport compared to the undoped ZnO resulting in efficiency enhancement in PSCs. Furthermore, treatment with amino functionalised organic compounds has proven beneficial as it induced the formation of negative interfacial barriers thus reducing the electron extraction barrier towards the anode contact [132,133]. Tin oxide (SnO2) has been the most established ETL in planar PSCs with the regular architecture [134-138]. It exhibits high transparency in the visible range and favorable energy level alignment with the perovskite absorber. Doping of SnO2 has been proven beneficial for the stable operation of PSCs. For example, Al-doping reduces the recombination losses originating by the trap states present on the surface of pristine SnO2 and improves the PCE compared with the undoped ETL-based device [139]. Furthermore, lanthanide (Ln) ions have recently enabled significant performance boosts in perovskite devices using SnO2 ETLs doped with these materials. In particular, PSCs using yttrium (Y)-doped SnO2 layers presented high efficiency combined...
with negligible hysteresis, while the device with the undoped oxide presented inferior performance [140]. Furthermore, surface modification of SnO₂ using, for example, polyethylene glycol (PEG) resulted in improved morphology of the oxide layer and better performance of the resultant PSC [141].

Recently, several other metal oxides, ternary metal oxides and transition metal dichalcogenides have been demonstrated as promising materials for HTLs in PSCs. Among them, Spiro-OMeTAD (2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamine)-9,9-spirobifluorene) is the most commonly used [142]. It enables fast hole transport under the requirement of sufficient doping to increase its low conductivity. This can be accomplished by using additives in the pristine solution, with the most common to be TBP (4-tert-butylypyridine) and Li-TFSI (lithium bis(trifluoromethylsulfonyl)imide) [146]. However, Spiro-acridine-fluorene and methoxy-O-Me substituted (in the para-, meta- and ortho- positions) Spiro-OMeTAD derivatives have demonstrated efficient device performance with no requirements for additional doping [147]. Moreover, thiophene-based materials have proven efficient HTLs due to their high electron mobility as revealed from steady-state and time-resolved photoluminescence measurements [148]. In addition, organic compounds using thiens(3,2-b) thiophene conjugated moieties or π-conjugated thiophene bridges attained enhanced PSC performance, even higher than that of the Spiro-MeOTAD based reference device [149,150]. Poly(triarylamine) (PTAA) the selection choice for the HTL in inverted PSCs [151-154]. One of the highest efficiencies in PTAA-based PSCs was obtained when applying p-doping of PTAA HTM with Li-TFSI and TBP [152]. However, despite the attractive electrical parameters of the fabricated device, p-doping of PTAA HTL has also led to faster degradation of the cell. Generally, PTAA enables stable operation when processed from chlorobenzene or toluene solutions, with the latter to be considered as the more effective in improving the PTAA solubility and thus the film quality of the HTL. However, the successful use of PTAA HTM in PSCs, significant differences in the device performance have been demonstrated dependent on the molecular weight of this polymer. PTAA's molecular weight severely affects the interfacial charge carrier losses in the cell, and it was found that reduced (TMDs) have been also employed as ETL in PSCs due to their attractive electron mobility and energy levels (Figure 7a) [142]. A precise control over the photovoltaic properties of these ETLs achieved by modified their deposition protocols and probing of the charge dynamics at the interface has led to enhanced performance of PSCs with the additional merit of long-term stability [143,144].

Hole transporting materials. Hole transporting materials are also indispensable in achieving high photovoltaic performance and stability as they facilitate hole extraction and block the photogenerated electrons simultaneously from reaching the cathode (Figure 7b). A large variety of organic and inorganic materials have been applied as HTLs in PSCs. Among them, Spiro-OMeTAD (2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenyl-aminio)-9,9-spirobifluorene) is the most commonly used [142]. It enables fast hole transport under the requirement of sufficient doping to increase its low conductivity. This can be accomplished by using additives in the pristine solution, with the most common to be TBP (4-tert-butylypyridine) and Li-TFSI (lithium bis(trifluoromethylsulfonyl)imide) [146]. However, Spiro-acridine-fluorene and methoxy-O-Me substituted (in the para-, meta- and ortho- positions) Spiro-OMeTAD derivatives have demonstrated efficient device performance with no requirements for additional doping [147]. Moreover, thiophene-based materials have proven efficient HTLs due to their high electron mobility as revealed from steady-state and time-resolved photoluminescence measurements [148]. In addition, organic compounds using thiens(3,2-b) thiophene conjugated moieties or π-conjugated thiophene bridges attained enhanced PSC performance, even higher than that of the Spiro-MeOTAD based reference device [149,150]. Poly(triarylamine) (PTAA) the selection choice for the HTL in inverted PSCs [151-154]. One of the highest efficiencies in PTAA-based PSCs was obtained when applying p-doping of PTAA HTM with Li-TFSI and TBP [152]. However, despite the attractive electrical parameters of the fabricated device, p-doping of PTAA HTL has also led to faster degradation of the cell. Generally, PTAA enables stable operation when processed from chlorobenzene or toluene solutions, with the latter to be considered as the more effective in improving the PTAA solubility and thus the film quality of the HTL. However, the successful use of PTAA HTM in PSCs, significant differences in the device performance have been demonstrated dependent on the molecular weight of this polymer. PTAA's molecular weight severely affects the interfacial charge carrier losses in the cell, and it was found that reduced (TMDs) have been also employed as ETL in PSCs due to their attractive electron mobility and energy levels (Figure 7a) [142]. A precise control over the photovoltaic properties of these ETLs achieved by modified their deposition protocols and probing of the charge dynamics at the interface has led to enhanced performance of PSCs with the additional merit of long-term stability [143,144].

Moreover, dopant-free triarylamidine-substituted spiro-cyclopentadithiophene (Spiro-CPDT) based materials have successfully applied as dopant-free HTLs in PSCs [156]. Moreover, materials based on thiens(3,2-b) thiophene conjugated moieties or π-conjugated thiophene bridges attained enhanced PSC performance, even higher than that of the Spiro-MeOTAD based reference device [149,150]. Poly(triarylamine) (PTAA) the selection choice for the HTL in inverted PSCs [151-154]. One of the highest efficiencies in PTAA-based PSCs was obtained when applying p-doping of PTAA HTM with Li-TFSI and TBP [152]. However, despite the attractive electrical parameters of the fabricated device, p-doping of PTAA HTL has also led to faster degradation of the cell. Generally, PTAA enables stable operation when processed from chlorobenzene or toluene solutions, with the latter to be considered as the more effective in improving the PTAA solubility and thus the film quality of the HTL. However, the successful use of PTAA HTM in PSCs, significant differences in the device performance have been demonstrated dependent on the molecular weight of this polymer. PTAA's molecular weight severely affects the interfacial charge carrier losses in the cell, and it was found that reduced (TMDs) have been also employed as ETL in PSCs due to their attractive electron mobility and energy levels (Figure 7a) [142]. A precise control over the photovoltaic properties of these ETLs achieved by modified their deposition protocols and probing of the charge dynamics at the interface has led to enhanced performance of PSCs with the additional merit of long-term stability [143,144].
COMPOSITIONAL AND INTERFACE ENGINEERING APPROACHES FOR EFFICIENCY STABILISATION OF PEROVSKITE SOLAR CELLS

Organic–inorganic hybrid perovskites are defect tolerant materials owing to the anti-bonding character of their valence band maximum (that consists of halogen p orbitals, in particular, Cl 3p, Br 4p or I 5p, with a small contribution from the Pb 6p) and conduction band minimum (which is mainly composed of Pb 6p with a small contribution from the anti-bonding halogen p*). Still, they exhibit a diversity of defects that are encountered on their surfaces at grain boundaries and interfaces (GBs) and can be classified into: halide anion (such as Cl, Br and I) and organic cation (such as MA⁺ and FA⁺) vacancies, under-coordinated lead cations (Pb⁺) and halide anions, lead-halide antisite defects, misfit halide and MA⁺ ions, Pb clusters, halide-excess and Pb-halogen antisites. Furthermore, many of these defects form deep trap states, which act as non-radiative recombination centers for the photogenerated charge carriers thus compromising the device efficiency and stability. PASSIVATION of bulk, surface and GB defects is therefore imperative to maximise and, importantly, stabilise the solar cell efficiency. In this context, various passivation and engineering approaches targeting to minimise defect density and, consequently, charge trapping at these defects are widely applied.

CATION OPTIMISATION

Methyl ammonium-based perovskites, such as the archetypal MAPbI₃, with a bandgap of 1.55 eV, have been the most intensively studied absorber in PSCs. However, they also undergo severe phase transition at 55°C and thermal degradation at 85°C, which necessitates the replacement of MA⁺ cation with more stable ones such as the larger FA⁺ [171]. Mixt cation MAFA-based or even single cation perovskites such as FAPbI₃, are shown great potential as alternative perovskite materials with superior thermal stability [172]. Moreover, FAPbI₃ presents broader absorption due to its narrower bandgap of 1.48 eV [173]. However, the large size of FA⁺ causes lattice disturbance thereby affecting the crystal structure of the obtained perovskite material which requires thermal annealing at elevated temperatures in order for the black perovskite 0-phase to be stabilised. Mixed cation (MA/FA) perovskites are more easily stabilised at room temperature [174]. Besides FA and mixtures with MA, the high efficiency of a Pb-free PSC was obtained with A-site substitution using a non-polar material bearing the guanidinium (GA⁺) organic cation. GA⁺ was added in varying ratios into the crystal structure of the FASnI₃ along with 1% ethylenediammonium diiodide (EDAI⁺) to form GA⁺[FASnI₃]ₓEDAI₁₋ₓ [175]. The optimised device performance was attributed to the presence of EDAI⁺, which passivated surface defects, controlled the film morphology, and suppressed the Sn⁺ oxidation to Sn⁰. Moreover, the GA co-cation, which has a zero electric dipolar moment, inside the FASnI₃ framework delayed the oxidation of perovskite in the presence of moisture. Furthermore, monovalent alkali cations such as Cs and Rb have been implemented for substitution in the A-site since their ionic radii fulfill the criteria of Goldschmidt’s empirical tolerance factor (0.8 < t < 1) to retain the 3D perovskite structure. Cs⁺ has been widely incorporated with either MA⁺ or FA⁺ or a mixture of both at the A-site in multi-cation perovskites along with the aim to alleviate the problem of undesired phase transition and improve their photo- and moisture stability [176]. The A-site substitution of Cs⁺ shrinks the cubic-octahedral volume of the perovskite crystal lattice, thereof inducing stronger chemical interaction between FA⁺ and I⁻ which prohibits the undesired halide segregation and facilitates the formation of perovskite crystals with enhanced thermal stability [177]. Rb⁺ can greatly enhance the optoelectronic properties of the resultant perovskite when incorporated in small amounts due to the enlarged grain size of the perovskite films along with entropic gains and small internal energy input required for the formation of mixed perovskite concerning thermodynamics [178]. Potassium (K⁺) has been also applied to confer enhanced device performance in PSCs. K⁺ addition can facilitate crystallisation due to the decreased activation energy and enable the production of larger grain sizes leading to lower defect density of GBs, longer carrier lifetimes and improved conductivity. K⁺ incorporation in mixed cation perovskites was found to induce a small decrease to the bandgap value due to both occupation of A-site and/or B-site in the lattice [179]. Generally, cation engineering represents one of the most effective approaches to tune the perovskite lattice and stabilise the photoactive black phase.

HALIDE OPTIMISATION

The structure and optoelectronic properties of perovskites can alternatively be tuned through substitution in the halide anion X position. Modification of the halide anion changes the Pb-X bond length and accordingly the angle between X–Pb–X thus demonstrating one of the most effective approaches to tune the energy bandgap. Compounds with I show the smaller bandgap (in the range of 1.55–1.61 eV) whilst those with Cl have the highest bandgap (2.88–3.13 eV). The bandgap values perovskites with Br (2.0–2.44 eV) are between those with I⁻ and those with Cl⁺ whereas those of the mixed halide perovskites vary between those of the single halide ones. Mixed-halide perovskites are ideal candidates for absorption in photovoltaics because their optoelectronic properties can be effectively controlled by adjusting the halide concentration in the precursors [180]. However, upon illumination these mixed-halide perovskites undergo several halide segregation resulting to the formation of high bandgap Br-rich and low-bandgap I-rich domains, which act as carrier traps, inducing non-radiative electron-hole recombination [181]. As a result,

ENGINEERING OF STOICHIOMETRY

The stoichiometry of the perovskite material, regardless of its composition, i.e., single or mixed cation and/or mixed halide, is known to govern the optoelectronic properties of the film and the device performance. For example, it has been shown that non-stoichiometric perovskites may exhibit better properties than the stoichiometric counterparts i.e., an excess of 5% of lead iodide (PbI₂) precursor in the perovskite solution can favorably impact the perovskite film morphology and optoelectronic properties when applying a two-step synthesis 

The optimised device performance was attributed to the incomplete transformation of the Pbi layer to perovskite (especially if this layer is quite thick) with Pbi residue to be accumulated at the underlying charge transport layer causing electronic insulation and poor device performance [167]. Notably, small amounts of Pbi can benefit the charge collection and transport from the perovskite layer to the corresponding electrode in both, forward and inverted cell architectures since it can passivate surface defects, enhance electron transport and block hole leakage (in forward device architectures) or it can improve hole injection and electron blocking (in inverted structures) [168]. In any case, control over the thickness of remaining at the interfaces is imperative for efficient device performance. The GBs of the perovskite film are also sub-stoichiometric compared to the bulk due to the dangling bonds and non-terminated surface. This deviation from stoichiometry results to the formation of defect states which negatively impact the device performance. Moreover, GBs are potential paths for ion migration within the perovskite matrix, which is generally considered as the main source of hysteresis and instability for the perovskite optoelectronics [169]. In general, the synthetic procedure followed strongly influences the stoichiometry, film forming and optoelectronic properties of the resultant perovskite layer [170], which has important implication in the fabricated PSCs.
significant voltage loss and reduced photostability is observed in PSCs based on mixed halide perovskites. The segregation of halide anions is generally initiated by halide defects in the perovskite structure, such as halide vacancies and interstitials, which provide low-energy migration pathways and cause the formation of iodide-rich and bromide-rich domains [182,183]. This defect-assisted halide migration has been proposed to be initiated by heat or light [184]. Once stored in the dark, entropically driven intermixing of halides returns the system to the initial homogeneous condition. Perovskite films with a low density of halide defects are more robust to halide migration and segregation phenomena.

PASSIVATION APPROACHES

Passivation of surface, grain boundaries (GB) and interface defects of perovskite films can be accomplished through the application of a wide variety of materials combined with different strategies and processes. Most of these passivation approaches include the use of organic small molecules, which exhibit tunable, optoelectronic properties and excellent stability and, therefore, they have been considered as efficient passivation agents.

Various organic donor-π-acceptor (D-π-A) small molecules with different electron density distributions were employed to efficiently passivate perovskite film defects [185]. Organic molecules, including functional groups, such as amino or carboxylate ones strongly coordinate with the under-coordinated Pb2+ especially when increasing electron density in the passivation moiety via employing nearby effective electron donor units [186]. Moreover, organic molecules with aromatic carboxylic acid groups also effectively coordinate with Pb2+ and passivate surface traps [187]. Upon controlling the –COOH content and optimising their concentration, the passivation effect of different defects can be rationalised [188]. Regarding amino functionalised molecules, their surface and GB defect passivation efficiency can be directly correlated to the alkyl chain length. An extended length of the alkyl chain in the amino bearing organic compounds results in multidimensional defect passivation and suppression of non-radiative charge carrier recombination [189].

Hydrophobic organic small molecules incorporated at the fullerene/perovskite interface of inverted planar PSCs reduce the density of the surface and interfacial traps and offer increased long-term stability by inhibiting moisture penetration into the perovskite film [190]. Multi-functional molecular materials represent effective means to passivate defects, regulate film crystallinity and enhance crystal grain size [200]. Molecules featuring hydrophobic (hetero) aromatic cores and functionalised by ammonium or/and thiol groups not only ensure defect passivation of the A cation vacancy defects and unsaturated Pb2+ but also increase the perovskite crystal grain size and improve crystallinity. Fluorinated organic compounds simultaneously passivate surface defects, enlarge grain size, and induce surface hydrophobicity thus being beneficial for the device efficiency and stability [191]. In general, passivation of perovskite defects has been widely applied to successfully prolong both the device performance and stability under various internal and external factors.

SOLVENT ENGINEERING

Solvation engineering is also considered to be one of the most efficient approaches to control crystal growth and defect passivation in perovskite thin films [192]. This process relies on the evaporation of most of the perovskite solvent(s) but also leaves enough residual solvent in order to induce the formation of the chemical adducts with the perovskite precursors that determine the mechanism of nucleation, grain size evolution and crystallisation. Some solvents used in this solvent engineering approach are diethyl ether (DEE), dichloromethane (DCM), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), Isopropl alcohol (IPA), acetone (ACE) and triethylenetetramine (TETA). The key strategies of solvent engineering can be categorised into the regulation of coordination ability of solvents by mixing solvents with high donor number (D) with those with low DN and reducing the toxicity of precursor solution by using alcoholic, aqueous or ionic liquids (Ils)-based solvent (Figure 8) [193]. This engineering approach starts with the application of the perovskite precursor onto the underlying charge transport layer, followed by the solvent engineering step that induces the formation of a highly compact, pinhole-free and smooth perovskite film with small surface roughness and full substrate coverage. Additionally, compositional engineering can also take place along with solvent engineering to enable optimal composition and optimised crystallisation of the perovskite film and accordingly to improved solar cell performance.

FIGURE 8. Illustration of current development on solvent engineering of precursor solution in PSCs.
PEROVSKITE SOLAR MODULES

Scaling up PSCs and producing efficient and stable modules is a prerequisite before this rapidly evolved technology enters the market. During the last years, many research groups have developed deposition techniques to scale-up fabrication from small cells (with areas below 1 cm²) to mini-modules with sizes ranging from 4 to 100 cm², and PCEs up to 21% [194-197]. It is evident that if PSC manufacturing can follow the pathways that have been developed for other thin-film solar cells, it will have serious potential for commercialisation in the near future.

However, these modules suffer from environmental stability problems and their efficiency are severely affected by humidity and constant illumination. Particular attention is therefore paid to fabrication methods and passivation approaches that result in perovskite modules that are simple, low-cost and relatively stable. For example, carbon allotropes such as graphite, graphene, black carbon and carbon nanotubes, possessing low-cost, facile fabrication, high chemical stability and high conductivity, have been successfully applied as counter electrodes in mesoscopic modules [198-200]. Notably, a such mesoscopic module with an active area of 198 cm² and an efficiency of 6% is the largest perovskite module reported so far [201].

Planar perovskite modules also present exciting characteristics such as ease of fabrication and high efficiency which makes the two technologies comparable to each other [202]. In both these cases, module fabrication involves additional step compared to single-junction devices. In particular, it requires scribing steps (i.e., P1, P2 and P3 scribes), to divide a large-area device into sub-cells and form the electrical interconnections between sub-cells (Figure 9a). The P1 scribe is applied after coating the bottom electrode aiming to remove stripes of this electrode to pattern sub-cells. The P2 scribe is applied to the device layer stack just before the deposition of the top electrode. P2 scribe exposes the bottom electrode within the P2 scribe lines. The subsequent deposition of the top electrode connects the top electrode of one sub-cell to the bottom electrode of the next sub-cell (i.e., series connection). Finally, the P3 scribe isolates the top electrode between neighboring sub-cells to complete the monolithic interconnections (Figure 9b). The sub-cells interconnection in the module is critical for the device performance, and the carbon dioxide laser patterning technique as well as copper or aluminium grids have been proven highly suitable to successfully interconnect the sub-modules [203].

The key design consideration for such module fabrication is to minimise the inactive area. Thus, it is important to minimise the fraction of the dead area (which is the area that does not contribute to the photogeneration of charge carriers) with respect to the total area that is the sum of the photoactive area and dead area, which is called the geometric fill factor (GFF). Several models and device designs have been considered leading to the module with a GFF of over 95% [204]. However, when increasing the module total area and GFF, a rapid decline in efficiency is commonly obtained. This indicates that further research efforts are still required to develop the large area but also efficient and stable perovskite modules as well as effective recycling protocols at the end of their life to secure a viable future for this rapidly evolved photovoltaic technology [205].

OUTLOOK AND PERSPECTIVES

Perovskite solar cells represent a rapidly advanced technology with an attractive figure of merits such as high efficiency, low material cost and short energy payback time. For further developments, however, significant advancements in efficiency stabilisation should be made while novel materials and alternative large-area fabrication techniques should be developed. Besides their impressive attributes, perovskite solar cells still present issues regarding their stable operation under various stresses such as exposure to ambient and continuous illumination. To this end, the application of several compositional and dimensionality engineering approaches for the perovskite absorber combined with existing and novel passivation materials and approaches seem to be in the right direction. Moreover, judicious device engineering to address the interface induced degradation is a prerequisite to improve PSCs overall stability. Furthermore, the degradation of the perovskite absorber caused by environmental moisture or oxygen can be successfully suppressed by suitable device encapsulation with materials and protocols borrowed by the more mature organic photovoltaic counterparts.

To realise their market entry, however, rapid advancements in the performance and stability of large-scale perovskite modules are urgently required. To this end, further improvements in the applied fabrication techniques and sophisticated design considerations that take into account the perovskite sub-cell structure, the sub-cells interconnection as well as the quality, recyclability and cost of used materials, including perovskites, interlayers, electrodes and substrate material, should be developed. Appropriate and reliable stability test protocols that researchers should subject their solar cells to are also needed in order for the literature results to be directly comparable. Up to now, scientific publications lack consistency in stability measurements adopted and this prevents the deeper understanding of degradation mechanisms that lead to the device failure. However, with the progress already made and rapid evolution of this technology, it is a common attribute that the remaining problems will be soon addressed thus facilitating immediate market entrance.


200. Y. Fu, S. A. Mei, Y. Rong, H. Liu, X. Li, H. Han, Solar RRL, 2017, 1, 1600019.


Over the past 135 years, petrol-fueled vehicles have contributed significantly to the way people live. However, they’ve also played a key role in polluting the environment, most notably with carbon dioxide (CO2) from fuel combustion, which is a key contributor to the “greenhouse effect” and climate change. Today, a typical passenger vehicle emits about 4.6 metric tons of carbon dioxide per year. This assumes the average gasoline vehicle on the road today has a fuel economy of about 22.0 miles per gallon and drives around 11,500 miles per year. Currently about 16% of global CO2 emission originate from the transportation sector (Figure 1), with about 60% coming from passenger vehicles (cars, motorcycles and buses) [3]. While energy production has started to significantly deviate more towards renewable energy production, particularly via wind and solar generation, the transportation sector has been moving toward electrification. Electric Vehicles (EV), not only provide a massive reduction of tailpipe emissions; but also present a massive improvement in vehicle performance and efficiency [4]. The Electric Power Research Institute (EPRI) envisions that EVs will contribute to 20%, 60%, or 80% of the entire U.S. vehicle fleet by 2050 using low, medium, and high vehicle fleet penetration scenarios [5].

While moving towards increasing adaptation of EVs is seen as mandatory, this step has to be tackled from different perspectives. A deeper dive into different technical aspects of transportation electrification need to be done before this technology becomes a reality. Optimising transportation electrification dictates several interlinked directions, some relating to the device design and others relating to system operation and practices.

On the device level, the innovative design of the power train to improve its efficiency and response is vital. Further, as charging speed and driving range are the main dilemmas in increasing the penetration of EVs, both fast chargers and wireless charging have key issues. On one hand, innovative converter topologies for fast chargers, along with their optimised control, should be designed. On the other hand, novel wireless charging circuits with increased power capacity and charge transfer efficiency would be far more convenient to use. In addressing this matter, important aspects such as increasing the distance between the power transmitter and receiving coils, mis-alignment, dynamic charging and bidirectional power transfer need be developed. On the system level, two main directions are of increasing importance, charging infrastructure and smart charging protocols. As seen from Figure 2, infrastructure planning, mainly charging stations’ locations and capacity, taking into consideration both power and transportation constraints, need to be investigated. Further, the development of optimised and intelligent charging protocols that take into consideration both customer and aggregators perspectives need to be considered. Furthermore, enhancing the system efficiency through the improvement of the energy management systems and regenerative protocols need to be addressed.
EFFICIENT DRIVETRAIN CONFIGURATIONS

This section discusses the basic architecture, key components, and different power train configurations of an EV. As depicted in Figure 3, the main components of an EV drivetrain system are the motor, controller, power source, and the transmission system [6]. The dc-ac converter along with the motor is responsible for converting the electrical energy stored in the battery to mechanical energy to drive the EV.


There are six types of drivetrain architectures with various mechanical arrangements and these are shown in Figure 4. Among them, the drivetrains shown in Figure 4b and 4c are the most popular configurations [7-8]. The main attributes of these architectures are highlighted below.

- The drivetrain architecture in Figure 4a consists of an electric motor (EM), a clutch (C), a gearbox (GB), and a differential (D). This drivetrain architecture is realised when transforming the existing IC engine-based vehicle to electric.
- Figure 4b shows a single electric motor drivetrain architecture along with fixed gearing (FG). Some conventional drivetrains without a transmission system utilise this configuration.
- The most widely used drivetrain architecture is depicted in Figure 4c. It is a single motor rear wheel drive system.
- Figure 4d shows a dual-motor drivetrain arrangement which has two separate electric motors on wheels, used via fixed gearing.
- Figure 4e presents an architecture which has a fixed planetary gear and is called an in-wheel drive system. This drivetrain is used to reduce the motor speed to the desired wheel speed.
- Figure 4f shows an electric drivetrain without a mechanical gear system.

EV DRIVETRAIN ARCHITECTURES BASED ON Mechanical Arrangement

FIGURE 4. EV Drivetrain Configurations based on Mechanical Arrangement: (a) with clutch (C), gear box (GB) and differential (D), (b) without clutch and gearbox, (c) with clutch, gear box and differential, (d) two motors (M), (e) in-wheel motor and mechanical gear, and (f) in-wheel motor and no mechanical gear.

FIGURE 5. EV Drivetrain Configuration based on Power Source: (a) one battery source, (b) two battery source, (c) battery passive and capacitor active, (d) both battery and capacitor passive, (e) battery active and capacitor passive, and (f) battery and capacitor both active.

FIGURE 5. EV Drivetrain Configuration based on Power Source: (a) one battery source, (b) two battery source, (c) battery passive and capacitor active, (d) both battery and capacitor passive, (e) battery active and capacitor passive, and (f) battery and capacitor both active.
As highlighted earlier, the EV drivetrain may use multiple motors, in which the speed of individual wheel can be controlled using a differential action between the wheels [11]. These multiple motor drives may be designed as four-wheel drive system as well as in-wheel drives by placing the drive motor inside the wheel. The selection of an appropriate drivetrain is done based on the application, size, weight, cost and performance constraints [12]. The Nissan Leaf, Chevrolet Spark, Kona and Ioniq from Hyundai, Soul EV, Verito from Mahindra, and Niro from Kia all employ the front wheel drivetrains. On the other hand, rear axle drive is used in E20 sport from Mahindra (Figure 6a), Reva, BYD E6 and Tesla model S. All-wheel drive architectures with in-wheel motor systems are utilised in cars like Nissan IMX (Figure 6b) to achieve an efficient driving performance. The Nissan Blade Glider uses an in-wheel motor structure with rear wheel drivetrain leading to better cornering performance.

The earlier choice for EV traction was direct as aspects of an electric motor for EV traction are mechanical energy and vice-versa. The critical the electrical energy stored in the battery to weight, cost and performance constraints [12]. The Nissan Leaf, Chevrolet Spark, Kona and Ioniq from Hyundai, Soul EV, Verito from Mahindra, and Niro from Kia all employ the front wheel drivetrains. On the other hand, rear axle drive is used in E20 sport from Mahindra (Figure 6a), Reva, BYD E6 and Tesla model S. All-wheel drive architectures with in-wheel motor systems are utilised in cars like Nissan IMX (Figure 6b) to achieve an efficient driving performance. The Nissan Blade Glider uses an in-wheel motor structure with rear wheel drivetrain leading to better cornering performance.

FIGURE 6. EVs in the Market: (a) Mahindra E20 with rear wheel drive with single motor, and (b) all-wheel drive Nissan IMX.

ELECTRIC MOTORS TYPES

Electric machines and drives convert the electrical energy stored in the battery to mechanical energy and vice-versa. The critical aspects of an electric motor for EV traction are higher power and torque, variable range of speed, higher efficiency, high reliability, and affordability. The earlier choice for EV traction was direct current (DC) motor drive, but their low efficiencies and low reliabilities have led to obsolescence. These days, the induction and permanent magnet synchronous machines (PMSM) are being commonly used due to the development of their power electronics control and design [13-14].

CHALLENGES AND FUTURE TRENDS

The successful adoption of EVs require highly efficient and high-power density drivetrain architectures. The development of advanced power devices and intelligent integrated circuit-based control may provide the required multi-goal optimisation of modular structure, improved efficiency and high power density. The driving range extension is achieved by using highly efficient machines for drives, which reduces battery drain [15]. Further, the design of the battery pack and battery management system should be done intelligently to achieve an optimised battery lifetime and operation. The electric motor propulsion is the best method for full torque from vehicle start while allowing for energy recovery during the regenerative braking. This offers a research platform for the futuristic EV drivetrain solutions. Other important research topics include efficient traction motors design, battery advancements, and optimisation of control strategies.

PLANNING THE EV CHARGING INFRASTRUCTURE

The location and size of electric vehicle charging stations (EVCS) affects the electrical grid in many aspects: power losses, voltage stability and system reliability. Similarly, the location and size of a station has an impact on road congestion, station utilisation, and the environment as well. There are two charging techniques: conductive charging and inductive charging. In conductive charging, power is transferred through direct contact, whereas power is transferred wirelessly in inductive charging. The first method is more efficient than the second one, while the second is safer than the first one under all weather conditions. EPRI defines three charging levels: level 1 (AC), level 2 (AC), and level 3 (DC fast charging), with the charging duration varying greatly between the three levels. The fastest is level 3 where the charger is located off-board and used to charge the battery directly with DC power. Because the current driving range of most EVs is below that their rival ICE vehicles, planning of the charging infrastructure is crucial for incentivising maximum EV penetration. The planning of EVCS determines the best location and size of the charging stations as well as the type of charging.

The EVCS planning problem has been studied in their recent years. Although this problem impacts the transportation network as well as the distribution network, few studies addressed both networks simultaneously. In the infrastructure planning, many researchers focused on the electrical network constraints and ignored transportation network operational constraints [16-19]. These studies focused only on electric networks taking different constraints, such as chargers types, arrival/departure times, transformer utilisation and battery charging characteristics, yet, they ignore any transportation aspects. On the other hand, other studies considered the transportation requirements through focusing on the user equilibrium model with the assumption of perfect knowledge of traveling costs and routes [20-24]. Nevertheless, as those two problems are interlinked, the accurate and efficient planning calls for the fusion of the two networks.

The planning problem of the EVCS is multi-objective and has a lot of aspects and dimensions. In most of the attempts made, there were assumptions and simplifications for the EV model, EVCS model, and the transportation network model. Therefore, the EVCS planning problem is not settled yet and more research is required to capture the details of all key players especially the transportation network. Figure 7 shows the coupling of distribution networks with transmission networks where the integration of the transportation network constraints and the distribution network constraints is the way to efficient resources allocation and the following aspects should be considered:

- Transportation network and distribution network should be modeled thoroughly
- Investment and operational costs of both networks should be included
- The convenience and satisfaction of EV users should be considered
As the demand for EVs is growing, a wide variety of chargers has been introduced to recharge EV batteries. Chargers are broadly categorised as on-board (OBC) and off-board chargers, which can be either unidirectional or bidirectional. Based on the type of input power, they are classified as AC charging systems and DC charging systems. The unidirectional chargers support battery charging only, whereas the bidirectional chargers can support vehicle to-grid power injection. The block diagram of an EV illustrating different charger options is shown in Figure 8. The OBC takes power input from the 1-phase/3-phase AC supply, either from the home or public charging point, whereas the off-board charger is usually connected to a medium-voltage (MV) grid and its output is directly supplied to battery terminals. Both OBC and off-board chargers typically have two conversion stages to feed the power from AC grid to EV battery. The OBCs can be either conductive or inductive and they have limited power rating because of weight, space, and cost constraints. The off-board chargers deliver dc power to the EV battery via an isolated converter located outside the vehicle. They provide the higher charging rates as they are not constrained by size and weight. These fast chargers can reduce the on-board energy storage requirements and thus, the overall cost of the vehicle.

The Society of Automotive Engineers (SAE) has developed the SAE J1772 standard to classify the conductive charging ratings of the EVs in North America, provided in Table 1 [25-27]. The on-board chargers are usually AC charging systems with peak power up to 19.2 kW and are normally used for overnight charging due to low power rating. On the other hand, DC charging systems are developed with peak power up to 350 kW to achieve fast charging. A charger is referred as fast charger if it can charge the vehicle battery in 30 minutes or less [26], whereas extreme fast chargers (XFC) stations are those that takes less than 10 minutes to add 200 miles range to the battery [28].

The main function of OBC is to transfer power from the grid to the battery and thus, the OBC must comply with the requirements of the grid codes. The foremost requirement for OBC is to have high unity power factor (> 0.9) and it should support both 1-phase and 3-phase operation. The block diagram of the generic single-phase OBC is shown in Figure 9. It consists of an AC input filter followed by a diode bridge rectifier and a dc-dc converter. The typical efficiency of single-phase and three-phase OBCs is greater than 90% and 94%, respectively [29].
Despite having high efficiency in the electric propulsion drivetrain, the driving range of EVs on one charge is still shorter than the range of the conventional gasoline vehicles due to the higher energy density of petroleum (12000 Wh/kg) compared to Li-ion batteries (200-300 Wh/kg) [30]. This is one of the major challenges for wider adoption of EVs and one of the solutions is to develop the extreme fast charging stations. However, as the power rating and the charging speed increases, the installation cost also increases significantly. The specifications of some of the commercial DC fast chargers is given in Table 2. These chargers have efficiency in the range of 91% to 95%. By using 350 kW XFC charger, it is possible to charge a vehicle battery in 10 minutes to add 200 miles range.

**Table 2. Specifications of some of the commercial DC fast chargers.**

<table>
<thead>
<tr>
<th>Name of the Charger</th>
<th>Power</th>
<th>Output Voltage (V)</th>
<th>Output Current (A)</th>
<th>Peak Efficiency</th>
<th>Time to add 200 miles</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABB Terra 53</td>
<td>50 kW</td>
<td>50-500 V</td>
<td>120 A</td>
<td>94%</td>
<td>72 min</td>
</tr>
<tr>
<td>Tesla Supercharger</td>
<td>135 kW</td>
<td>50-410 V</td>
<td>330 A</td>
<td>91%</td>
<td>27 min</td>
</tr>
<tr>
<td>EVTEC</td>
<td>150 kW</td>
<td>170-500 V</td>
<td>300 A</td>
<td>93%</td>
<td>24 min</td>
</tr>
<tr>
<td>ABB Terra HP</td>
<td>350 kW</td>
<td>150-920 V</td>
<td>375 A</td>
<td>95%</td>
<td>10 min</td>
</tr>
</tbody>
</table>

The different architectures of the dc fast charging stations are shown in Figure 10a-c. These chargers that convert 3-phase AC voltage into required dc voltage have the following conversion stages: AC/DC rectification with power factor correction (PFC) and DC/DC conversion to achieve the desired battery voltage. The galvanic isolation between the grid and EV battery can be provided by either using line-frequency transformer before the AC-to-Dc converter as shown in Figure 11a or by using a high-frequency transformer inside DC/DC converter as shown in Figure 10b. It should be noted that multiple identical modules are connected in parallel to meet the required power demand. To give an example, the Tesla supercharger is made of 12 parallel modules to meet the power demand. The solid-state transformer (SST) based architecture shown in Figure 10c consists of rectification, voltage step-down, and isolation function in a single unit. This architecture provides significant reduction in overall size and total losses in the conversion.

RESEARCH CHALLENGES AND OPPORTUNITIES

As the power range of OBCs is increasing along with stringent requirements for efficient and compact designs, the need for utilisation of wide bandgap (WBG) semiconductor devices, such as Silicon carbide (SiC) and Gallium Nitride (GaN), becomes crucial. By operating WBG devices at high switching frequency, the size of passives circuit elements, including transformers, inductors, and capacitors, can be significantly reduced. Companies such as Tesla has moved to SiC in their designs, but further research and development is required to make commercial utilisation of GaN devices a viable solution. Other important research topics for achieving high power density OBCs include auxiliary power module integrated OBCs with new control strategies to avoid cross-regulation, wireless integrated OBCs with higher circuit efficiency, and efficient integrated dc-dc converters for motor-drive and inverter in all operating modes. In addition, these OBCs must also minimise the severe power quality impacts on the power grid, such as overvoltage, components overloading, system losses, and stability issues.

The bottleneck for the fast charging stations is their high installation cost. This can be addressed by combining multiple XFCs in one charging station along with load diversification based on the different battery capacities and charging state of batteries. In addition, new architectures with higher efficiency and lower control complexity need to be developed to integrate battery storage and renewable energy sources and hence reduce charges during peak hours of grid demand. One major challenge for the power electronics converters of XFC stations is achieving higher efficiency across the wide voltage and power rating of EVs. Another emerging research topic for XFC is the development of new modular converter topologies and architectures that can significantly reduce overall size as well as provide higher efficiency.
Charging EV batteries can be time-consuming as mentioned previously, which has prompted a number of ideas to deal with this issue. Some of these ideas can be categorized as direct solutions, for example fast charging. However, development of extreme fast charging (XFC) infrastructure will require huge investments and resources. On the other hand, there are also indirect solutions that don’t provide high power charging solutions but do create a charging experience that is convenient and autonomous. One of these solutions is Wireless Power Transfer (WPT), which is increasingly finding interest in electric vehicle charging. WPT can help mitigate the charging time issue by:

- Offering a convenient, charging experience in which the user doesn’t need to interfere or plug any cables
- Allowing dynamic charging, which refers to charging the vehicle while moving on the road.

Wireless chargers for EVs can be classified into two main broad categories depending on coupling method between the power sending system and the power receiving system on-board of the car. In the first category, coils off-board and on-board the EV are coupled magnetically in a very similar manner to the coupling that occurs between transformers. However, the main difference here is the absence of a magnetic core that forms a close path between the power sending and receiving systems. Magnetic cores can still be used, but again they don’t form a closed magnetic path. Figure 11 shows an example of a WPT system [33].

**FIGURE 11.** Example of a WPT couplers.

The second category is known as capacitively-coupled WPT systems, where electric fields couple the power sending and receiving systems. This method of WPT is not as popular in EV charging application as inductive WPT for a number of reasons, such as its relatively low power density and sensitivity to background interference from the car chassis and the road material [34]. For this reason, the focus of this section is on inductively-coupled WPT systems. In the following, some important metrics relevant to inductively coupled WPT systems are briefly discussed.

**WIRELESS CHARGING, BENEFITS AND CHALLENGES**

A block-diagram that describes the main electrical stages involved in a conventional inductively coupled WPT system, including the Ground System and the Vehicle System, is depicted in Figure 12. Starting from the ground system, power from the grid is first converted from ac to dc using a rectifier, typically a full-wave rectifier. The dc-voltage is then fed to a high-frequency inverter to generate an ac-voltage with frequencies within accepted standards. The high-frequency signal passes through a reactive power compensation circuit and then to the primary coil to generate a high-frequency time changing magnetic field. The field induces a voltage in the secondary coil located in the vehicle, which is then rectified and eventually supplied to the vehicle’s battery. A dc/dc converter is often added to increase the power transfer efficiency [35]. Compensation blocks on both the primary and secondary sides often consist of capacitors connected in series or in parallel. Their values are chosen such that resonance is achieved, which minimises the VA rating of the power electronics circuits and improves the power transfer efficiency. Some of the important design metrics and aspects related to WPT systems are discussed in the following section.

**FIGURE 12.** Block diagram of main components in a conventional WPT system.

The SAE J2954 standard is one of the widely used standards for WPT applied to light-duty vehicles. It classifies WPT systems into three main categories, distinguishable by their power transfer capabilities [36]. These levels are shown in Table 3 along with the required minimum efficiency. Note that WPT 1 and WPT 2 chargers fall in the same power range category of ac-level 1 and 2 conductive chargers. Standards for power levels higher than WPT 3 are still under development as high power transfer is getting more attention. There are also three standard airgap ranges (Z-classes) between the transmitting and receiving coils, with the maximum distance being 250 mm, as shown in Table 4. In terms of frequency, the SAE J2954 standard mandates that the frequency should be within the range of 79 kHz to 90 kHz, with 85 kHz being the nominal operating point.

**TABLE 3.** WPT power classifications SAE J2954.

<table>
<thead>
<tr>
<th>Type of system</th>
<th>Power Level</th>
<th>Minimum Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPT 1</td>
<td>3.7 kVA</td>
<td>85%</td>
</tr>
<tr>
<td>WPT 2</td>
<td>7.7 kVA</td>
<td>85%</td>
</tr>
<tr>
<td>WPT 3</td>
<td>11.1 kVA</td>
<td>85%</td>
</tr>
</tbody>
</table>

**WIRELESS POWER TRANSFER SYSTEMS**

The SAE J2954 standard is one of the widely used standards for WPT applied to light-duty vehicles. It classifies WPT systems into three main categories, distinguishable by their power transfer capabilities [36]. These levels are shown in Table 3 along with the required minimum efficiency. Note that WPT 1 and WPT 2 chargers fall in the same power range category of ac-level 1 and 2 conductive chargers. Standards for power levels higher than WPT 3 are still under development as high power transfer is getting more attention. There are also three standard airgap ranges (Z-classes) between the transmitting and receiving coils, with the maximum distance being 250 mm, as shown in Table 4. In terms of frequency, the SAE J2954 standard mandates that the frequency should be within the range of 79 kHz to 90 kHz, with 85 kHz being the nominal operating point.

**TABLE 3.** WPT power classifications SAE J2954.
The most basic compensation blocks consist of capacitors connected either in series or in parallel with the coils. This results in the common and classical series-series (SS), series-parallel (SP), parallel-series (PS) and parallel-parallel (PP) compensation topologies. Compared to these four topologies, the SS compensation is the most widely used because the switching frequency needed to achieve resonance is independent of the loading and coupling factor between the coils. When designing and choosing a compensation circuit topology, some additional factors that have to be considered are the constant-voltage or constant-current output mode at the battery, the implementation of soft-switching at the primary-side inverter to minimise semiconductor switching losses and avoiding bifurcation, which can affect the stability of the system [37]. More details and discussion on these and more advanced compensation networks can be found in [35, 38].

<table>
<thead>
<tr>
<th>Type of system</th>
<th>Airgap (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>100 to 150</td>
</tr>
<tr>
<td>Z2</td>
<td>140 to 210</td>
</tr>
<tr>
<td>Z3</td>
<td>170 to 250</td>
</tr>
</tbody>
</table>

### Compensation Topologies

A very common challenge in inductive WPT systems is lateral misalignment between the primary and secondary coils, which is measured with the respect to the centers of both coils. Misalignment reduces the coupling factor between the two coils and hence decreases the power transfer efficiency. Designing WPT system tolerant to misalignment is one active research front and some ideas that have been proposed in this regard include novel compensation networks such as the LCL compensation topology [37], novel coil shapes such as the DDQ coils [38], and mechanical-alignment systems that adjust the position of either the primary coil, secondary coil or sometimes the vehicle autonomously. In terms of safety from stray electromagnetic fields, circular and rectangular coils perform better, while with respect to misalignment tolerance DD and DDQ coils give better performance [40].

### Coil Design

The primary and secondary coil shape and geometry is detrimental to the system operation. The magnetic coupling is significantly affected by the design of these coils, and an optimum coupler design may lead to 50%-100% improvement compared with some non-optimal designs [39]. At the moment, the most common coil shapes are circular coils, rectangular coils, DD coils, and DDQ coils, which are shown in Figure 13 [38]. Note that ferrite bars are usually added to increase the magnetic coupling between both systems, yet they don’t form a closed magnetic path between the primary and secondary systems.

### Misalignment Tolerance

WPT produces electromagnetic fields at relatively high-frequencies, such as 85 kHz, according to the SAE J2954 standard. These fields can present a safety threat to a human, animals, electronics and even passengers on-board of the charging vehicle. For instance, at 85 kHz charging in regions where passengers are located, the SAE J2954 standard mandates that the flux density magnitude should be lower than 28 μT [36]. Passive and active methods of protection have been suggested to limit the field value. For example, the use of copper or aluminum plates is very common for this purpose, but can affect the WPT efficiency [40].

### Stray Field Protection

Charging electric vehicles can be achieved through different protocols as simple as ‘first come first serve’. However, this kind of protocol doesn’t take into consideration any factors related to the customers (time commitment, state of charge, price, etc.) or related to the electrical network. Therefore, this simple charging protocol can lead to either customer dissatisfaction, network overloading, or both. Other charging protocols are mainly focused on achieving the maximum revenue for charging station owners while meeting the energy system constraints. However, those protocols are not centered around customer need and satisfaction. Developing intelligent charging protocols that take both the customer requirements and charging station owners into consideration along with the network constraints is required.
CUSTOMER-CENTERED SMART CHARGING STRATEGY CONSIDERING VIRTUAL CHARGING SYSTEM

Electric vehicle (EV) charging is considered as one of the main challenges that face EV drivers. The routing process of EVs is typically implemented centrally based on the charging station/operator perspective. On the contrary, a smarter charging strategy that routes EVs drivers to the best charging station based on their priorities is needed. To achieve a smart charging strategy, various charging stations need to cooperate through a virtual charging system (VCS) to serve all EVs charging requests with a high satisfaction level. The drivers’ requirements are achieved through a new scoring criterion which ranks the participating charging stations based on EV driver’s perspective. Then, the EV driver will select individually the charging station based on his/her priorities. The data required for the scoring criterion are computed through two stages: offline (day-ahead) and online stages. The expected waiting time at each charging station within the VCS is computed during the offline stage based on the forecasted arrivals. The integration between offline and online stages aims to reduce the data flow, calculated data, and finally the communication bandwidth during the online stage.

Charging stations with different ownerships participating in VCS will cooperate rather than compete in a conventional charging system to act as one charging station for EV drivers. This cooperation will benefit both parties; the participating charging stations benefit by increasing their profit through serving all EVs' requests and EV drivers benefit by having satisfied their requirements. However, coordination between multiple VCSs can be used to maximise the profit gained by each VCS as well as to minimise the cost incurred by the customer. Different charging stations with different chargers’ ratings will cooperate through a VCS to offer various charging options for EV drivers including: different charging prices, different traveling times and various waiting times at these charging stations. The VCS will route the EV centrally to the most suitable charging station by ranking the participating charging stations based on the driver’s priorities. This allows the EVs to select individually the most suitable charging stations according to their requirements. Therefore, the proposed strategy guarantees a high level of customer satisfaction compared to the methods introduced in the literature since the routing process in the proposed strategy is based on customer’s perspective and not based on the operator’s perspective. Moreover, the smart charging strategy proposes another option for EVs, which is Vehicle-to-Vehicle (V2V) charging mode. This option will be inevitable if the current state-of-charge (SOC) isn’t sufficient to reach the nearest charging station. The required data for the routing process is computed through two stages: offline stage and online stage as shown in Figure 14.

CONCLUSIONS

Electric vehicles are an essential means of mitigating carbon emissions from the transportation sector. However, achieving this mitigation via seamless integration of electric vehicles into the transportation sector requires several interlinked efforts. The industry needs to not only focus on improving the drive-train efficiency of electric vehicles, but also needs to develop competent charging devices (wired and wireless) and optimise charging infrastructure with both energy and transportation constraints taken into consideration. Finally, intelligent charging protocols that prioritise driver benefits while also providing financial gains to investors need to be developed.
3. E. Steinitz, Max Roser (2020) - CO2 and other greenhouse-gas emissions
17. X. Wang, H. Yang, and J. Hu, "Optimal planning of electric vehicle charging stations in the active distribution network," IEEE Access, 8, pp. 68124-68134.
HYDROGEN PRODUCTION FROM COAL-MINE METHANE

INTRODUCTION

At present, the volume of hydrogen production in the world is estimated at 75 million tons/year. A 50% increase is expected in the next five years [1]. More effective refining, together with the advances in output of ammonia, methanol, and synthetic liquid fuels, have caused a steady increase in hydrogen consumption. Along with the conventional areas of domestic hydrogen consumption is predicted in the energy sector, where hydrogen, due to its high energy saturation and environmental friendliness, is considered one of the promising energy carriers (Figure 1).

Bloomberg New Energy Finance offers three scenarios for achieving zero emissions by 2050. They refer to the contribution of the primary energy resources: fossil fuels, renewable energy, nuclear energy to the energy supply mix (Figure 2). The "green" and "red" scenarios are far and forward R&D and nuclear energy, respectively, as priority sources of clean electricity, while the share of fossil fuels is brought down to 10% from the current 85%. According to the "green" scenario, in 2030 the demand for hydrogen in the transport industry will approximately reach 115 million tons per year, and its contribution to the structure of electricity consumption will increase from 3% to 24%. According to the "gray" scenario, where coal and gas will still be used to generate electricity, and where CO2 capture and storage technologies will be implemented, the demand for hydrogen will approximately reach 190 million tons a year in 2050.

On the one hand, coal is seen as the dirtiest fuel with a high carbon footprint. In the bargain, the contribution of CO2 emissions to greenhouse gases and global warming is quite significant. On the other hand, with the increasing role of hydrogen as an energy carrier, the coal industry has a very high potential for its production from both coal and methanol.

FIGURE 2. Present and future contributions of the major energy resources to the energy supply mix, depending on the energy development scenario.

FIGURE 3. The cost of hydrogen depending on its production technology.
At present, the cost of renewable hydrogen is significantly higher than the cost of hydrogen obtained using traditional technologies (Figure 3). The cost of hydrogen produced specifically from coal is minimal even with the combined use of carbon capture and storage (CCS) technology. In Australia, the Latrobe Valley Project (also called the Hydrogen Energy Supply Chain Project) is being developed. It represents a pilot plant for the gasification of lignite to produce hydrogen [4]. The plan is to integrate H₂ production into CO₂ utilisation technologies, with its subsequent delivery to consumers in liquefied form (Figure 4). In China, coal already plays a key role in the production of hydrogen (62% against the global contribution of 18%), and this trend continues to intensify [6]. The world’s largest plant for the production of hydrogen from coal is located in Inner Mongolia (China) and includes two reactors for coal gasification, processing 2250 tons of coal per day [6].

This review looks at the scientific basis and promising technologies for hydrogen production from coal-bed methane and coal production.

**FIGURE 4.** Hydrogen energy supply chain pilot project between Australia and Japan: hydrogen production from brown coal.

**FIGURE 5.** Coal-bed methane and its production in the world.

**COAL-BED METHANE RESOURCES**

Coal beds contain significant hydrocarbon wealth, consisting mainly of methane (80–98%) and small amounts of carbon dioxide, nitrogen, ethane, propane, and butane. In November 2011, coal-bed methane (CBM) was recognised as an independent mineral and included in the All-Russian Classifier of Minerals and Subsoil Waters (code 11102111, additionally included by amendment No.1/2011) [9]. The world coal-bed methane supplies are estimated at 113–201 trillion m³, of which 30 to 42 trillion m³ are considered to have good extraction potential [10]. The largest volumes of CBM are found in Russia, China, USA, Canada, Australia, Indonesia, Poland, Germany and France (Figure 5).

In Russia, CBM reserves reach approximately 80 trillion m³ [11]. More than half of those resources are concentrated in the West Siberian (40%) and Tunguska (24%) coal basins, followed by Kuznetsk (16%), Leninsky (12%), Taimyr (5%) and Pechora (2%) basins (Figure 6). Among the deposits potentially fit for industrial development, there are Kuznetsk and Pechora basins, since they are well-explored, and they have optimal coal-bed depth and sufficient gas content [12].

**FIGURE 6.** Resources of coal-bed methane in Russia.

**COAL INDUSTRY METHANE: CHARACTERISATION AND CLASSIFICATION**

Coal-bed gas properties, in particular its origin, composition and quantity, are determined by the coal rank and vary greatly. The content of methane per ton of coal may vary from low (4–6 m³/ton) to high (15–20 m³/ton) (Figure 7).

International and Russian classifiers offer several terminology sets to designate coal industry methane depending on the process flow stage. Currently, the most established are the four main terms describing the various stages of the coal mining process and referring to the differing methane content, and, accordingly, to the ratio of methane and air concentrations:
FIGURE 7. Ratio between coal gas content, its grade and mining depth.

In Russia, coal-bed methane is extracted mainly as by-product, in the existing mine fields, by mine degassing systems. The only exception is the joint innovation project of the Administration of the Kemerovo Region and Gazprom PJSC for the extraction of coal-bed methane in Kuzbass, where methane is recovered as an independent mineral [14]. Coal bed methane (CBM) is used in gas-fired power plants that provide electricity to manufacturing facilities [15]. Projects for capturing gas from the degassing systems of existing mines (methane type is CMM, coal mine methane), its recovery and use are implemented only by a few coal industry companies. In particular, in 2020, SUEK reclaimed 4.8 million m³ (equivalent to 67,651 tons of CO₂) of methane, which amounted to no more than 2% of total methane emissions. Higher rates were achieved at the enterprises of OA Vorkutaugol, where, according to data for 2018, 77.5 million m³ of methane was processed, which was equal to 73% of the total volume of degassed methane [16]. Sibur has outlined an environmental development strategy that includes a program for coal mine methane utilisation [17]. In Russia, methane recovered from the degassing systems of operating mines (CMM), as well as the CBM considered above, is mainly used for the generation of electrical and thermal energy.

In the gross structure of global greenhouse gas emissions, methane ranks second after CO₂ (Figure 9). Its annual volume released is equal to about 8046 Mt of CO₂ equivalent in total, with the coal industry contributing 967 Mt of CO₂ equivalent (12%) or 34.5 Mt of CH₄. As noted above, CH₄ enters the atmosphere from coal beds as a result of natural erosion, ground fissures or coal mining. It is believed [22] that 98% of the coal industry methane emissions occur during the underground mining. The contribution of the coal industry to the emissions of greenhouse gases other than CO₂ is 8.1% (Figure 10).
According to the International Energy Agency (IEA) figures over the year 2020, China ranks first in terms of methane emissions from coal industry facilities with 22.31 Mt [23]. Emissions in the Russian Federation are lower and reach only 5.7 Mt; still, they exceed coal industry methane emissions of the EU (2.74 Mt), USA (2.10 Mt), India (1.27 Mt), Indonesia (1.18 Mt) and Australia (1.13 Mt). Given the present-day rates of coal production, a further increase in the release of methane into the atmosphere can be predicted.

The target indicators of the environmental safety of the coal industry (CI) are set up in policy papers of the Russian Federation. According to [18], the emission factor of CI pollutants into the atmosphere in 2019 amounted to 2.5 kg per ton of production; of those, less than 5% of harmful substances were captured and neutralised.

According to the Global Methane Initiative (GMI) database, there are more than 300 coal mine / dump methane (CMM) utilisation projects [24]. These projects have different statuses (starting, operating, completed) and are being implemented in 15 countries of the world, of which China, the USA and Germany are the leaders. As of 2021, there were 260 active projects, of which 152 projects were related to CMM utilisation, 4 projects were related to VAM (coal mine ventilation air methane) and 104 projects were related to AMM (abandoned mine methane) (Figure 11).

Mainly, these are projects for CMM and AMM use for heat and power generation (Figure 11).

Low-concentration methane-air mixtures (VAM) are also used to generate electricity or, more often, are simply burned with the release of carbon dioxide into the atmosphere [20, 25–27]. For example, during coal mining in China, Shanxi Province, a number of projects (TUNLAN, MALAN, DUERPING) are being implemented to minimise coal mine methane (CMM, VAM) emissions and its optimal utilisation [28].

The principles of a multifaceted approach to efficient methane capture and recycle into energy through combustion are illustrated in Figure 12. We should emphasise that in this case, another greenhouse gas, CO₂, will enter the atmosphere instead of CH₄.

At the laboratory level, a number of VAM utilisation technologies are being developed (Figure 13), in particular, low-temperature and more environmentally friendly catalytic combustion processes [30–32].
Production of Hydrogen from Coal-Bed Methane

A distinctive feature of CBM is its significant flow rate fluctuations and composition heterogeneity. Methane content depends on the type of gas (VAM, CMM, AMM, CBM) and varies over a very wide range, which imposes certain restrictions on the use of traditional technologies employed in natural gas processing. Thus, there are two main options. The first is conditioning (purification, concentration) of the gas until it becomes suitable for further chemical processing by traditional methods to produce hydrogen. The second option is the processing of the existing methane-air mixture.

The first option can be implemented for gases with high methane concentration (i.e. CBM, AMM). In this case, with rational methods of deoxygenation, separation and concentration, 100% gaseous methane is obtained, which can be pumped into an existing natural gas pipeline or chemically processed by conversion into useful products, primarily hydrogen, or into synthesis gas, carbon nanomaterials, C1 oxygenates, C2 and aromatic hydrocarbons (Figure 14) [33–42].

The second option is for obtaining hydrogen from less methane-concentrated gases (SMM, AMM) and it will require development and mastering of technologies for processing gas of variable composition, including methane (30–80%), air, water vapour, and carbon dioxide. This option is attractive because, in essence, there is a reaction mixture containing methane and oxygen, and the most promising methods in this case are the methods of partial and combined catalytic reforming of methane into a hydrogen-containing gas. An extremely important issue of today is the development of catalytic processes that will provide high and stable conversion of a methane and air mixture of variable composition [33, 34, 44–53, 35, 54–62, 36–42].
The production of hydrogen by decomposition of methane is an effective way to avoid releasing carbon dioxide into the atmosphere [44–56]. A huge amount of research has been devoted to this method and several innovative catalytic technologies are being developed, since the principal advantage of this method is the production of pure hydrogen with the simultaneous production of a wide range of unique carbon materials: carbon nanofibers (CNF), carbon nanotubes (CNTs), graphene, various types of amorphous carbon etc.

The opportunity of obtaining hydrogen and the second useful product, graphene, via methane pyrolysis in an electric arc plasma has been considered [67, 68]. Among the advantages of the method, the authors mention the possibility to use CBM as a raw material without its preliminary purification. The method allows for the presence of small impurities of nitrogen and carbon dioxide; in the plasma, those are effectively converted into active radical species, which, in turn, have some catalytic effect in the conversion of CBM (Figure 16).

Lots of studies are devoted to the production of hydrogen. Catalytic systems based on wastes (by-products, semi-products) of the coal industry look advantageous from the point of view of creation of low-waste technologies [69–71]. For instance, a strategy has been proposed for preparing Ni/C catalysts for methane decomposition by adding nickel oxide and K$_2$CO$_3$ during the steam gasification of coal char (Figure 17). Gasification yields Ni0 nickel crystallites, with the concurrent production of hydrogen rich gas and nickel-carbon composite materials. In general, these catalysts achieve high methane conversion (up to 80–87% at 850°C) with the combined formation of hydrogen and filamentous carbon.

**METHANE DECOMPOSITION**

To obtain hydrogen from highly concentrated coal bed gases (CBM, AMM), it is advisable to improve the gas quality by removing impurities (e.g. nitrogen, oxygen, water vapour, carbon oxides), which will make it possible to process them by standard gas chemistry methods. The most technically challenging stage, namely separation of methane from nitrogen, is possible with molecular sieves, pressure swing adsorption (PSA), solvent absorption, cryogenic or membrane technologies [63]. Following the removal of nitrogen, the most technically complex and expensive procedure is the removal of oxygen, deoxygenation. Commercial technologies are available for extraction of carbon dioxide from coal-bed gas, including amine scrubbing, membrane technology, and selective adsorption. Dehydration of coal gas is mainly performed on molecular sieves.

For purification and concentration of the ventilation air methane (VAM), special adsorbents are being developed that are distinguished by high capacity and methane selectivity, as well as by their resistance to water vapour (Figure 15) [64, 65].

Worth mentioning is the method of non-catalytic CMM deoxygenation by passing gas through heated dead rock, which allows simultaneous use of two types of coal mine by-products [66]. At higher temperatures, oxygen will interact with carbon contained in the dump waste and the intermediate product which primarily consists of oxides of silicon (23.8 wt. %), aluminum (17.7 wt. %), iron (0.8 wt. %) and titanium (1.0 wt. %). Both temperature and gas flow rate have been shown to affect deoxygenation efficiency. Complete removal of oxygen from the CMM simulating mixture (CH$_4$ = 43%, O$_2$ = 12%, N$_2$ = 45%) was achieved at a temperature of 650°C and a rate of 15 l/h. In this case, the loss of methane due to its decomposition amounted to maximum 0.2% [66].

**FIGURE 16.** Schematic representation of hydrogen production from coal-bed methane using rotating gliding arc (RGA) plasma.

**FIGURE 17.** Production of hydrogen by decomposition of methane on nickel-carbon catalysts obtained in situ during the steam gasification of coal char.
Methane reforming is one of the major traditional methods of hydrogen production in gas chemistry. It consists of three stages: (1) reforming of methane with the formation of a CO + H2 mixture (synthetic gas); (2) conversion of CO to obtain H2 and CO2; (3) purification from CO2. This is the cheapest and most energy efficient method, but in order to avoid CO2 emissions, capture and storage technologies will be required [72, 73]. Each of these methods has its own advantages and disadvantages and yields gas with different hydrogen content. As a rule the exact method is chosen depending on the further use of the resulting synthetic gas. From Table 1 it can be seen that the maximum hydrogen content is achieved in the case of steam reforming of methane, while the minimum content is achieved in carbon dioxide reforming.

### TABLE 1. H2/CO ratio in synthetic gas obtained through various methane reforming processes and its main applications.

<table>
<thead>
<tr>
<th>Methane reforming process</th>
<th>H2/CO ratio in the reforming gas</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming with further CO conversion with steam</td>
<td>&gt; 3</td>
<td>Production of H2 and ammonia</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>2~3</td>
<td>Methanol synthesis</td>
</tr>
<tr>
<td>Steam reforming or partial oxidation</td>
<td>2~2.5</td>
<td>Fischer-Tropsch synthesis for gasoline and light olefins production</td>
</tr>
<tr>
<td>Steam reforming or partial oxidation</td>
<td>1.7~2</td>
<td>Fischer-Tropsch synthesis for the production of paraffins and diesel fuel</td>
</tr>
<tr>
<td>Carbon dioxide reforming</td>
<td>≤ 1</td>
<td>Production of acetic acid and polycarbonates</td>
</tr>
</tbody>
</table>

### STEAM REFORMING OF METHANE

Steam reforming of methane (1) is an endothermic process carried out in the presence of catalysts at temperatures of 800 to 1000°C, pressures of 0.3 to 2.5 MPa, and a high ratio of H2O to CH4 = 2.5~3.0. This process yields synthetic gas with a high hydrogen content H2/CO = 3. However, it has certain disadvantages, as it requires big capital investments, has low energy efficiency, and displays rapid catalyst deactivation due to coke formation and hydrogen sulfide poisoning.

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_{\text{298}}^{\text{o}} = +226 \text{ kJ/mol}
\]

Despite the fact that the process of hydrogen production by steam reforming of methane has been successfully put into practice, further work is underway to optimise the characteristics of the catalyst and the process as a whole. Advanced methods for improving the methane steam reforming process also include its coupling with CO2 adsorption [78, 79], the employment of microreactor units [80, 81] or chemical cycling technologies using complex oxide materials as oxygen carriers instead of molecular oxygen from the gas phase: LaFe1-xCoxO3 [82], Ce-Fe-Zr-O/MgO [83], Fe 2O3/Al2O3 with additions of Ce and Ca [84], SrFeO 3-δ [85]. In [86], calcite modified with nickel and iron was proposed as an affordable and efficient oxygen carrier. As seen on the diagram in Figure 19, during its reaction CH4 interacts with lattice oxygen CaFeO3 to form H2, CO2, CO and C. The process yields a mixture of CaO and Ni3Fe, whose oxidation closes the cycle. The treatment of oxide materials in the reactor with water vapour yields additional portions of hydrogen due to the conversion of carbonaceous deposits (3). A high selectivity of hydrogen production (93%) at methane conversion of 96% is reported.

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2, \quad \Delta H_{\text{298}}^{\text{o}} = -41 \text{ kJ/mol}
\]
The use of bifunctional materials with a core-shell structure, combining the adsorbent and catalyst features, for steam reforming of methane makes it possible to increase the yield of hydrogen and to reduce the carbon footprint of production [79, 87, 88]. CaO-Ca$_9$Al$_6$O$_{18}$@Ca$_5$Al$_6$O$_{14}$/Ni material has been developed containing 13 wt. % CaO, with a core-to-shell ratio (CaO-Ca$_9$Al$_6$O$_{18}$ to Ni/Ca$_5$Al$_6$O$_{14}$) of 0.2 (Figure 20). The material offers 100% CO$_2$ sorption within 60 reaction-regeneration cycles.

**Figure 19.** Flowchart of hydrogen production by steam reforming of methane in the chemical cycling mode.

**Figure 20.** Process design of bifunctional material and its mode of operation in the hydrogen process by methane steam reforming reaction.

The composition of CMM varies over a wide range, but its main components are methane and air, which is fully suitable for hydrogen production by the reaction of partial oxidation of methane. The partial oxidation of methane (4) is a weakly exothermal process ($\Delta H^\circ = -44$ kJ/mol), which is carried out over catalysts at temperatures of 800 to 900°C and pressure of 2 to 4 MPa. This process yields synthetic gas with molar ratio of H$_2$/CO = 2, which is favorable for its further conversion into methanol or hydrocarbons by the Fischer-Tropsch reaction, but not sufficiently advantageous in terms of hydrogen production. It does not require extra heat supply, but is characterised by low stability and safety due to the high probability of mixture ignition, the formation of overheating zones, sintering, and catalyst deactivation.

**Partial Oxidation of Methane**

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**Figure 21.** Composition of a two-layer reactor (a) for the conversion of a methane-air mixture into a hydrogen-containing gas and its principle of operation (b).

With catalysts, the process temperature required to achieve high methane conversion and product yields may be below 1000°C. To intensify the process, membrane reactors are being developed that combine the functions of air separation and catalytic partial oxidation of methane [91-94]. In this event, the air oxygen passes through the oxygen-permeable membrane and is used to oxidise methane, into synthesis gas and hydrogen was proposed [99]. Carrying out the CMM conversion reaction in a burner with porous filler ensures the simultaneous production of heat and hydrogen, which can be used as the main raw material for solid oxide fuel cells (SOFC) (Figure 21). Structural optimisation of two-layer “matrix” burners has made it possible to obtain gas with a maximum hydrogen concentration of 12.3% by means of partial CMM reforming. It was demonstrated [90] that the process efficiency depends on the geometry of porous fillers, flow rate, and the temperature of preheating of the reaction mixture. The efficiency of the device is approximately 50%.

**Equation 4**

$$\text{CH}_4 + 0.5\text{O}_2 \leftrightarrow 2\text{CO} + 3\text{H}_2$$

$$\Delta H^\circ_{298} = -44 \text{ kJ/mol}$$
A process of CMM oxidative conversion in an SOFC electrochemical cell with a catalytically active anode [95, 96], with the removal of oxygen from the CMM mixture by the PSA method was proposed to control the composition of the mixture and prevent the risk of explosion (Figure 23).


FIGURE 23. Flowchart of methane-air mixture (CMM) utilisation using SOFC.

methane to synthetic gas (Figure 22). The use of air reduces operating costs and minimises the hazards associated with the handling of pure oxygen. An additional advantage of catalytic membrane reactors is the uniform distribution of the temperature profile, which solves the problem of overheating the inlet part of the catalyst bed, where gas phase oxygen is consumed for the complete oxidation of methane.

A well-established approach is based on the in-situ formation of catalytically active particles by activating complex oxides in a reducing or reaction medium. The targeted thermal activation of complex oxides/hydroxides leads to the destruction of their original structure, and to nucleation, growth, and formation of metal nanoparticles and clusters stabilised on the oxide surface of the carrier (Figure 24).

FIGURE 24. Generation of catalytically active NiFeCo nanoparticles upon reduction of La (Fe,Ni,Co) O₃ for carbon dioxide conversion of methane.

An increase in the dispersion ability of the active component and the strength of its interaction with the oxide matrix of the carrier makes it possible to enhance the system resistance to carbonisation. A well-established approach is based on the in-situ formation of catalytically active particles by activating complex oxides in a reducing or reaction medium. The targeted thermal activation of complex oxides/hydroxides leads to the destruction of their original structure, and to nucleation, growth, and formation of metal nanoparticles and clusters stabilised on the oxide surface of the carrier (Figure 24).

Carbon dioxide (dry) reforming of methane (5) is an endothermic process carried out in the presence of catalysts at temperatures of 900 to 1000°C. Its essential advantage is the simultaneous utilisation of the two major greenhouse gases, CO₂ and CH₄.

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{\text{f}}^{\circ} = +261 \text{ kJ/mol} \]

(5)

Since this process is characterised by side reactions of carbon deposits formation which are more pronounced than those occurring in other reforming processes [6–9], catalysts with improved composition and structure are being developed to reduce the deactivation rate [97].

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{\text{f}}^{\circ} = +74.6 \text{ kJ/mol} \]

(6)

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad \Delta H_{\text{f}}^{\circ} = -172.5 \text{ kJ/mol} \]

(7)

\[
\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \quad \Delta H_{\text{f}}^{\circ} = -131.3 \text{ kJ/mol} \]

(8)

\[
\text{CO}_2 + 2\text{H}_2 \rightarrow \text{C} + 2\text{H}_2\text{O} \quad \Delta H_{\text{f}}^{\circ} = -90.1 \text{ kJ/mol} \]

(9)

However, the process requires heat supply and can be complicated by a high rate of carbon deposits formation and catalyst deactivation. This technology, unlike steam reforming and partial oxidation of methane, is not yet employed on an industrial scale.
COMBINED METHODS

To overcome certain shortcomings inherent with the traditional methods of methane conversion, alternative combined methods for processing coal-bed methane are being developed. Under the 7th Framework European Program, Design and Manufacture of Catalytic Membrane Reactors by Developing New Nanoarchitectured Catalytic and Selective Membrane Materials (DEMCAMER), we have developed catalysts for autothermal reforming and dimerisation of coal mine methane [33, 34, 39, 40, 42, 57–62]. A large study cycle on catalytic membranes and micoreactors has been completed. Pilot tests of the ATR process with a PdNi/Ce0.5Zr0.5O2/Al2O3 catalyst developed by the Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences in a combined ATR and membrane reactor have shown hydrogen productivity of 650 to 850 Nm3/h.

AUTOTHERMAL REFORMING OF METHANE

Autothermal reforming of methane (ATR CH4) is deemed to be the most promising catalytic process for hydrogen production.

\[ 2\text{CH}_4 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{CO} + 5\text{H}_2 \]  

ATR CH4 is a combination of several exothermic (10-12) and endothermic (13) processes, which makes it energy efficient compared to other processes of methane conversion into a hydrogen-containing gas.

\[
\begin{align*}
\Delta \text{H}^{\circ}_{298} &= -35.6 \text{ kJ/mol}^{-1} \\
\Delta \text{H}^{\circ}_{298} &= -802 \text{ kJ/mol}^{-1} \\
\Delta \text{H}^{\circ}_{298} &= -41.2 \text{ kJ/mol}^{-1} \\
\Delta \text{H}^{\circ}_{298} &= 206.2 \text{ kJ/mol}^{-1}
\end{align*}
\]

Along with the optimum power balance, this process is characterised by a fairly high yield of H2 and by resistance to the formation of carbon deposits, due to the presence of oxygen in the reaction mixture. For this process, the methane-air mixture from the degassing system of the mine does not require special preparation, only water vapour dosage [99].

Topsoe offers SynCOR™ technology based on autothermal reforming [100]. SynCOR™ units are more compact compared to steam reformers. They can operate at a steam/carbon ratio of 0.6, which reduces capital and operating costs. Effective catalysts are being developed for better autothermal methane reforming performance in terms of hydrogen yield or volume concentration of hydrogen in hydrogen-containing gas [57–62].

Within the novel process flow of sorption-enhanced autothermal reforming, SE-ATR (sorption-enhanced autothermal reforming), methane is first recovered from the gas flow of the coal mine drainage system, and then it is reformed autothermally with CO2 capture (Figure 25). From the experimental results of the enrichment process [101] it is evident that a single-stage adsorption process involving carbon-containing sorbents can boost the concentration of the vent gas from 4.5% to 31.7%, and the concentration of methane, from 20.3% to 79.3% respectively. Autothermal reforming of a 30% CH4 and air mixture over a nickel catalyst, yields gas mixture with H2 concentration of about 45 to 47% (for dry gas).

STEAM-CARBON DIOXIDE REFORMING OF METHANE

Steam-carbon dioxide reforming of methane (14) is an environmentally friendly process making it possible to simultaneously utilise three greenhouse gases (carbon dioxide, methane, water vapour) and to produce hydrogen within synthetic gas (a mixture of H2 and CO).

Steam consumption within synthetic gas (a mixture of H2 and CO). The process is characterised by the possibility of flexible regulation of the H2/CO ratio by varying the feedstock composition CH4/CO2/H2O [102].

Linde is developing a DRYREF™ synthetic gas process powered by a BASF SYNSPIRE™ G1-110 catalyst. With DRYREF technology, production costs are significantly reduced due to steam consumption reduction.

FIGURE 25. Utilisation of CMM by ATR, with preliminary concentration of methane and in situ utilisation of CO2.
TRI-REFORMING OF METHANE

Tri-reforming of methane combining endothermic reactions of steam and carbon dioxide reforming with exothermic reactions of partial and complete oxidation deserves special attention. This method has a number of advantages, such as (1) high energy efficiency: energy costs are compensated by the intrinsic energy of the initial hydrocarbon feedstock; (2) good process versatility: by changing the ratio between the initial reagents, it is possible to obtain a product of a given component composition; (3) lesser coke formation as side process; (4) chemical utilisation of CO₂. Also of interest is the possibility of using carbonaceous materials for methane tri-reforming (Figure 26). For instance, a mixture of CH₄, CO, H₂, O₂, N₂ = 1:0.34:0.23:0.5:2.12 at 750°C in the presence of a 5% Ni@MWCNT/5%Ce catalyst increases conversion of the reagents, that is, 96.8% CH₄, 38.7% CO₂. The H₂/CO mole ratio in the reaction products is 1.9 [103]. In [104], CBM is modeled by a mixture with the composition CH₄/CO₂/H₂O/O₂/N₂=1.0/0.45/0.45/0.1/0.4. Its processing at 800°C in the presence of a Ni-Mg-ZrO₂ catalyst achieves a high conversion of methane (99%) and CO₂ (65%) with good performance in terms of H₂/CO = 1.5.


Another important aspect is the production of hydrogen by aromatisation of methane over zeolite catalysts [15]. From six molecules of methane, nine molecules of hydrogen are formed, together with one by-product benzene molecule which is a valuable chemical product. The non-oxidising nature of the process ensures high selectivity of the target products formation (minimum 70%). We have found that Mo-zeolite catalysts are the most active systems [106], and performed research in order to identify the nature of the active centers and to improve the catalyst formula with the aim to increase the systems' carbonisation resistance [35–38, 41, 43].

DEHYDROAROMATISATION OF METHANE

Very attractive is the method of coal mine methane co-processing with fossil coal. Hydrogen production via coal gasification is advantageous due to the low cost of raw materials, but is regarded as problematic due to the low H₂/CO ratio in the resulting synthetic gas yield. Therefore, modern applications are focused on the process of partial oxidation of coal to produce a gas mainly consisting of hydrogen and carbon monoxide (reactions 16–20) rather than on direct pyrolysis yielding a wide mixture of hydrocarbons (Figure 28).
For various grades of coal, i.e. those of different composition and, accordingly, different reactivity, the H₂/CO ratio of the gas obtained as a result of coal gasification will be in the range of 0.9 to 1.5 (Figure 29).

The research results [108, 110] have revealed that coal gasification in the presence of coal mine methane makes conversion of coal more efficient, yielding gas of optimal composition (H₂/CO = 2) for further use. At the same time, coal ash and coal char formed during gasification have a catalytic effect and increase the yield of products in methane reforming reactions. The diagram of the installation for coal gasification is shown in Figure 31. When coal is gasified with a mixture of H₂O+CH₄, a decrease in the molar ratio of H₂/CO [111] is observed. The composition of the hydrogen-containing gas obtained from coal is characterised by a high CO₂ content. This imposes restrictions on the use of standard cleaning methods, such as PSA method. Therefore, absorption of CO₂ and subsequent methanation of residual amounts of carbon oxides is considered as an effective approach [6].
CONCLUSION

Given the increasing role of hydrogen as energy carrier, coal industry has a very strong potential for its production. Coal bed methane is an important unconventional hydrocarbon feedstock with a high economic potential. In the recent years, research and development of technologies for production of hydrogen from coal mine methane (VAM, CMM, AMM and CBM), differing in methane concentration and methane-to-air ratio.

For highly concentrated CMM, AMM and CBM, methane (VAM, CMM, AMM and CBM), differing in production of hydrogen from all types of coal mine methane. We define the last two methods of hydrogen production as “Green Glus” grade, because, firstly, the method is “green”, as it does not lead formation of nanomaterials; (3) “Green Plus” hydrogen obtained by catalytic conversion of methane into hydrogen and benzene. We define the last two methods of hydrogen production as “Green Glus” grade, because, firstly, the method is “green”, as it does not lead formation of carbon dioxide, and secondly, it is “plus” because it yields additional valuable products, namely coal nanomaterials and benzene.

REFERENCES


be superfluous to recall that the combustion of oil and natural gas in energy consumption was primary energy consumed \[2,3\]. The share of coal, slightly decreased and amounted to 71.4 GJ of 75.7 GJ of primary energy. In 2020, despite the little more than 1% of the annual increase. Moreover, the past few years, it has been increasing by nearly 30-35% per year. It has been increasing by nearly 90-95 million people per year which accounts for a little more than 1% of the annual increase. Moreover, the world’s population is likely to cross the 8 billion mark in 2022.

Well-being of people living in the country, as a rule, tends to well correlate with per capita energy consumption. The more energy is consumed, the higher the standard of living and income of the population. At the same time, we should take into account a constant population growth throughout the world, and the fact that the new inhabitants of our planet would require new energy capacities. The world’s population stood at approximately 7.85 billion \[1\] at the start of January 01, 2021 and over the past few years, it has been increasing by nearly 90-95 million people per year which accounts for a little more than 1% of the annual increase. Moreover, the world’s population is likely to cross the 8 billion mark in 2022.

In 2019, each inhabitant of the Earth consumed 75.7 GJ of primary energy. In 2020, despite the COVID-19 pandemic, global consumption only slightly decreased and amounted to 71.4 GJ of primary energy released \[2,3\]. The share of coal, oil and natural gas in energy consumption was 84.3% in 2019 and 83.1% in 2020. It would not be superfluous to recall that the combustion of hydrocarbons releases carbon dioxide (\(\text{CO}_2\)) into the atmosphere in huge amounts accounting for billions of tons. According to the World Energy Agency, human energy activities result in over 30 Gt of carbon dioxide released annually into the air during the last decade \[4\].

The world’s population stood at approximately 7.85 billion \[1\] at the start of January 01, 2021 and over the past few years, it has been increasing by nearly 90-95 million people per year which accounts for a little more than 1% of the annual increase. Moreover, the world’s population is likely to cross the 8 billion mark in 2022.

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INTRODUCTION

Table 1 shows that nuclear power industry is a prominent player in the carbon-free electric power generation market. It should be noted that the low worldwide-average ICUF of wind and solar is due, among other things, to rapid growth of the installed capacity and commissioning work at new power plants. However, the weather dependency of the wind and solar plants requires either availability of the backup fossil fuel capacity with a reserve of hydrocarbons or availability of large, energy storage capacities which will inevitably increase the cost of the produced power.

So, the nuclear power generation is the one producing no greenhouse gas emissions during its fuel cycle and a mastered technology for power generation on an industrial scale.

Nowadays electric power is a versatile energy resource that can be generated in a variety of ways. The share of primary energy involved in electricity production in 2020 was 43% and has steadily been growing over the past decades. This figure is easy to obtain from BP reports \[2,3\] if you know the nuclear generation share in primary energy, which is calculated on the basis of the efficiency of the NPPs in operation, and the NPP share in electric power generation, calculated on the basis of generated power.

According to \[3\], 26.823 TWh of electric power was produced throughout the world in 2020, 10% of which - at NPPs. The RES share accounted for a little over 11% given that in terms of the installed capacity, RES is already more than four times the capacity of NPPs. The capacity growth of wind and solar power plants in the world over the past decade is very similar to the one of NPPs in the world from 1975 to 1985 \[6\]. During this period, the capacity of the installed power units was increasing by dozens of GW annually. The growth rate of NPPs capacity reached its peak in 1984 when over 30 new power units with a total capacity of more than 30 GW were put into operation. At the same time, we must take into account that the world population in 1975 climbed to a little more than 4 billion people, almost twice as less than in 2021. Therefore, the annual growth of renewable energy capacity at the level of dozens of GW does not seem to be surprising. Sooner or later, the growth rate will slow down. Various reasons will affect it: decommissioning of previously installed capacities, a decrease in the state support for the sector due to the limited funds, consumers’ dissatisfaction with a low installed capacity utilisation factor (ICUF) and weather dependable performance conditions, the price rise for materials and components, etc. In any case, it is desirable to have alternative energy sources, and in this context, politicians are increasingly turning to nuclear power as a reliable source of baseload power.

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Over the past decades, actually, all the experts have recognised the need to curb human-caused greenhouse gas emissions. In 2015, the UN developed the Paris Climate Agreement under which nations have committed to limiting their annual greenhouse gas emissions to the level of the early 21st century which requires development of carbon-free energy production. In 2020, the World Energy Agency published its outlook for reaching net-zero carbon dioxide emissions by 2050.

Recognising the importance of reduction of greenhouse gas emissions in the power industry, the issue of a new energy policy arises, the policy that will rely on carbon-free energy sources. One of the carbon-free ways of energy production is nuclear generation. High calorific value of nuclear fuel, which is a million times more caloric than fossil fuel, gives us hope that nuclear energy development will help humanity meet its energy needs without greenhouse gas emissions into the atmosphere.

However, the available technologies for power generation in thermal neutron reactors are not provided with fuel reserves making possible the development of a large-scale nuclear generation. According to IAEA experts, with regard to the current growth rates of nuclear generation, raw material reserves for thermal neutron power generation at using an open nuclear fuel cycle would last about 130-150 years \[5\]. Therefore, transition of mankind to large-scale nuclear power with the resources provided for thousands of years requires transfer to a closed nuclear fuel cycle and a new generation nuclear reactors with a fast neutron spectrum.

TABLE 1. Electric power generation by generation type.

<table>
<thead>
<tr>
<th>Source</th>
<th>Capacity 2020, GW</th>
<th>Generation in 2020, TWh</th>
<th>Average annual ICUF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydropower plants</td>
<td>1 330</td>
<td>3 147</td>
<td>27.0</td>
</tr>
<tr>
<td>Nuclear power plants</td>
<td>394</td>
<td>2 700</td>
<td>78.2</td>
</tr>
<tr>
<td>Wind power plants</td>
<td>733</td>
<td>1 591</td>
<td>24.8</td>
</tr>
<tr>
<td>Solar power plants</td>
<td>708</td>
<td>856</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Table 1 shows performance data of all power generation types in 2020 \[3\].
The content of the document is too long to be provided in this format. However, the text likely discusses the current state of nuclear power industry, focusing on recycling and reprocessing of spent fuel, and the development of new technologies for nuclear power generation. It mentions the potential for recycling uranium and plutonium, with a focus on the utilization of these materials in various reactor types, including fast reactors and water-water energetic reactors. The text also touches on the importance of energy security and the role of nuclear power in the world's energy mix, along with the challenges and opportunities presented by the evolving nuclear landscape.
natural or regenerated uranium. The use of this mixture will reduce consumption of the enriched uranium by about 25% for each fuel cycle [15].

It should particularly be noted that the technologies of the CNFC and fast neutron nuclear power generation must be able to compete economically with other ways of power generation. In all the above-mentioned projects, economic calculations occupy an important place and show that the cost of disposal of the irradiated fuel without its reprocessing and the cost of SNF reprocessing with a subsequent high-level radioactive waste (without uranium and plutonium) disposal are comparable, while the cost of electric power generated by new models of fast reactors is not higher than that of the power generated by fast-neutron reactors.

THE CONCLUSION

Closed nuclear fuel cycle technologies must be developed for creation of a reliable carbon-free energy future. Mastering of CNFC technologies and developing of two-component nuclear power generation will make possible elimination of coal and natural gas by the end of this century and provision of mankind with a reliable source of energy with a fuel base for thousands of years of operation.

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From consumer electronics to electric vehicles and grid storage, the market share of Li-ion batteries is quickly growing throughout the world. While this poses as mostly good news in terms of the electrification of various transportation fleets and its impact in slowing climate change, a rather lesser known problem of Li-ion battery waste quietly lurks in the wake of the expanding Li-ion battery production.

Although the use of Li-ion powered smartphones is ubiquitous in nearly almost every country for many years now, the newer Li-ion battery users, the EV market, requires a significantly larger mass of battery per consumer. Accordingly, with the seemingly inevitable growth of EV's market share and the associated production and decommissioning of old EV vehicles, the battery waste generated from Li-ion batteries derived from EVs are expected to grow very quickly in the coming years. If left unchecked, the waste generated will without a doubt, become a major environment and sustainability concern and directly conflicts with the entire initial motivation for the electrification of the transportation sector. Fortunately, the recycling of Li-ion batteries at various stages and with various techniques, is also steadily tracking the progress of Li-ion growth.

Each Li-ion cell is composed of various materials with varying value and impact on environment. The cathode and anode sheets are separated by a plastic membrane (separator), all of which, is soaked in electrolyte containing organic solvent and Li salt (as shown in Figure 1) [1]. The cathode sheet is composed of a Al foil coated with Li- transition metal (Co, Ni, Mn, Fe) oxides, conductive agents such as carbon black and carbon nanotubes and polymeric binder whereas the anode sheet is composed of a Cu foil coated with graphite, conductive agents and polymeric bind. The casing of cylindrical Li-ion batteries are typically made from stainless steel-based material. The most valuable parts of a Li-ion battery are the transition metal (Co & Ni) and Lithium in the cathode and the electrolyte salt. The battery industry is concerned about sustainability of both Co and Ni and its impact on overall cost of the battery when mass vehicle electrification take shape. Therefore, recycling not only address the accumulated waist from used battery but significantly impact the overall cost of the battery and insure sustainable availability of critical materials used in the cathode.

State-of-the-art Li-ion battery recycling strategies can be divided into two paths: 1) metallurgy-based and 2) direct recycling (schematically shown in Figure 2) [4]. Like most recycling process, there is a large trade-off between the cost and the recycling efficiency. The recycling efficiency is a function of the amount of value the recycler is retrieving from the battery. For example, in the case of direct recycling, obtaining regenerated LiCoO$_2$ powder that is ready for battery slurry formulation is more valuable than producing the Li and transition metal salts. The value is then balanced by the cost of the process both in terms of the environment and economics.
The more straightforward recycling strategy are the metallurgy-based processes. These are typically less involved and as such, are more scalable and easier to implement. The battery is first shredded mechanically and either heat treated (pyrometallurgical) and/or (hydrometallurgical) chemically treated. The premise of this method is to more or less dissolve the valuable metals in the batteries rather than separating the active material compounds. These metal usually include Co, Ni, and Li. The output of this metallurgical recycling is not a usable battery electrode but raw materials in the form of Li and transition metal salts/ alloy/ slags that can be used as feedstock in the battery active material manufacturing process. Unfortunately, this type of recycling is very costly in terms of its environmental footprint. The separation of the metal ions is usually achieved by the removal of carbonaceous compounds using thermal treatment. This produces a significant amount of toxic and carbon-positive off-gasses. The dissolution of the metal-ion are usually done in strong acid/alkali solutions that produce a significant amount of wastewater. Pyrometallurgical tend to be costly, which stems from the smelting process while hydrometallurgical is the cheapest.

Direct recycling typically involves the physical separation of battery components by human hands followed by the selective removal and regeneration of the cathode active material particles. Pursued by Argonne’s ReCell Center, this recycling pathway produces Li-ion battery active material that can be used directly in electrode laminates. Since the battery being recycled are obviously “used” with an expected high degree of performance degradation, a key step to human-directed recycling is to regenerate the active materials. For examples, used cathode materials such as LiCoO₂ typically degrades by losing its lithium content and phase change over the course of long cycling. To regenerate the LiCoO₂ layered structure, spent LiCoO₂ can be sintered with Li₂CO₃ (source of Li-ion) [2]. Performance can be expected to be upward of 95% of fresh cathode active material, making it rather promising. Although the output of this recycling process is at a high level of value (cathode active material rather than Li and transition metal salts), the added value might not be enough to compensate for the high cost associated with human intervention. The separation of battery components is very involved and not likely to be automated in the near future. Since active material is the retrieval target, the specific chemistry type and even separation of Cu and Al current collectors are necessary to prevent contamination. Accordingly, the cost associated to this direct recycling is currently considered high.

There is also a third type of recycling “technology”. Grid storage has a lower standard for energy density but instead, focusses on the cost of the battery. Reusing/refurbishing old battery cells from electric vehicles and reselling them at a significantly lower cost for grid storage is also a possible avenue of recycling. Obviously, this type of recycling (“second life”) is not fundamentally a material recycling and can be seen as more of a means to extend the battery service life. Ultimately, the battery will eventually underperform even for grid storage application and will be classified as battery waste, and fed into a recycling process. However, it still does significantly alleviate the environment stress that Li-ion battery waste creates [3].

**ECONOMICS OF RECYCLING**

The aforementioned recycling technologies are critical in ensuring the sustainability of Li-ion batteries. Like most engineering problems, it is not technically challenging to recycle Li-ions. The difficulty lies in doing so at a profit margin that make it economically viable. A recent study by Offer et al conducted a techno-economic analysis of a lithium-nickel-cobalt-aluminum oxide recycling plant in the United Kingdom[5]. Main cost contributors for every recycling process include: utilities, labour, materials and overhead expenses (such as maintenance, rent, etc.). The cost of the recycling varies between the recycling technologies. Pyrometallurgical processes would result in a higher utilities cost. Interestingly, the transportation of the used-Li-ion batteries incurs a large cost to the recycling process.

The revenue was found to be higher for direct recycling processes, which is expected due to the higher value of the recycling product. Also expected is the strong correlation of the revenue with the amount of Co in the battery. In fact, Co and Ni make up the majority of the revenue from the direct recycling process. Currently, there is a global notion of moving towards low-Co cathode throughout the Li-ion battery field to increase the sustainability of Li-ion battery raw material mining. This might, ironically, negatively affect the profitability of recycling facilities and delay the creation of recycling capacity throughout the world. The dynamics of this relationship are unclear. The next most impactful source of revenue is Cu, which represent about ~15-20% of the revenue (depending on Co content in cathode) in the direct recycling process. While the Cu current collector is not as critical for Co-containing-direct battery recycling processes, pyro metallurgical process of Co-free cathode such as lithium iron phosphate almost entirely rely on the Cu revenue, representing ~100% of the revenues. The profitability of Li-ion battery recycling is heavily dependent on the market prices of the transition metal retrieved, especially Co.

Beyond the recycling technology used, one major recycling cost contributor is the transportation cost of delivering the spent battery from its drop-off point to the recycling facility. Long range transportation incurs a very high cost due to high safety requirements for transporting Li-ion batteries. Sorting of the batteries is also a critical problem that incurs cost. Standardisation of battery systems will assist in the development of cheaper and more scalable direct recycling processes. For example, a simple battery identification tag that contains its material list and recycling protocol. This can be used for assisting recyclers in implementing an automatic battery sorting process, allowing for recycling centres to accept varying battery technologies from the consumer. Fortunately, while there is a degree of variety in battery chemistries, they are mostly centered on materials that contain lithium, nickel, manganese, aluminum, and cobalt (at varying proportions), and lithium iron phosphate.
As the electrification of the transportation sector becomes more widespread, the production and subsequent waste generation from spent Li-ion batteries will start to take centre stage as one of the leading challenges in the industry. Accordingly, the recycling of Li-ion batteries is starting to gain immense traction to solve this problem of battery waste. While current techniques exist to recycle battery components, their scalability in terms of environmental impact and cost is unclear. Standardisation among battery packs could be an extremely helpful method to facilitate the downstream recycling processes. For example, introduction of a battery passport could help not only to state the composition of the battery and recycling recommendations, but also to help track the health of the battery through retrieving its complete service life. Such as battery identification systems is extremely valuable in first identifying if the battery is suitable for a second-life service role (such as grid storage) and also in allowing for automatic sorting for a recycling facility based on its composition and disassembly process. Furthermore, rises in raw material cost might give some leeway for direct recycling. As mining of transition metals and lithium will eventually taper off, their market price will increase. This might provide a stronger incentive for industry to invest more into recycling Li-ion batteries.

CONCLUSION

As the electrification of the transportation sector becomes more widespread, the production and subsequent waste generation from spent Li-ion batteries will start to take centre stage as one of the leading challenges in the industry. Accordingly, the recycling of Li-ion batteries is starting to gain immense traction to solve this problem of battery waste. While current techniques exist to recycle battery components, their scalability in terms of environmental impact and cost is unclear. Standardisation among battery packs could be an extremely helpful method to facilitate the downstream recycling processes. For example, introduction of a battery passport could help not only to state the composition of the battery and recycling recommendations, but also to help track the health of the battery through retrieving its complete service life. Such as battery identification systems is extremely valuable in first identifying if the battery is suitable for a second-life service role (such as grid storage) and also in allowing for automatic sorting for a recycling facility based on its composition and disassembly process. Furthermore, rises in raw material cost might give some leeway for direct recycling. As mining of transition metals and lithium will eventually taper off, their market price will increase. This might provide a stronger incentive for industry to invest more into recycling Li-ion batteries.
total CO₂ emission in 1900 worldwide (1.95 billion tons) [9,10], but it largely resulted from the COVID-19 pandemic which affected human life and economic activities in an unforgettable way. In a similar way, it is impractical to decarbonize the world’s energy systems solely through restricting human activities or lowering the well-being of human to mitigate the situation. Instead, developing carbon capture, sequestration, and conversion technologies that directly treat and utilise the anthropogenic CO₂ emission offers the most straightforward solutions to the problem, which is thus of immediate importance.

Among these techniques, carbon capture is the prerequisite for all downstream steps, including sequestration and conversion, one that determines the maximum throughput of the whole process. Generally, carbon capture involves the selective separation of CO₂ from a gas mixture and the collection of CO₂ in high purity, suitable for storage, transportation, and conversion.

The overarching challenge is the feasibility of rapid, large-scale development of such techniques around the world. In some cases, manipulation of the energy generation process generates high-concentration CO₂, already suitable for storage or utilisation. This is exemplified by oxy-fuel combustion, where oxygen or oxygen-rich air are used for the fossil fuel combustion, resulting in a flue gas mostly containing mostly CO₂ and condensable H₂O. [12] However, this process requires pre-combustion separation of oxygen from air, which is unavoidably another energy-consuming process. The adaptability of this technique to existing facilities are also relatively low. In most cases, the source CO₂ concentration is low, and the central challenge is the separation of CO₂ from a low concentration and release into a much higher concentration with minimal consumption of energy. In this contribution, we focus on discussing two most promising schemes of carbon capture – the separation of CO₂ from flue gas (post-combustion capture, PCC) and directly from air (direct air capture, DAC), as they exhibit the advantages in wide applicability – the ease of retrofitting into existing power plants (PCC) or the flexibility of location selection (DAC).

To unravel the separation challenge, we start by looking into the structure of CO₂. Gaseous CO₂ consists of linear-shaped CO₂ molecules with zero dipole moment. This results in a sublimation point of -78.5°C (194.5 K) and a 6.5 MPa (~64 atm) saturation pressure at 25°C, leaving the collection of low-concentration CO₂ through direct condensation in ambient conditions not feasible. Nevertheless, the polar C=O bonds (a σ bond and two π3/4 delocalised bonds) of CO₂ create partial positive charges (δ+) on the C atom and partial negative charges (δ-) on the oxygen, leaving the opportunities to utilise polar interactions to selective separate CO₂ through physisorption. The electrophilic character of the central carbon also renders CO₂ a slightly acidic molecule, thus chemical reactions between basic compounds and CO₂ can be employed for chemisorption (Scheme 1).

**SCHEME 1.** Illustration of Physisorption and Chemisorption of Carbon Dioxide.

Based on these, we discuss the development of sorbent materials for efficiently capture CO₂ from flue gas an air, focusing on how the challenge can be resolved with minimum consumption of energy. We then briefly introduce the concepts and procedures of common technical processes utilising these sorbents for PCC or DAC, commenting on their advantage and disadvantages in a general scheme. To conclude, we envision how reticular chemistry can potentially contribute to solving the carbon capture challenge through developing next-generation sorbent materials with optimal overall performances in terms of capacity, selectivity, regenerability, stability, and thus economic feasibility.

**PHYSIOSORBENTS**

Carbon-based materials used in PCC include activated carbon and carbon nanomaterials, generally characterised by high specific surface area and non-polar nature of the surfaces. Activated carbons can be obtained through pyrolysis (often combined with physical or chemical treatments) of inexpensive carbon precursors such as coal and biomass, allowing for wide availability and facile upscalability. Comparatively, synthetic carbon nanomaterials such as carbon nanotubes, nanofibers, or nanosheets, have higher structural uniformity, but are produced in higher cost and limited scales [17].

Generally, CO₂ interacts with the carbon surface majorly through van der Waals forces, rendering relatively lower uptake in flue gas-relevant conditions, which is further reduced in the presence of moisture. To improve this, various functionalities can be introduced through altering precursor compositions or chemical activation onto the carbon surfaces, which enhances the affinity through increasing binding energy (Figure 1).

Large-scale, fossil-fuel-burning facilities such as power plants are discrete point sources of CO₂ emission. Typically, a coal flue gas consists of 12–15% CO₂ in N₂, O₂ (3–4%), SOx, NOx at 25-40°C with various levels of humidity [13-16]. The CO₂ concentration in natural gas flue gases ranges from 3% (natural gas combined cycle, NGCC, 3-4%) to 10% (natural gas fired boilers, 7-10%) [16]. If the CO₂ in flue gas were released to the atmosphere, the CO₂ concentrations would drop by several hundred folds (0.04% in air) [5], which poses much higher demand upon the sorbents, including much stronger binding affinity to CO₂ and increased energy consumption per batch of regeneration. Thus, it is very meaningful to capture the CO₂ directly from the flue gas.

As such, compared to DAC, post-combustion capture scenarios allow the use of more available chemical tools to design and optimise sorbents toward cost-effective and scalable capture solutions, where both physiosorbents and chemisorbents can achieve considerable uptake of CO₂ in flue gas-relevant conditions. However, the other components in the flue gas have posed two major challenges to PCC sorbents: the material must be able to capture CO₂ in the presence of significant amounts of water vapour, and be regenerable over numerous cycles without losing capacity [6]. Therefore, an ideal CO₂ capture material would have a high capture capacity, high selectivity, low energy requirement, fast kinetics, and long cycling lifetime, which together are expected to reduce the unit cost of operation. We herein categorise post-combustion capture sorbents by the kind of major sorbent-CO₂ interaction (physisorption or chemisorption) and then provide brief introductions about their composition, as well as their advantages and disadvantages in terms of resolving these two challenges.
FIGURE 2. Examples of surface functionalities in porous carbon and their calculated binding energies to CO₂. Shown in the figure are DFT-optimised configurations of CO₂ adsorption on carbon clusters with different polar groups (cyan, C; white, H; blue, N; red, O; light green, K) and the corresponding contour plots of the differential charge density. The contour value is ±0.001 au. The purple and lime regions represent the charge accumulation and charge depletion regions, respectively.

Zeolites. Zeolites are a class of natural or synthetic crystalline microporous aluminosilicate structures, characterised by highly ordered, narrow pores with polar oxide surfaces, which strongly interact with CO₂ through polar interactions. In addition, the chemical compositions of the zeolites influence their CO₂ uptake capacity. Generally, a lower Si/Al ratio increases the CO₂ uptake performance, through increasing the negative charges of the backbone and subsequently the amount of extra-framework cations, typically alkali metal cations. These cations interact strongly with CO₂, which can be further enhanced through cation exchange to other alkali metal cations including Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ [21], or alkaline earth metal ions such as Ca²⁺ [22]. The strong cation-CO₂ interaction allows these zeolites to achieve high uptake capacity in low pressures of CO₂ (Figure 3) [23], and their rigid backbones supports numerous cycles of uptake and release without significant loss of capacity. However, these structures exhibit even stronger binding affinity to water, which competes with CO₂ and result in close-to-zero uptake of the latter under humid conditions and requires much higher temperature (>200°C) to regenerate. This limits the use of zeolites for CO₂ capture to rigorously dry conditions, such as pre-combustion capture of CO₂ from CH₄.

Metal-organic frameworks (MOFs). MOFs are a class of porous, crystalline, extended solids comprising metal ions or clusters and organic molecules linked through coordination bonds [24]. Physisorptive capture of CO₂ in MOFs mostly adopts two major mechanisms: open (coordinatively unsaturated) metal sites and polar interactions in micropores. The former, exemplified by Mg₂(dobdc) (Mg-MOF-74), utilises the strong electric field around coordinatively unsaturated metal ions to bind CO₂ with a high heat of adsorption (~40 kJ/mol in Mg₂(dobdc), Figure 4a) [25]. These frameworks are capable of capturing CO₂ even at elevated temperatures (60°C), but concomitantly require a regeneration temperature as high as 140°C for removal of CO₂. Moreover, many open metal sites are reactive to various species including water, resulting in reduced uptake and framework decomposition under humid conditions [26]. The second mechanism, exemplified by NbOFFIVE-1-Ni, feature micropores suitable for CO₂ to fit in, and polar functional groups cooperatively increasing the binding affinity toward CO₂ molecules (54 kJ/mol heat of adsorption in NbOFFIVE-1-Ni, Figure 4b) [27]. These frameworks exhibit less jeopardised uptake capacity under humid conditions compared to the former type, but many examples show slight reduction of performance over repeated cycling.
Amine-functionalised silica and resins. Combining the thermally-reversible amine-CO₂ chemistry with solid supports is of particular interests as it provides promising candidates that operates with lower energy consumption (lower heat capacity and water content), high stability, and facile handling [5,11,12]. Silica are highly porous structures with large pore volumes, allowing for physical impregnation or chemical functionalisation of amine species in considerable loadings [37-40]. Some solid resins contain primary amines themselves, thus suitable for CO₂ capture without further modifications, and can withstand long-term cycling in pilot-scale tests with only small reduction of performance [41,42]. Compared to bulk, liquid amines, surface supported amines are better exposed to the feed gas, and display characteristically enhanced CO₂ uptake under humid conditions. These materials are also DAC-capable, and their structures and chemistry are further discussed in Section 3.

Amine-appended MOFs. Coordinative binding of primary or secondary amines to the open metal sites of MOFs leads to the formation of amine-appended MOF complexes. In some scenarios, the metal-binding amines are innocent to CO₂ capture while other amines in the appended moieties react with CO₂ in the same way as amine-functionalised silica or resins (Figure 5a), such as a dry uptake of 6.06 mmol/g (15% CO₂ in N₂, 60°C) observed in Mg₂(dobdc)-TEPA-40 (TEPA, tetraethylenepentamine), and a further enhanced capacity of 8.31 mmol/g with heavy humidification, characteristic of the nature of its amine-CO₂ chemistry [26].

FIGURE 5. (a) Structure of mmen-Mg₂(dobpdc) (mmen = N,N′-dimethylentriamine; dobpdc = 4,4′-dioxido-3,3′-biphenyldicarboxylate) from single-crystal structure of its Zn analog, highlighting the CO₂ binding mechanism proposed at the terminal amine of mmen. (b) Depiction of the mechanism for CO₂ adsorption at four neighboring M-mmen sites within an infinite one-dimensional chain of such sites in a mmen-M₄(dobpdc) compound resolved from single-crystal structure.

Covalent organic frameworks (COFs). COFs are porous, crystalline, two- or three-dimensional extended structures built by linking organic building units through covalent bonds [28]. The majority of COFs are comprised of aromatic backbones that are relatively non-polar, similar to that of carbon surfaces but with higher pore uniformity as a result of crystallisation. However, COFs hold great potential of functionalisation through covalent organic chemistry, which provides opportunities to tune the pore environments, and more importantly, to introduce chemically reactive sites for CO₂ chemisorption while maintain robust chemical stability [29].

CHEMISORBENTS

Inorganic bases. Some reactions between CO₂ and strong inorganic bases such as hydroxides, oxides, and carbonates happen readily even in low CO₂ concentrations, thus they have been used to design chemical looping systems where hydroxide, oxide, or carbonate reagents react with CO₂ in the flue gas in a low-temperature reactor (such as a fluidised contactor), and the products (carbonate or bicarbonate) are then transferred to a high-temperature reactor (such as a calciner) to regenerate the reagent and collect CO₂. The regeneration step is energy-consuming as it requires heating up to 400–1000°C [30], and the solid management process in a multicomponent system likely requires more maintenance costs.

Liquid amines. The most common industrial CO₂ capture processes involve the use of aqueous amine solutions (such as 20–30 wt% monoethanoamine solutions) as a liquid absorbent to extract CO₂ from gas mixtures [31]. The chemistry primarily involves the carbamate formation and bicarbonate formation reactions, both reversible when heated:

\[
\begin{align*}
2R_1R_2NH + CO_2 & \leftrightarrow (R_1R_2NH_2)(R_1R_2NCOO^-) \\
R_1R_2N + CO_2 + H_2O & \leftrightarrow (R_1R_2NH^+)(HCO_3^-)
\end{align*}
\]

where \(R_1\) is -H for primary and secondary amines, and \(R_2\) is -H for primary amines [32]. The major challenge of this approach is the high energy consumption in regenerating such liquid sorbents due to (1) the high temperature required to reverse the CO₂-carbamate chemistry (typically over 90–100°C), (2) the high apparent heat capacity as a result of high water content, and (3) the high viscosity that impedes diffusion during CO₂ release [7-10]. The scrubbing process also suffers from reaction vessel corrosion and complexed handling of liquid chemicals.

Alternative absorbents include nonaqueous, low-vapour-pressure amines such as aminosilicones, which effectively reduces the energy consumption by reducing the apparent heat capacities [33-35]. However, the regeneration are carried out around >120°C, which still requires considerable energy. This also caused long-term amine volatilisation and degradation. Ionic amine species such as amino acid salts also provide viable solutions in reducing volatilisation, but the oxidative degradation remains issues to be resolved [36].

In other scenarios where CO₂ molecules were found inserted to the metal-amine coordination bonds to form metal carbamate complexes (Figure 5b), the heat of adsorption is drastically increased to 80–110 kJ/mol, resulting in a high CO₂ affinity even at elevated temperatures, a step-shaped isotherm, and the absence of a significant uptake increase in the presence of humidity [43,44]. The inflection step of the isotherm varies with the temperature, allowing for temperature swing adsorption (TSA) in a relatively small range. The unique mechanism also brings about disadvantages of the necessity of heating up to >140°C for regeneration, which requires the system to operate at high temperatures, where amine volatilisation, framework hydrolysis, and oxidation are likely to take place in a faster pace. Recent progress was made through appending tetramines with high boiling points into Mg₄(dobdc), which reduced the volatilisation while preserving the cooperative insertion mechanism [45]. Overall, the energy-demanding high operating temperature remains an issue to be resolved.
Amine-functionalised MOFs. Functionalisation of MOFs with covalently attached amine species provides solutions to resolving the disadvantages related to the weak binding of metal-amine coordination bonds. Through covalently binding amines to linkers [46,47] or strong-binding ligands during framework crystallisation or post-synthetically, amines are permanently bound to the frameworks and thus resistant to volatilisation and hydrolysis. With proper activation, the amine species are exposed to the pore surfaces and the amine-CO$_2$ chemisorption mechanism can be utilised for capture (Figure 6). The major challenge of covalent functionalisation of MOFs with amines is resolving the synthetic compatibility. For the introduction of amines prior to crystallisation, the amines or their precursors need to be compatible with the crystallisation of MOF [46,47], while for the post-synthetic modification approach, the framework needs to be stable in the amination conditions, which can be harsher than the operational conditions of CO$_2$ capture. With the rich library of organic synthetic tools, such as protecting groups and the control of chemoselectivity, this approach holds high promise for yielding highly stable, chemically tunable, amine-functionalised MOF sorbents toward post-combustion carbon capture.

**DIRECT AIR CAPTURE**

The major portion of anthropogenic CO$_2$ emission is from distributed sources such as residential utilities and transportation, or point sources that are unretrofittable or not yet equipped with post-combustion capture[7]. Therefore, direct capture of CO$_2$ from air is of immediate importance and plays a crucial role to achieve negative emissions. However, the capturing cost is still much higher than economic demand to date. The major challenge arises from the low feed CO$_2$ concentration (~0.04% in ambient air) that requires strong interactions, such as physisorption with large heat of sorption, or highly selective chemisorption, to achieve efficient capture. This is typically coupled with high energy consumption in cycling capture processes, which accounts for the major portion of the cost per unit CO$_2$ capture. Besides, the low CO$_2$ concentration also requires a much larger volume of air to contact the mixture for the same amount of CO$_2$ uptake. For example, comparing air (0.04% CO$_2$, 21% O$_2$, 50% RH assumed at 25°C) to NGCC flue gas (4% CO$_2$, 4% O$_2$, 100% RH assumed at 25°C), at least 100 times more volume of air needs to be treated, and moreover, 525 times more O$_2$ and 50 times more H$_2$O contacts the sorbent during this process. Compared to PCC, the capture rate (effluent/feed CO$_2$ %) is of less importance, which also results in more necessary volume of air to process per unit CO$_2$ capture. As a result, the sorbent's capabilities of maintaining their uptake performance in moisture and against hydrolysis and oxidation are undoubtedly crucial to DAC.

Overall, in the effort to achieve practical upscalability and economic feasibility, even stricter requirements on chemisorbent candidates are in terms of simultaneously improved capturing capacity, selectivity, energy consumption, kinetics, and cycling stability. We herein describe the most prominent classes of materials for direct air capture of CO$_2$ to date. Sorbent classes that have been introduced in Section 2 are left out to avoid repetition, or briefly discussed.

**Inorganic Bases.** The high reactivity of strong hydroxide bases with CO$_2$ makes it a useful process to capture CO$_2$ from extremely low concentrations. Adapted from existing chemical engineering process, a continuous adsorption-precipitation-calcination-regeneration process has been established first among the various DAC techniques.

**A representative solution is provided by Carbon Engineering Ltd., which has been upscaled to megaton scale (Figure 7) [48]. The process involves (1) capture of CO$_2$ from air with an aqueous solution containing 1 mol/L KOH and 0.5 mol/L K$_2$CO$_3$, (2) precipitation of the CO$_3^{2-}$ products with CaCO$_3$, (3) calcination of the product CaCO$_3$ to release and collect high-purity CO$_2$, and (4) hydration of solid CaO in step (2) to regenerate OH$^-$ [49]. The process is powered by either heat from the burning of natural gas (10 GJ/t) or electric energy (1.5 kWh/t), rendering a cost of $94 or $232 per ton of CO$_2$ capture. The hydroxide-CO$_2$ chemistry uses very inexpensive reagents to achieve highly efficient toward low-concentration (400 ppm) CO$_2$, which is supported by a heat of absorption value of 120 kJ/mol in a similar scheme using LiOH [27], but the process runs at a very high temperature for decomposing carbonate salts to regenerate the base. It would require a fundamental change of the chemistry to resolve this issue to further reduce the energy cost.
Amine solutions. Directly applying liquid amine scrubbing process to direct air capture provides a viable solution but with reduced capture rate and up to 60 wt% [52]. The morphology of the polyamines in sorbent, and in some cases occupying more than large amount, often achieving >10 mmol amines/g resin, Figure 8a). The polyamine can be loaded in the pores of meso- or microporous substrates adsorption (TVSA) cycling processes [57,58]. These has been employed by Climeworks for large-scale uptake capacity due to the reversible nature of scrubbing process to direct air capture provides a generally high regeneration temperature and applying lowest electricity and heat prices[30]. The energetics and costs are comparable to that of hydroxide process, and the most potential is in the optimisation of sorbent-air contacting and liquid handling.

Solid-supported amines/polyamines. Porous solid-supported amines are of the most developed class of DAC sorbents. To functionalise the pore surfaces with amine groups, three different strategies are used to produce three classes of supported amine sorbents (Figure 8a)[50,51]:

CLASS 1 consists of physically impregnated polyamines (such as polyethyleneimine, PEI) into the pores of meso- or microporous substrates (such as mesoporous silica, fumed silica, and resin, Figure 8a). The polyamine can be loaded in large amount, often achieving >10 mmol amines/g sorbent, and in some cases occupying more than 60 wt% [52]. The morphology of the polyamines in the pore surface also influences the CO₂ capture performance through influencing the kinetics. At a lower loading, the amines are possible to form thin layer due to strong intermolecular forces (such as hydrogen bonding) with the pore surface, while at increased loadings, the amines form aggregates, which significantly impedes the diffusion of CO₂ through the body of the viscous polyamine, affecting the apparent amine efficiency (defined as the molar ratio between CO₂ adsorbed and total amino groups in the sorbent) and thus the performance (Figure 8b) [53]. Upon contact with air, the amines chemically capture CO₂ through the aforementioned amine-CO₂ chemistry, which exhibits enhanced CO₂ uptake under humid conditions. The introduction of other functional groups by impregnating a mixture of polymers, such as polyethylene glycol (PEG) with PEI, helps modulating the polyamine layers and thus their CO₂ uptake [52]. Nevertheless, similar to other physically impregnated materials, the body of polyamines are not strongly bonded, of which the loss of amines or additive polymers are observed over the long run [52].

CLASS 2 includes complex sorbents where small-molecular amines are covalently tethered to the supports’ surface (Figure 8a). An example is the exchange reaction between (3-aminopropyl)triethoxysilane (APTES) and –OH groups on the silica surface [54]. By controlling the amount of the reagent, the amines are loaded only a single layer on the pore surface, largely alleviating the amine loss and diffusion issues. Nonetheless, the loadings of amines are lower than the polyamine method due to limited total surface area and –OH population of the support, as well as the limited amine-layer thickness after functionalisation. A generally high regeneration temperature and slight decrease of cycling capacities are still observed in experiments [55].

CLASS 3 contains the sorbents obtained by polymerising amines from the pore surfaces of solid supports, which features both high amine loading and covalent bonding between the body of amines and the support (Figure 8a). For example, this method can be achieved through ring-opening polymerisation of aziridines in silica to form hyperbranched aminosilica (HAS) [56]. Experiment showed that increasing the extent of polymerisation increases the DAC CO₂ uptake in humid conditions, but the adsorption halftime exhibits an increasing trend after significant accumulation of amines in the pores. It can be inferred that the diffusion of CO₂ is also impeded in the highly aminated samples, similar to that of Class 1 materials, while the most populations of the amines are secondary amines instead of primary amines, as a result of the ring-opening polymerisation.

Except for silica and resins, covalent amine functionalisation of cellulose fibers and aerogels also afford Class 2 or 3 sorbents with considerable CO₂ uptake in DAC-relevant conditions. The former has been employed by Climeworks for large-scale air contactors running in temperature-vacuum-swing adsorption (TVSA) cycling processes [57,58]. These sorbents exhibit considerable uptake performance of CO₂ from air and stability for cycling over 100 TVSA cycles. An existing issue is that these materials have very low densities of 40–60 kg/m³, resulting in a low volumetric uptake and extra contrator space required to contain, which also affects heat conduction due to the hollow nature of the materials.

MOFs. MOF sorbents employed in DAC so far include those with strong physisorption (such as NbOFFIVE-1-Ni) [27] and chemisorptive M₄(dobdc)/M₄(dobpdc)-amine complexes [43]. In both cases, the strong interactions between the framework and CO₂ are adequate to uptake CO₂ from DAC-relevant concentration. Especially Class 2 or 3 sorbents with highly ordered crystalline structure, these sorbents possess amine (or metal-amine complex) species in more uniformed chemical environments, thus promising for achieving uniform capture and release with high efficiency. In most cases, the pore apertures of MOF sorbents are only a few nanometers, much smaller than mesoporous silica, which likely have slower diffusion comparatively, but more examples and further observations need to be examined to reveal this relationship.

FIGURE 8. (a) Representations of the three classes of amine adsorbent materials. (b) Schematic of a SBA-15 morphology with various PEI-filling motifs. PEI may fill the pore (i) conformally, (ii) in aggregates, (iii) or as a mixture of these modes.

CAPTURE PROCESSES

The dedicatedly designed sorbents for CO₂ capture, especially solid sorbents for direct air capture, mostly cost much higher than common chemical reagents such as KOH, which are thus much suitable for repetitive use through cycling processes to dilute the materials cost per unit volume. Cycling processes typically involve two or more steps of operations to carry out the adsorption and desorption/regeneration in batches. Judging by the major driving force of the regeneration, the most prevalent cycling processes include temperature swing adsorption (TSA), pressure swing adsorption (PSA), and vacuum swing adsorption (VSA), and combined driving forces such as the aforementioned temperature-vacuum swing adsorption (TVSA).

TSA involves an adsorption step at a lower temperature and regeneration at a higher temperature in an isobaric environment. For strong physisorbers or chemisorbents, CO₂ is released at a lower temperature and regeneration at a higher temperature. For weak physisorbers, CO₂ capture mostly cost much higher than common chemical reagents such as KOH, which are thus much suitable for repetitive use through cycling processes to dilute the materials cost per unit volume. Cycling processes typically involve two or more steps of operations to carry out the adsorption and desorption/regeneration in batches. Judging by the major driving force of the regeneration, the most prevalent cycling processes include temperature swing adsorption (TSA), pressure swing adsorption (PSA), and vacuum swing adsorption (VSA), and combined driving forces such as the aforementioned temperature-vacuum swing adsorption (TVSA).

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118


INTRODUCTION

Microgrids as "sections of electricity distribution systems containing loads and Distributed Energy Resources (DER), (such as Distributed Generators (DG), storage devices and controllable loads) can be operated in a controlled, coordinated way either while connected to the main power network and/or while islanded" [1]. In all definitions, the two distinct features that distinguish them from any distribution lines with DER, are their capabilities to: a) operate islanded, thus achieving increased reliability and resilience, b) appear to the upstream network as controlled, coordinated units.

These characteristics pose significant technical challenges to their operation and control [2], especially during the islanded mode of operation. Thus, the transfer from interconnected to islanded operation might face relatively large imbalances between generation and load, that have to be managed seamlessly by efficient demand participation and use of new technologies. Power electronics converters interfacing the interconnected DER allow the application of versatile solutions, e.g. they allow to relax the strict boundaries of voltage and frequency imposed mainly by the stability of directly coupled rotating electrical machines in large interconnected systems. This makes the operation of Direct Current (DC) and hybrid Alternating Current/ Direct Current (AC/DC) solutions viable alternatives for Microgrids. Nevertheless, the dominant presence of Power Electronics significantly increases control complexities. The absence of inertia and the speed of reaction open new stability problems and together with the relatively short lines of Microgrids structures increase considerably the difficulties of frequency and voltage control. The particular distribution network characteristics, e.g. the relatively large resistance to reactance ratios, lead to strong coupling between active and reactive power with important control and market implications, especially for voltage. As a result, a large number of technical solutions have been designed for the coordinated control of the interconnected DER, ranging from decentralised communication-free approaches to centralised ones, where decisions are taken at a central point [3].

Despite the technical challenges, the integration of Microgrids in the power system opens many opportunities, as widely recognised today by all involved stakeholders, namely, consumers, DER owners and Distribution System operators. The technical, economic, social and environmental advantages associated with Microgrids are increased energy efficiency, minimisation of overall energy consumption, reduced environmental impacts and improvements of energy system reliability and power quality thanks to their ability to switch seamlessly to islanded operation. From a microgrid point of view, benefits include reduced losses, support in congestion management, ancillary services in voltage problems and increased flexibility in planning by allowing cost efficient infrastructure replacement strategies, etc. [2]. Microgrids have gained increasing importance by their potential role in enhancing power system resilience against natural disasters [4]. Thus, in cases of extensive damages in the upstream network infrastructure due to extreme weather phenomena, like windstorms and floods, but also earthquakes, wildfires, etc, Microgrids can operate islanded supplying critical loads, reducing electricity outages to citizens and aiding system restoration. Microgrids are also perfect technical infrastructures to support Local Energy Communities and Local Markets operation.

LOCAL ENERGY COMMUNITIES – LOCAL ENERGY MARKETS

Local Energy Communities have a long tradition in European countries, e.g. Germany, Denmark, the Netherlands, Spain, etc. and other parts of the world in the form of local cooperatives that are involved in electricity production by RES and community district heating systems. Currently the role of active citizens, as prosumers that are able to shape their energy consumption profiles and produce their energy locally, is recognised as an important factor in the energy transition to a sustainable future. Local Energy Communities are an ideal means to facilitate and enhance this role. According to the EC Electricity Directive COM (2016) 864/2 a Local Energy Community is defined as an association, a cooperative, a partnership, a non-profit organisation or other legal entity which is effectively controlled by local shareholders or members, generally value – rather than profit-driven, involved in distributed generation and in performing activities of a distribution system operator, supplier or aggregator at local level, including across borders.

According to this definition, local energy communities can play simultaneously many roles in the electricity market, among others the role of retailer, producer, etc., enabling this way local pools of electricity exchanges and the operation of local or decentralised electricity markets. From the wholesale market and distribution grid operation side, local energy communities enable the aggregation and coordination of DG and a portfolio of flexible loads, acting essentially as brokers for their participation in the central energy market. Of course, their operational goals might differ significantly, a fact that dictates the investigation of the impact of different business models on the system economics and on the consumer revenues. It is obvious however that this role requires the optimal internal coordination of their energy resources and consumption, optimising...
the energy exchanges with the wholesale electricity market, which is one of the fundamental functions of Microgrids. From a market perspective, the Microgrid can be viewed as an aggregator of distributed energy resources operated behind a Point of Common Coupling (PCC). This concept is shown in Figure 1, with examples of controllable resources that may include Electric Vehicles (EVs), Energy Storage Systems (ESS), renewable (and small-scale conventional) DG units, flexible loads, but most importantly, the telecommunication infrastructure for coordinating all those resources.

From the overall market operation perspective, the formation of local energy markets applying decentralised techniques provides distinct advantages for a more efficient system operation. This is similar to the overall system control, as discussed in [3]. A decentralised market refers to a case where buyers and sellers have the ability to trade commodities directly with each other, without necessarily procuring them from the central market. In the economic sense, decentralised market structures can adopt fully decentralised, peer-to-peer (P2P) market models, where trades are conducted bilaterally without central control and local energy or community markets, where the main goal is the collective social welfare of the community, even at expense of some individual participants’ profits. Decentralised (peer-to-peer or local) markets, while not yet specifically regulated or widely facilitated by Distribution System Operators, are beginning to emerge as a future, viable development path. Perhaps the most glaring example is the proliferation of energy cooperatives/communities that have the ability to participate directly in the wholesale energy market. An energy community that can be seen as an aggregation of prosumers in the market layer, makes it possible to trade locally the energy that is produced and consumed and if required, represents an aggregation to the centralised market according to the objectives of the community. The operation of peer-to-peer markets brings multiple benefits to the members of the energy community, such as reduced costs for consumers, increased profits for producers and overall significant savings in the energy costs of the community.

Depending on the technological maturity of the Local Energy Community members and the grid’s infrastructure, real-time tools can be employed, such as advanced load and production forecasting techniques, energy consumption profiling, stochastic scheduling of the available resources, etc., that can increase the energy efficiency of each prosumer and of the aggregation in total. The necessary tools for this real-time, peer-to-peer energy trading and coordination, constitute a local trading platform that provides the required data access and facilitates the coordination of the peers, by providing and securing linkages between the local grid infrastructure, the prosumer’s energy gateway and the central market. Particularly relevant to the development and support of decentralised energy markets appear to be the emerging blockchain and distributed ledger technologies (Figure 3) [5-6]. Typically, blockchain technologies refer to distributed computer network protocols that can securely manage and maintain the data imported and processed by their users, without the need of a centralised authority. Cryptocurrencies applications are currently becoming more and more established, but the technology itself is not considered mature enough for large-scale energy trading due to various limitations. However, several of their advantages indicate a great potential for the development of decentralised trading platforms that is under investigation. Such characteristics comprise, the decentralised nature of the technology, the possibility for simplified development of economic settlement and automation protocols (without requiring third parties), the enhanced cyber security and for certain blockchain technologies, the possibility to preserve the privacy of user data.

**Blockchain Technology**

The blockchain was first introduced as the underlying technology of the digital cryptocurrency Bitcoin, as a way to eliminate the need of central financial organisations operating as trusted third parties, to secure the transactions [5]. Blockchain protocols ensure the security of the users’ transactions using various cryptographic mechanisms. Every transaction is digitally signed with the private key of the sender. All other nodes can verify the integrity and the validity of the digital signature through the sender’s public key [5]. A network user after creating a transaction transmits it to other nodes of the network. A valid transaction is then circulated to the whole network to be registered in a block and be finalised. This procedure is called mining and is performed by the nodes which support the network, called the miners. The Ethereum blockchain protocol can be used for the creation of “smart contracts”, that is computer code guaranteed to be executed in the exact same way by all nodes, enabling the creation of the so-called Decentralised applications (Dapps). The users can this way write their own code and develop their own applications for managing data in the blockchain. Ethereum can be seen as a state transition machine, where the “state” consists of objects called accounts and the associated data [6]. The smart contract code can be seen as an agent that is executed in the Ethereum Virtual Machine (EVM). EVM runs the contracts’ code after being first compiled into a low-level stack-based language called EVM bytecode. The EVM is a quasi-Turing Complete machine. It can execute any program, providing it with resources and memory. The calculations however are bound by one parameter, their execution cost. The reasons for penalising the computational steps are, amongst others, to motivate miners to support the network and to prevent malicious users from wasting network resources (e.g., through infinite loops). The unit by which the computational steps are measured is referred to as “gas” and is translated into actual monetary costs that the users need to pay for their transactions to be processed.
PRACTICAL EXAMPLES

Despite the promising perspectives of blockchain powered Microgrids, there are very few actual applications today. The most prominent pilot projects for community energy and peer to peer exchanges have been successfully run by the Brooklyn Microgrid in New York [7]. In this study peer-to-peer energy transactions, control of DERs for grid balancing, demand response, and emergency management have been implemented in a real physical microgrid on a platform, based on Ethereum and smart contracts. In Europe and most parts of the world such experiments are limited to pilot projects in the context of R&I projects and some are performed under regulatory exemptions or private microgrids. In the following, a simplified R&I experiment in a practical Microgrid with 6 DG units is presented to outline the approach and demonstrate its complexities. A key function for the overall optimal operation of a Local Energy Market within a Microgrid is Economic Dispatch of DGs using a decentralised solution. Among the large number of distributed optimisation models developed, a very popular method is the Alternating Direction Method of Multipliers (ADMM), which is based on the augmented Lagrangian function and duality theorem. ADMM decomposes a convex optimisation problem in simpler subproblems, which are coordinated through an aggregation step. The implementation of the ADMM algorithm in a blockchain environment can be applied in a typical Microgrid, as shown in Figure 4 and described in [8, 9]. Each DG unit is assumed to be equipped with a microcontroller able to interact with the blockchain. Each microcontroller solves the local optimisation problem, i.e., calculates its output power, so that the augmented Lagrangian is minimised taking into account the technical constraints of each DG unit. After the calculation of its power, each node stores this value in the smart contract deployed on the blockchain, by triggering a respective transaction. The smart contract also plays the role of authenticating the DG based on a lookup table, that contains the respective addresses. After the smart contract has received the local information for the production from all nodes participating in the procedure, it calculates its updated dual variable and Lagrange multiplier. Then, it checks for convergence, in order to inform the nodes that the problem was solved. If the problem is solved, then the optimal power output for every node is implemented, otherwise, every node reads from the smart contract the values of the dual variable and the Lagrange multiplier and continues the iterations in order to update its output power, until the optimum solution is reached. Figure 5 shows the production of the DGs after each iteration.

As discussed before, the smart contract plays the role of the data aggregator, but also of the authenticator. It is also able to perform simple calculations, and once the smart contract code is executed, the results of the global values, are openly available to each DG unit. The blockchain and the deployed Dapp provide a decentralised platform that securely coordinates and enables the economical operation of the DG units. Moreover, the results of the optimisation can be stored in the smart contract, offering transparency (possibly for future auditing) or even for triggering transactions that will transfer the actual funds at the later stage of economic settlement. As a protocol design choice, the nodes need to compete for writing their values on the blockchain, since the last node will pay a significantly larger fee. This motivates the nodes to follow the protocol minimising any possible delays (that could delay the execution of the whole procedure).

FIGURE 4 The blockchain-enabled decentralised Economic Dispatch problem.

FIGURE 5 Evolution of the output power of the DG units after each iteration.

CONCLUSIONS

The tremendous complexity in managing efficiently huge numbers of distributed energy resources makes the application of more decentralised or distributed control technologies particularly appealing. Decentralisation of the power system operation can effectively deal with these complexities, is more resilient to cyber-attacks and more robust to equipment or communication failures answering the challenges for transitioning to a fully digitised and sustainable power system. Microgrid, as the underlying technical infrastructure of Local Energy Communities is one of the basic building blocks of future decentralised energy systems. The operation of local energy markets in particular, increases the efficiency of the whole power system operation and empowers active consumers to assume a central role in the transition to sustainable energy systems. Emerging Blockchain technologies can decentralise the data management process, while offering a security and authentication layer for operating local electricity markets in the context of Microgrids. They avoid the need for a centralised responsible authority to secure the data and energy transactions and they promote high transparency and traceability. Blockchain powered microgrids based on peer-to-peer energy trading and optimal use of their distributed energy resources can increase market efficiency and aid power system operation. They disrupt however the current power system structures, since they critically challenge the traditional roles of today’s market players, including distribution system operators, retailers, suppliers, metering point operators and balancing groups. A new equilibrium to a more sustainable, secure, efficient and decentralised energy system needs to be sought for, while the practical limitations of using blockchain platforms in real-world implementations need to be further investigated.
REFERENCES


INTRODUCTION – HIGH ENTROPY ENERGY

Based on the laws of thermodynamics: the energy is transformed from concentrated and high quality fossil fuels into electric power, which is transmitted via cables to millions of homes and will eventually be dissipated into environment, becoming low quality and not readily reusable energy such as heat and mechanical turbulences. In other words, the energy is transformed from high quality sources into distributed and low-quality energy sources (Figure 1), which are referred as high entropy energy [1]. The high entropy energy is in the form of heat, wind, ocean water wave, human activities etc. Although the total amount of such energy is huge, it cannot be efficiently reused. Therefore, a disruptive technology is required for effectively harvesting such high entropy energy. Just using green and renewable energy may not meet the sustainable development of the world due to their instability and interrupters. The future of the world should be run by a conjunction of fossil energy dominated power grid together with the renewable/distributed energy dominated micro-grids.

FIGURE 1. Schematic diagram showing the transformation of energy from concentrated, high quality fossil energy into distributed and not readily reusable “high entropy” energy. Once there is fossil energy shortage, we will face a true energy crisis.
MECHANISM OF THE TRIBOELECTRIC NANOGENERATORS

The traditional approach for converting mechanical energy into electric power relies on the electromagnetic generator (EMG). EMG relies on the Faraday's law of electromagnetic induction and its output has the characteristics of low output voltage and high output current, because the output voltage is a product of the current and the inner resistance of the metal coils (Figure 2a). The output power of EMG is proportional to the operation frequency of the EMG, so that it is not effective for converting low-frequency and low amplitude mechanical energy into electric power.

A revolutionary approach is required for effectively harvesting low-amplitude, low quality and low-frequency high entropy energy to meet the needs of the world. Triboelectric nanogenerator (TENG) was invented for such purposes [1]. TENG utilises a conjunction of triboelectrification and electrostatic induction effects (Figure 2b), and it can convert any form of mechanical energy into electric power with high energy conversion efficiency. TENG has the advantages of low cost, easiness of fabrication, diverse choice of materials, and broad range of applications. [1,2] Using the electrostatic charges created on surfaces due to media contacts, a space variation in the arrangement of the electrostatic charges results in a displacement current that induces the flow of electrons connected to the two electrodes as driven by an external force. TENG is a field that uses Maxwell’s displacement current as the driving force for effectively converting mechanical energy into electric power/signal, regardless if nanomaterials are used or not.

FIGURE 2. A comparison about the mechanisms of (a) the electromagnetic generator (EMG) based on the Faraday’s electromagnetic induction law and (b) the triboelectric nanogenerator (TENG) that is based on a conjunction of triboelectrification and electrostatic induction effects. EMG has the characteristic of high current but low voltage, TENG has a high output voltage but low current. Both EMG and TENG can be applied in complementary.

The driving force for TENG is the Maxwell’s displacement current, which is caused by a time variation of electric field plus a media polarisation term. However, for power generation, the polarisation should include a term that is contributed by the mechanical strain/deformation owing to piezoelectric effect and/or triboelectric effect. Piezoelectric effect is about the crystal lattice polarisation of piezoelectric materials once they are subjected to having a mechanical strain, the anions and cations in the crystal will be polarised and distributed, respectively, at the two ends of the crystal along the polarisation direction. Triboelectric effect is about the electrostatic charges created on the surface of the media once they are in physical contacts. Such charges are usually created due to the movement of the media. In the case of TENGs, triboelectric charges are produced on surfaces simply due to contact-electrification between two different materials. To account for the contribution made by the contact electrification induced electrostatic charges in the Maxwell’s equations, an additional term $P_s$ is added in displacement vector $D$ by Wang [1,2], that is

$$D = \varepsilon_0 E + P + P_s$$

Here, the first term polarisation vector $P$ is due to the existence of an external electric field, and the added term $P_s$ is mainly due to the existence of the surface charges that are independent of the presence of electric field. Substituting Eq. (1) into Maxwell’s equations, and define

$$D' = \varepsilon_0 E + P$$

The reformulated Maxwell's equations are [3]:

\[
\begin{align*}
\nabla \cdot D' &= \rho - \frac{\partial P_s}{\partial t} \\
\nabla \times B &= \mu_0 \varepsilon_0 \frac{\partial D'}{\partial t} \\
\nabla \times E &= -\frac{\partial B}{\partial t} \\
\n\nabla \times H &= J + \frac{\partial D'}{\partial t}
\end{align*}
\]

The term that contributes to the output current of TENG is $\frac{\partial D'}{\partial t}$, which has been applied to simulate the output of TENG [1,2].

APPLICATION FIELDS OF TENG

Ever since its invention in 2012, a vast effort has been devoted worldwide to TENG research for demonstrating its applications in medical science, environmental science, wearable electronics, textile based sensors and systems, internet of things, security, and many more. The applications of TENG are summarised in Figure 3, as elaborated in following.

As nano- and micro- power sources for small, wearable, distributed and possibly flexible electronics, internet of things and sensor networks. Since the fast development of internet of things and sensor networks, all of the small electronics have to be powered. With considering their large mobility, harvesting energy from the environment is essential for the sustainable operation of these distributed electronics [3]. With considering the high output voltage and low output current of TENG, a power management circuit is required in order to effectively using...
As self-powered sensors, with a range of applications in internet of things and sensor networks. The development of artificial intelligence and big data rely on sensor networks that provide the huge data needed. But most of the sensors requires external power to operate. It is essential to have sensors that response to the environmental changes without power, e.g., active sensors. As for motion, vibration and triggering sensors, TENG can be an ideal choice, which produces output signals as it is mechanically triggered. The signals can be wirelessly transmitted even without an external power source.

**C. For blue energy.** Since TENG has an outstanding output efficiency at low-frequency and low impact amplitude in comparison to those for electromagnetic generator, it is unique for harvesting water wave energy from ocean. By integrating many units of TENG into networks, it is possible to harvest energy from ocean water waves, which is referred as the blue energy that is expected stable, dependent and sustainable.

**D. As high voltage sources.** Since a unique characteristic of TENG is high output voltage, it can be used in many occasions that requires a high voltage, such as driving electrostatics and excitation of plasma.

**E. As a probe for studying the charge transfer at liquid-solid interface.** By using the principle of a single electrode TENG, one can probe the charge exchange between a water droplet with a solid surface using the charge transport in TENG. This provides a basic tool for fundamental studies of liquid-solid interfaces.

**FIGURE 3.** Five major application fields of TENG covering flexible electronics, human-machine interfacing, robotics, wearable electronics, medical sciences, environmental sciences, defence, and blue energy.

**FIGURE 4.** Quantified triboelectric series for over 50 different polymer materials, which can be used for TENGs.

**CHOICES OF MATERIALS**

Triboelectrification is a universal effect that occurs anywhere and anytime for all the materials in solid, liquid, and gas states. Therefore, the choices of materials for TENGs are rather broad. We recently introduced a universal standard method to quantify the triboelectric series for a wide range of polymers. This method standardises the experimental setup for uniformly quantifying the surface charges of general materials. The normalised triboelectric charge density (TECD) was defined and derived to reveal the intrinsic tendency of polymers to gain or lose electrons. A table is given regarding the TECD of over 50 organic materials (Figure 4), all of which can be used for fabricating TENGs.
TENG has established the principle and technology road map as a new and distinct discipline in energy science, and has inspired a global effort for developing self-powered systems and sensors for environmental/infrastructure monitoring, national security, and wearable/flexible electronics. Major multinational corporations are investing extensively in this technology. The technologies originating from TENG have the potential of significant impact in addressing societal challenges such as those related to energy harvesting from large scale motions, security through embedded sensors, and human lifestyle and welfare with self-powered gadgets as well as medical devices. TENG sets a power technology for driving internet of things, robotics and artificial intelligence, which is referred to as the energy for the new era.

According to the retrieval results from Web of Science database by Jan. 25, 2022, the TENG research is being conducted by over 7200 scientists distributed in 800 units in 61 countries/region, which suggests the global impact of the TENG research and its innovation [Figure 5].

The areas to be impacted by TENG include but not limited to powering wearable electronics, touch sensors for robotics, sensors for artificial intelligence, air purification and degradation of pollutant molecules in water, implantable medical devices for health care, triggers and tracking systems for security, self-powered microphone, voice recognition and typing recognition, mobile powers for internet of things, and large-area harvesting energy from ocean wave as sustainable energy.

US-based IDTechEx company published a report on Triboelectric Energy Harvesting and Sensing (TENG) as transducers with $billions market by 2040. The report outlines many opportunities for commercialisation of the TENG technologies [1]. TENG is an important part of the distributed energy. According the BCC Research, the global market for distributed generation technologies will reach nearly $350 billion by 2040 [2].

The energy for the future may largely come from ocean. Ocean covers more than 70% of the earth's surface and there are exceedingly abundant resources in water. The ocean energy is regarded as an important renewable and clean energy source, which has been estimated to be totally over 75 TW (1 terawatt = 1012 W) around the world. Large-scale commercial applications of ocean energy, if possible, will bring huge changes for global energy structure, political balance, and economic and society developments. Ocean energy is typically regarded as having five specific forms, i.e., tidal energy, wave energy, ocean current energy, temperature gradient energy, and salinity gradient energy, among which ocean wave energy referring to the kinetic and potential energy from ocean surface waves exhibits advantages of high power density and wide distribution. The global power by waves around the coastlines worldwide has been estimated to be about 2-3 TW. Therefore, the wave energy is one of the key directions of ocean energy development. However, it has rarely been exploited.
due to lack of economical energy scavenging technologies.

Internet is one of the most important drive for today’s economy. Internet is not only for people-to-people, but also for people-to-object and object-to-object. Billions of moving objects around the world would be interconnected via wireless signals, and each need to be powered. This is the concept of distributed energy for sensor networks. Different from the traditional energy technology for concentrated power supply via cables, the newly distributed energy would involve energy harvesting from local area and used locally without long distance transmission. With considering the limited lifetime of batteries, building self-powered system would be vitally important. TENG was invented for harvesting mechanical energy from our living environment. TENG has a broad range of applications, which can be classified into four major areas: micro, nano-power sources; self-powered sensors, blue energy and high-voltage sources (Figure 6). We look forward to a great contribution of the triboelectric nanogenerators to the world energy technologies in many years to come.

REFERENCES

GEOTHERMAL ENERGY

INTRODUCTION

Geothermal energy belongs to renewable energy sources and is considered the most environmentally friendly type of energy since its generation does not lead to the emission of greenhouse gases as well as does not require large areas of land. Other advantages concern the possibility of continuous energy production, extracting energy anywhere on Earth, no need to store primary energy, and availability of an almost inexhaustible source of energy. Geothermal resources are divided into hydrothermal and petrothermal. Hydrothermal resources are enclosed in natural reservoirs and are represented by natural dynamic thermal energy carriers of the subsurface – geothermal fluids or geofluids (water, steam, and water-steam mixture). Their reserves are relatively small. Petrothermal resources (or deep heat) are a part of thermal energy that is contained in the skeleton of water-bearing rocks and practically waterproof dry rocks. Dry hot rocks are located at depths of 3-10 km (or deeper), and their temperature reaches 350°C. The reserves of exactly petrothermal energy are practically inexhaustible. However, the development of this type of energy is at the stage of scientific research and pilot projects due to the enormous complexity, comparable in scale to coping with thermonuclear energy. Geothermal energy is used both for producing electrical energy and supplying heat, including direct utilisation of heat. Geothermal energy is among the cheapest energy sources. Despite the obvious attractiveness, the contribution of Earth’s heat to world energy is negligible, which definitely does not correspond to its potential. In this section, geothermal energy development analysis is presented hopefully for the predominant contribution of this type of energy in the future, especially due to the need to make drastic decisions in the fight against climate change.
Subterranean heat is associated with the history of Earth's evolution [12,18]. Earth was formed 4.56 billion years ago by accretion of material from a protoplanetary disk, which contained a significant amount of short half-life radioactive elements. The release of heat due to radioactive decay and other processes led to forming a multi-layered planet with a hot liquid metal core (iron and nickel) inside which a solid inner core with a radius of 1,220 km and a temperature of 4,500-6,600 °C was subsequently formed. The outer liquid core stretches for approximately 3,480 km from the center of Earth, which makes it about 2,200 km thick. The temperature at the outer boundary of the liquid core lies within 3,700-4,500 °C. The internal structure of Earth is shown in Figure 2a. Outside, the core is surrounded by the mantle, which has a thickness of about 2,890 km and consists of molten silicate minerals and oxides. The temperature at the outer boundary of the mantle is 1,100 °C. A feature of the mantle is the presence of powerful convective flows forming convective cells. It is in this way that heat is transferred from the hot core to Earth's crust, which floats on the mantle. Earth's crust is of two types. The oceanic crust has a thickness of 6 to 10 km and is formed in areas where the ascending parts of convective cells in the mantle reach the surface. The continental crust, consisting mainly of granite and basalt, has a thickness of 30 to 60 km and contains a significant amount of long-lived radioactive isotopes of K, Rb, Th, and U. Approximately 60% of the heat flux that comes out of Earth's surface of the continents is generated by the radioactive decay of these four elements. The background heat flux, formed due to heat, stored in Earth's core is 40 mW/m². The average heat flux for the whole planet is 87 mW/m². Compared with the average energy flux from solar radiation over Earth's surface (341 W/m²), this is a very small value. However, for the entire surface of Earth, this heat flux is equivalent to a total heat output of more than 4.4 × 10¹³ W. For comparison, the total average power consumed by all human activity is approximately 1.8 × 10¹³ W. It is more important to note that in geothermal energy, heat is accumulated from volumetric underground reservoirs, rather than from the surface of Earth, which is much more efficient in terms of technology. The predominant heat transfer mechanism in Earth's crust is thermal conductivity.

Due to the complexity of Earth's structure, namely, the presence of convective cells in the mantle and moving tectonic plates in Earth's crust (Figure 1a), the heat flux on Earth's surface varies greatly (Figure 1b). The relationship between plate tectonics and heat on Earth's surface is fundamental. The main structural elements of plate tectonics are spreading centers, subduction zones, and faults (boundaries between tectonic plates). In Figure 1b, the brown line shows crust faults between tectonic plates. It can be seen that it is in these zones that the maximum heat fluxes – up to 350 mW/m² are observed. Such crust faults pass through (or along) well-known geothermal zones, involving Iceland, western North America, Indonesia, the Philippines, Kamchatka, etc. From the map indicating the location of existing geothermal power stations (Figure 6), it follows that most of them are situated in the area of crust fractures, or regions associated with subduction zone volcanoes and spreading centres.

Important characteristics for assessing geothermal resources are temperature distributions at different depths and the magnitude of the temperature gradient over depth. In Earth's crust, the average temperature gradient is 30 °C/km, and in the town of Larderello (Tuscany, Italy) it is an order of magnitude higher – 300 °C/km. An example of the temperature distribution at a depth of 10 km, which is already of interest for petrothermal energy, is shown in Figure 3 for the USA. As follows from the Figure, the entire Western USA has huge reserves of petrothermal energy with temperatures of dry rocks exceeding 250 °C. Such data form the basis for forecasting and developing geothermal energy.
GLOBAL PRACTICES IN DEVELOPING HYDROGEOTHERMAL HEAT

To date, only hydrogeothermal resources in the form of underground hot water and (or) steam are used on a large scale for energy needs. Electricity is produced at geothermal plants (GPP) at sufficiently high temperatures of the heat carrier. At a temperature of about 100°C, the geothermal heat carrier is used for direct heat supply, and at lower temperatures, it is necessary to employ heat pumps. Heat pumps are widely used for heating individual houses also by using ground heat, that is, not only underground water [15]. Geothermal heat utilisation methods are discussed in more detail in the following sections.

The first generation of electricity using geothermal steam was carried out in Larderello, Italy, in 1904. This year should be considered the year of the geothermal energy origin. Larderello is located in the province of Tuscany, which is characterised by significant volcanic activity. Here, Prince Piero Ginori Conti used a small steam generator, to lighten four light bulbs as part of a demonstration project (Figure 3a). In 1916, the generating capacity of 2,500 kW was already connected to the grid for the commercial supply of electricity to consumers. A general view of a modern GPP with a capacity of 100 MW is shown in Figure 3b (Reykjanes, Iceland). Data on the installed electric capacity of geothermal plants in the world are shown in Figure 4. Large-scale use of geothermal power plants began in the 1960s. At that, the generated capacity grew linearly with an increment of 250 MW per year (Figure 4a). Over the past five years, the increment amounted to 733 MWe per year (Figure 4b), which is much higher than the average in previous years. However, the share of geothermal heat in the global energy sector is still insignificant. Table 1 shows data on installed capacity and electricity production by GPPs in the top ten leading countries in 2020, as well as total figures. A total of 29 countries produce 95,098 GWh/year with a total installed capacity of 15,950 MWe. By 2025, 10 more countries will join, and the total capacity will increase to 19,361 MWe, by an average of 3.9% per year, which cannot be called impressive given the huge potential and undeniable advantages of geothermal energy. The undoubted leader in all indicators is the United States, followed by Indonesia, the Philippines, and Turkey. However, if talking about the contribution of subterranean heat to the national economy, the indicators here are completely different. For example, in Iceland, the share of electricity production at GPPs is quite noticeable amounting to 30%. In Russia, hydrogeothermal resources are huge and higher than the reserves of organic fuel by about 10 times. However, this potential is practically not utilised, since the installed capacity of the GPPs amounts to a negligible value of 82 MWe [23]. The global GPP arrangement diagram is shown in Figure 5 [19]. As already noted, GPPs are situated mainly in places of faults of tectonic plates and near foci of volcanic activity. Typical geothermal energy generation costs range from $1,870 to $5,050 per kilowatt. The levelised cost of electricity (LCOE) of geothermal power plants is 0.04-0.14 US dollars per kilowatt-hour [17].

FIGURE 3. Geothermal power plants (GPP): (a) Prince Piero Ginori Conti built the first GPP in 1904 at the Larderello dry steam field in Tuscany (Italy); (b) modern GPP with a capacity of 100 MW in Iceland.

FIGURE 4. Installed electric capacity of geothermal power plants in the world: (a) from 1916 to 2012; (b) from 2010 to 2025.
TABLE 1. Installed electric capacity and energy production at GPP in various countries in 2020.

<table>
<thead>
<tr>
<th>Country</th>
<th>Installed MWe</th>
<th>Energy GWh/yr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 USA</td>
<td>3 700</td>
<td>18 366</td>
</tr>
<tr>
<td>2 Indonesia</td>
<td>2 289</td>
<td>15 315</td>
</tr>
<tr>
<td>3 Philippines</td>
<td>1 918</td>
<td>9 893</td>
</tr>
<tr>
<td>4 Turkey</td>
<td>1 549</td>
<td>8 168</td>
</tr>
<tr>
<td>5 Kenya</td>
<td>1 193</td>
<td>9 930</td>
</tr>
<tr>
<td>6 New Zealand</td>
<td>1 064</td>
<td>7 728</td>
</tr>
<tr>
<td>7 Mexico</td>
<td>1 006</td>
<td>5 375</td>
</tr>
<tr>
<td>8 Italy</td>
<td>916</td>
<td>6 100</td>
</tr>
<tr>
<td>9 Iceland</td>
<td>755</td>
<td>6 010</td>
</tr>
<tr>
<td>10 Japan</td>
<td>550</td>
<td>2 409</td>
</tr>
<tr>
<td>TOTALS</td>
<td>15 950</td>
<td>95 098</td>
</tr>
</tbody>
</table>

FIGURE 5. The GPP arrangement pattern in the world.

Geothermal heat is widely used in heat supply systems both directly and using heat pumps [10,15,28]. It should be noted that for closed circulation systems, coolant circulation is possible even with disconnected pumps (residual flow rate effect [11]), which significantly increases the efficiency of geothermal installations. In 2015, the installed capacity of geothermal heat supply in the world amounted to 70.3 GW (of which geothermal heat pumps account for 50 GW, and direct heating = 7.5 GW), while heat generation reached 163 TWh/year (heat pumps = 90.1 TWh/year, direct heating = 24.5 TWh/year). Among the leading countries are China (installed capacity of 17.9 GW, heat generation of 48.4 TWh/year), the USA (17.4 and 21.1, respectively), and Sweden (5.6 and 14.4). Geothermal heat supply makes the greatest contribution to the economy in countries, such as Iceland, Japan, Sweden, Switzerland, Tunisia, Turkey, and the USA. In Iceland, more than 90% of buildings are heated by geothermal heat, and in Sweden, 20% of buildings are heated by geothermal heat pumps. The largest number of heat pumps are installed in the USA; in 2020, their total number amounted to two million (28 million are planned by 2050).

One of the main problems of using thermal waters is their high mineralisation, which reaches 200 g/l (and even 700 g/l) [4]. Natural waters contain six main ions, which include three anions, namely, chloride Cl—, sulfate SO₄²—, and hydrocarbonate HC₃O₃—, and three cations — sodium Na⁺, calcium Ca⁺², and magnesium Mg⁺². This results in intense processes of contamination and corrosion of equipment. However, brines from different deposits may contain valuable chemicals (lithium, rubidium, cesium, bromine, potassium, and others) that can be extracted on an industrial scale. This is especially true of rare earth elements.

PETROTHERMAL ENERGY

Undoubtedly, the greatest prospects in the future geothermal energy are associated with the development of petrothermal energy — deep heat, which is accumulated in dry rocks at technically accessible depths from 3 to 10 km [18,24]. Apparently, the idea of extracting geothermal energy from solid hot rocks was first expressed by K.E. Tsiolkovsky in 1897 and described in more detail in 1914 [14]. Tsiolkovsky considered the heating of water due to heat exchange with rocks having a temperature of 120°C at a depth of more than 4 km, and its circulation in two vertical channels. About the same time, the Hell Fire Exploration Project was developed, which was initiated in 1904 by Charles Parsons, the famous English engineer, and inventor of the steam turbine. The project provided for building a zigzag mine at a depth of 19 km to the high-temperature horizons of the subsurface. The first flow diagram of the geothermal circulation system (GCS) was proposed by academicians V.A. Obruchev in 1920 in his novel “Thermal Mine”. The first geothermal circulation system, extracting heat from layers with natural permeability was built in Paris in 1963. By 1985, 64 GCSs with a total thermal capacity of 450 MW provided heat to 154 thousand urban apartments.

The schematic diagram of the petrothermal energy utilisation is shown in Figure 6. Cold water enters the reservoir, situated in permeable hot dry rocks with a temperature of 120°C, and then heats up, comes out to Earth surface through production wells, and then enters the electric power plant in the form of hot water or steam. From the GPP the water returns to the injection well again, thereby creating a closed circulation system. Since natural permeability at great depths is rare due to the predominance of solid granite and basalt rocks, a need arises to create an artificial permeable reservoir. In 1970, the Los Alamos National Laboratory (USA) proposed a GCS with an artificial collector representing vertical cracks created by hydraulic fracturing in a monolith. In hydraulic fracturing, the bottom-hole pressure should be 1.8-2.5 times higher than the hydrostatic pressure. To prevent cracks, produced by hydraulic fracturing, from closing when the pressure decreases, they are fixed with a proppant, which is usually quartz sand with a fraction of 0.5-0.8 mm, pumped into the cracks by a viscous liquid. Similar hydraulic fracturing is also used in oil production, however, the water consumption in geothermal wells should be ten times greater than in oil production. This project was called Hot Dry Rock (HDR). It was implemented in the town of Fenton Hill in the Valles Caldera in New Mexico in 1973-1996. At the first stage of the project, two wells were successfully drilled to a depth of about 2,600 m. The wells were communicated through a rupture field in an artificially created reservoir and were capable of producing hot liquid at a temperature of 135-140°C with a flow rate ranging from 7 to 16 kg/s. A binary plant with a capacity of 60 kW was installed as a means of generating electricity from hot water circulating through the loop. During the second stage, two more wells were drilled at a distance of 50 m from each other. The deeper well extended to 4,390 m, where the temperature reached 327°C. Unfortunately, two new wells were not communicated, and it took a lot of effort to close the hydraulic loop. Thus, certain challenging problems of creating GCSs were identified. In particular, the standard method of hydraulic fracturing gave an insufficient number of cracks to achieve necessary permeability and good heat exchange. Therefore, further projects were oriented toward creating extensive reservoirs with many cracks arising by stimulating natural defects of the rock. Such projects are called Enhanced...
Geothermal Systems (EGS) [18,24]. The difference between HDR and EGS is shown in Figure 7. In total, about twenty experimental HDR or EGS systems were implemented, which confirmed the technological ability to extract deep heat from depths up to 5.1 km. The characteristics of the major projects are shown in Table 2. Among the participating countries are the USA, Japan, Great Britain, France, Germany, and Australia. Even small commercial stations were operating, such as Desert Peak Demonstration Project in Nevada with a capacity of 1.7 MW (since 2013) and Landau in Germany.


FIGURE 7. Types of circulation systems: (a) Hot Dry Rock (HDR); (b) Enhanced Geothermal Systems (EGS).

<table>
<thead>
<tr>
<th>Location</th>
<th>Years</th>
<th>Depth (m)</th>
<th>Temperature of Producing Fluid (°C)</th>
<th>Flow Rate (l/s)</th>
<th>Power (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton Hill, New Mexico</td>
<td>1972-1996</td>
<td>3 600</td>
<td>191</td>
<td>13</td>
<td>–</td>
</tr>
<tr>
<td>Rosemanowes, United Kingdom</td>
<td>1984-1991</td>
<td>2 200</td>
<td>70</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>La Mayet, France</td>
<td>1984-1994</td>
<td>800</td>
<td>22</td>
<td>5.2</td>
<td>–</td>
</tr>
<tr>
<td>Hijiori, Japan</td>
<td>1985-2002</td>
<td>2 200</td>
<td>180</td>
<td>2.8</td>
<td>–</td>
</tr>
<tr>
<td>Soultz-sous-Forêts (I), France</td>
<td>1987-1995</td>
<td>3 800</td>
<td>135</td>
<td>21</td>
<td>–</td>
</tr>
<tr>
<td>Soultz-sous-Forêts (II), France</td>
<td>1996-present</td>
<td>5 000</td>
<td>155</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>Landau, Germany</td>
<td>2005-present</td>
<td>2 600</td>
<td>160</td>
<td>76</td>
<td>1.5</td>
</tr>
<tr>
<td>Habanero, Australia</td>
<td>2003-present</td>
<td>4 250</td>
<td>212</td>
<td>30</td>
<td>1.5</td>
</tr>
<tr>
<td>Newberry, Oregon</td>
<td>2009-present</td>
<td>3 075</td>
<td>290</td>
<td>25</td>
<td>–</td>
</tr>
<tr>
<td>Desert Peak, Nevada</td>
<td>2002-present</td>
<td>1 800</td>
<td>200</td>
<td>32-101</td>
<td>–</td>
</tr>
</tbody>
</table>

The following conclusions can be drawn based on the analysis of Enhanced Geothermal Systems. Typical EGS must meet the following requirements: the well depth should be more than 3 km; the generated power – more than 3-10 MW; the temperature in the reservoir – more than 250°C; water flow rate – 50-100 kg/s; the service life – more than 25 years; the distance between wells – 0.5-2 km; and the volume of the underground permeable reservoir – 0.1 - 0.3 km³.

There is a range of technical problems:

- High drilling cost (growing exponentially with depth);
- Creating an underground reservoir with sufficient permeability;
- Uncertainty and short lifetime of a paired wells;
- Temperature drop over time (decrease in EGS efficiency);
- Low efficiency of heat extraction amounting to 1 - 5% of the available reserve;
- The need for water for EGS and its loss in the system;
- Creating a closed circulation system (drilling of subsequent wells);
- Induced seismicity;
- Corrosion of equipment due to HCl, H₂S, and carbonates.
The first two fundamental problems are the most important. Drilling wells is very expensive for any industry. More than 60% of the total capital expenditure for EGS may fall on drilling. Thus, the price of drilling a 10 km deep well is estimated at 15-30 million dollars. Typical parameters of a geothermal well are as follows: diameter at the well inlet - 500 mm, at the well bottom - 150 mm, drill penetration rate - up to 10 m/h. For monitoring purposes, so-called "microholes" with an inlet diameter of 120 mm, and 50 mm at the bottom, and a very high drill penetration rate of up to 60 m/h (1.5 km/day) have recently been applied. Placing geophones along the "microhole" allows conducting tomographic monitoring which is fundamentally important for decision-making on the construction of EGS. Thus, the search for new technologies for high-speed and cheap drilling is of fundamental importance for many industries. As a result of the implementation of the Department of Energy (DOE) Geothermal Energy Program, various technologies for drilling "microholes" were developed and tested in 2005-2007. These technologies include resonant drilling, high-pressure fluid enhanced cutting, and high-speed drilling at 5000 rpm. Laser and microwave drilling methods have also been considered but have not yet found application. Another technology could be based on using plasma to soften basalt rocks before drilling, but this approach is currently at the stage of scientific research.

Attention should be drawn to the low efficiency of heat extraction (just 1-5% of the available reserve) and the drop in the temperature of the heat carrier over time, which leads to a decrease in the efficiency of EGS. In this regard, the analysis of heat transfer in EGS is very important. Figure 8 illustrates the results of calculating the parameters of a GCS with several fractures for model conditions [1], which can be used for service evaluations. The following are shown in the Figure: (a) the heat carrier temperature at the outlet of the GCS with the number of cracks n and the flow rate of 43 m³/h; (b) the dependence of the GCS service life on the flow rate of the heat carrier at n = 5; (c) the dependence of the GCS capacity on time t at n = 5 and the total flow rate of the coolant, equal to 43 m³/h. It can be seen that the electrical power varies over time. Three phases of power change at a constant water velocity were identified in [20]: 1. constant power; 2. power decrease over time according to the law of t⁻¹/₂; 3. power decrease according to the law of t⁻¹. To increase efficiency, a strategy is proposed: at stage 3, reduce the speed of water pumping in order to reduce the power drop to the law of stage 2.

FIGURE 8. Parameters of the GCS under different conditions: (a) The temperature of the heat carrier at the outlet of the GCS with the number of cracks n and the flow rate of 43 m³/hour. Solid line — numerical computation, dashed line — analytical calculation; (b) The dependence of the GCS service life on the heat carrier flow rate at n = 5; (c) The dependence of the GCS capacity on time at n = 5 and the total flow rate of heat carrier of 43 m³/hour.

The following recommendations can be suggested to further develop EGS:

1. Creating integration programs for laboratory and field research, including experimental and theoretical studies, as well as numerical simulations to study heat transfer, permeability, mechanical properties of rocks, etc.

2. Applying and developing modern geophysical diagnostic methods, such as deep micro-drilling with sensors installed along the depth; visualising seismic data; carrying out electromagnetic monitoring; and applying tracer methods.

3. Interacting with traditional geothermal systems, especially in the field of power equipment (GPPs driven by dry steam and steam-water mixture, binary GPPs, and heat pumps), as well as with the oil and gas industry (exploration, drilling).
Let's highlight the undeniable advantages of petrothermal energy, which are not peculiar in other energy sources:

- Continuous energy production;
- Energy can be produced anywhere on Earth;
- The renewable energy source (RES);
- No environmental impacts;
- No emission of gases, including CO₂;
- No need to store primary energy;
- Energy production does not need large land areas;
- An inexhaustible source of energy;
- Cheap energy source.

Below are a few more facts to confirm the advantage of petrothermal energy. Using the example of the USA, it is shown in [24] that petrothermal energy just at depths up to 10 km contains 130 thousand times more energy than the annual energy consumption of the USA. With an extraction efficiency of 1.5%, this energy source will last for two thousand years, and if applying advanced technologies – for 20,000 years, even without taking into account its renewal. This leads to a global conclusion: petrothermal energy is enough to provide humanity with energy forever (taking into account the finite time of the existence of civilisations). As for prices, the same estimates [24] show that by 2030, it is possible to achieve a levelised cost of petrothermal energy (LCOE) of up to $69 million, which is at the level of the lowest indicators for the energy sector.

Although the above information concerns mainly scientific research and experimental setups, nevertheless there is no doubt about the reality of the large-scale application of petrothermal energy in practice. It is enough to cite the recently published impressive plans of the USA, the leader in this area, stated in the program “GeoVision: Harnessing the Heat Beneath Our Feet, 2019.” By 2050, it is planned to reach 60 GWe due to petrothermal sources. This will amount to 3.7% of the total installed capacity of the USA in 2050, and in terms of total energy production – 8.5% of all electricity generation in the country (20.4% of energy, produced by all RES). Moreover, ambitious targets concern direct use of heat – 320 GW instead of today’s 0.1 GW. The stated targets are confirmed financially – the federal budget for geothermal research in 2020 amounted to an impressive figure of $110 million, of which $69 million were allocated for petrothermal energy.

An unusual project, related to an attempt to use the heat of magma near active volcanoes is being implemented in Iceland under the name of Iceland Deep Drilling Project (IDDP) [6]. If successful, this project could open a new era in the development of geothermal energy. The main goal is to find out whether it is economically feasible to extract energy and chemicals from hydrothermal systems under supercritical conditions. To do this, it is necessary to penetrate an extensive reservoir with supercritical water with a temperature t = 400-600°C, located at a depth of 4.5 km. At the first well in Krafla with a depth of 2.1 km, superheated steam (with a pressure of 140 bar and a temperature of 450°C) was extracted at a pressure of 140 bar and a temperature of 450°C with a potential capacity of 40 MW(e). Thus, the world’s first Magma-EGS system (IDDP-1) was launched. However, the water reservoir was not very large, and therefore, a second IDDP-2 well was drilled in Reykjanes in 2017. As a result, supercritical conditions were achieved at a depth of 4,659 m at a temperature of 427°C and a pressure of 340 bar. According to a plan, a third IDDP-3 well will be drilled in the Hengill area. The possibilities of using magma heat and the analysis of volcanic activity are discussed in [21].

### Geothermal Heat Utilisation Methods

In the case of dry steam, the flow diagram for generating electricity is the simplest (Figure 9a), and the main problems are related to the corrosion of equipment [4,12]. For a liquid or two-phase medium, the technical solutions for organising a geofluid thermal energy conversion system into electricity are largely determined by medium temperature. In this regard, geofluids can be conveniently divided into five groups. Table 3 shows the most promising energy conversion systems for geofluids of different temperatures [24], although the classification may differ markedly from one author to another. Figure 11 shows the installed capacity of geothermal power plants of various types in the world and the USA.

#### TABLE 3. Methods of geothermal heat recovery.

<table>
<thead>
<tr>
<th>Geofluid temperature, °C</th>
<th>Energy-converting systems</th>
<th>Typical application</th>
<th>Working fluid</th>
<th>Cooling system</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>basic binary</td>
<td>the water of gas and oil wells</td>
<td>R-134a</td>
<td>water (evaporative condenser)</td>
</tr>
<tr>
<td>150</td>
<td>binary with recovery</td>
<td>the water of gas and oil wells</td>
<td>isobutane</td>
<td>air</td>
</tr>
<tr>
<td>200</td>
<td>binary or single-flash rapid boiling</td>
<td>enhanced geothermal systems</td>
<td>isobutane or geofluid</td>
<td>air or water</td>
</tr>
<tr>
<td>250</td>
<td>double-flash rapid boiling</td>
<td>enhanced geothermal systems</td>
<td>geofluid</td>
<td>water</td>
</tr>
<tr>
<td>400</td>
<td>single-flash or three-stage expansion</td>
<td>supercritical enhanced geothermal systems</td>
<td>geofluid</td>
<td>water</td>
</tr>
</tbody>
</table>

Binary systems-based GPPs are successfully used for low- and medium-temperature geofluids and will be discussed in detail below. At a geofluid temperature of 200°C and above, it is possible to use relatively simple single-flash rapid boiling stations. The schematic diagram of such a station is shown in Figure 9b. The process of rapid boiling-up consists in transforming a liquid under pressure into a two-phase liquid-vapor medium by sharply reducing the pressure below the saturation pressure. Geofluid flows from a geothermal well through a system of valves tangentially into a cyclone separator, where the liquid fraction is separated from steam. The liquid is returned to the underground loop through an injection well. Steam passes to the inlet of the turbine that drives the electric generator. Turbines must be made of corrosion-resistant steel due to the presence of gases, such as hydrogen sulfide in the steam. The pressure of saturated steam at the turbine inlet is 5-10 bar, which is significantly different from the conditions that occur at organic fuel-fired thermal power plants using highly superheated steam. This results in the emergence of a large amount of liquid in the turbine, which contributes to erosion on the turbine blades. Turbines for single-flash geothermal plants are usually manufactured with a capacity of 25-55 MW. After the turbine, the steam condenses in a surface condenser. Gases, such as CO₂ and H₂S do not condense in the surface condenser, increase the overall pressure, and reduce the operating efficiency of the turbine. They can be removed using steam injectors and vacuum pumps. Single-flash technologies are the dominant type in the global geothermal energy industry (see Figure 10a).
At a geofluid temperature above 250°C, a rapid boiling up double-flash geothermal power plant is used [12]. In contrast to the single-flash flow diagram, an instantaneous evaporation unit and a low-pressure steam line connecting the latter with the turbine are added to the double-flash flow diagram. The turbine has two inputs – for low pressure and higher pressure vapor. In such a flow diagram, two different turbines can be used. For a relatively high-power geothermal plant (55 MW and above), employing turbines with a double steam flow is considered a successful solution that allows significantly reducing the height of the outlet turbine blades. It is such stations that dominate among the flash-based technologies in the USA (see Figure 11b).

For the case where the geofluid has supercritical parameters, that is, a temperature above 374°C and pressure above 22 MPa, it is promising to use a three-stage expansion flow diagram in a GPP [24]. This flow diagram differs from the conventional double-flash flow diagram by adding a back pressure turbine at the inlet. Such a turbine is similar to the supercritical double-heating turbines, typical of fossil-fuel-fired power plants. It should be noted that this flow diagram requires a certain composition of steam to avoid problems with erosion of the turbine blades.

The schematic diagram of the basic binary GPP is shown in Figure 11a [12]. Geofluid is pumped into the evaporating heat exchanger from a geothermal well through the sand filter. In this device, the energy of the geofluid is transferred to a low-boiling working fluid. The vapors of the working fluid rotate the turbine with an electric generator. The waste steam enters the condenser, where it is converted into a liquid, which is pumped into the heater. The number of binary stations is growing most rapidly in comparison with other types of geothermal stations (see Figure 10). They are the most promising not only for geothermal energy but also for other industries where low-potential heat recovery is required since energy can be generated even at temperatures of the order of 70°C [8]. The main manufacturer of binary stations equipment is ORMAT (http://www.ormat.com/).

In the simplest and most common version of a binary power unit, the usual Rankine cycle for overheating steam is used, whose T-S diagram is shown in Figure 12d. Here, 1-2-3-4-5-6-7 is the working fluid cycle: 1-2 corresponds to compression in the pump; 2-3 – heating in the economiser; 3-4 – evaporation at a constant temperature; 4-5 – overheating in the superheater; 5-6 – expansion in the turbine; 6-7-1 – cooling and condensation in the condenser. The ТА-ТВ line shows the temperature change of the separated liquid, and ΔТ means the minimum temperature difference between the separator and the working fluid. The world’s first geothermal binary power unit was implemented according to this diagram at the Paratunskaya Geothermal Experimental Industrial Power Plant in Kamchatka, Russia in 1967 [12,22]. The binary unit with a power of 750 kW was operating using freon R12; the temperature of the separation liquid was 80°C (Figure 11b). Operational research was carried out in the period from 1967 to 1974 by the specialists of the Institute of Thermophysics, Siberian Branch of the USSR Academy of Sciences. Subsequently, new diagrams were developed and a wide variety of working fluids were used [7,12,27, etc.]. Despite a fairly large number of publications on binary cycles,
there is practically no information on the experience of commercial use of binary power units. Most of the works are devoted to theoretical studies of binary cycles. The greatest attention is paid to the selection of working fluid for the Organic Rankine Cycle (ORC), as the Rankine cycle is commonly called when using non-aqueous working fluids [2,3,7,9,27, etc.].

However, today the problem of choosing working fluids remains open for the following reasons. There is a huge number (more than a hundred) of potential liquids, which can be used as working fluids in the ORC. Implementing ORC requires a wide range of conditions, primarily associated with the temperature of the heat source. When choosing a working fluid, various selection criteria are applied, including thermal efficiency, exergetic efficiency, heat utilisation factor, heat exchanger area per unit of power, and efficiency. Depending on the criterion, the working fluids under consideration were ranked completely differently each time.

Among the most important characteristics of working fluid (WF) is the saturation curve. Three types of curves in the temperature-entropy (T-S) coordinates are distinguished: “dry” liquid with a positive slope of the curve on the right; “wet” liquid with a negative slope, dS/dT < 0, and isentropic liquid with an infinitely large slope, dT/dS → ∞ (see Figure 12a-c).

In the case of a “wet” liquid, the steam in front of the turbine should be overheated to such an extent as to avoid unacceptable droplet formation in the turbine. For this purpose, an expensive superheater is used (see process 4-5 in Figure 12d). It is recommended to maintain the steam dryness value at the turbine outlet at a level above 85% [7]. Isentropic and “dry” liquids do not require overheating; therefore they are more preferable for ORC. However, if the liquid is "too dry", the steam leaves the turbine significantly overheated, so additional heat removal is necessary before the condensation process begins (see process 6-7 in Figure 12d). A possible solution to this problem is using heat recovery in the cycle [3,16]. As for the steam overheating in front of the turbine, it has little effect on thermal efficiency. Therefore, for organic liquids, there is no need for excessive overheating [7]. Below are examples of various working fluids according to the classification, given in [27]: R21, R22, R32, R134a, R152a, R143a are...
allows significantly reducing the dimensions of the dual-fluid binary cycle where two interrelated working fluids are used at binary stations in Guatemala (Zunil, 20 MW), etc. Such technological flow diagrams are transferred to the liquid heat carrier in front of the turbine, taken away using an economiser, is irreversible losses are reduced and the efficiency of power plants is increased [12,13]. The most striking example is the so-called Kalina cycle, which uses a water-ammonia solution. This cycle has been successfully tested in several pilot projects. By comparing pure substances and their mixtures for subcritical and supercritical Rankine cycles, it is shown that non-azeotropic mixtures (for example, R134a/R32) demonstrate the best efficiency in supercritical conditions [9].

Below are several specific examples of commercial binary stations for which any data are known:

1. A double-cycle GPP in the USA [4] uses steam in the first cycle and isobutane — in the second cycle. Isobutane cycle parameters are as follows: the temperature of the separated liquid at the inlet is 167°C, at the outlet — 66°C, the temperature of saturated isobutane vapor at the turbine inlet — 125°C; the outlet — 60°C, the flow rate of the separated liquid — 278 kg/s; the flow rate of isobutane — 45 kg/s; the turbine power — 22.3 MW; cycle efficiency — 11.9%.

2. Geothermal Demonstration Power Plant [12]. In the early 1980s, the first station was built with a mixed coolant: 90% isobutane + 10% isopentane. A supercritical cycle at a pressure of 40 bar was implemented. At a separated liquid temperature of 182°C and a flow rate of 614 kg/s, the gross power reached 36 MW, but the net power was only 21 MW. Due to heavy losses, this station was shut down. In 1993, the second station was launched with 12 binary power units and a total capacity of 44 MW (31 MW net). Here, isopentane was used in the subcritical cycle. The separated liquid temperature was 165°C. The gross thermal efficiency reached 12.7%.

3. Geothermal Power Plant, Alaska [5]. The separated liquid temperature is 73.3°C, the flow rate — 33.4 kg/s. A supercritical Rankine cycle with a slightly overheated freon R134a has been implemented. The vapor pressure in front of the turbine is 16 bar, behind the turbine — 4.4 bar. Gross power amounts to 230 kW, net power — to 210 kW. The thermal efficiency is 8%.

Thus, the following conclusions can be drawn from the presented analysis:

1. Binary cycles occupy a leading position in terms of growth rates among energy technologies (both in geothermal energy and other energy sectors) being among the most promising technologies for future energy, especially for distributed generation.

2. The prevailing schemes of binary power units are based on the organic Rankine cycle (ORC) with several variations, including subcritical cycles with overheating, as well as supercritical cycles.

3. There is a huge variety of potential working fluids (many dozens) for ORC but only a limited number of fluids are used for commercial purposes. Preference is given to so-called "isentropic" as well as "dry" working fluids.

4. Due to many criteria for selecting working fluids and a wide range of conditions to be met, there are no universal working fluids like water in the heat power industry. In each specific case, it is necessary to perform multivariate optimisation studies to make a suitable choice of working fluids, as well as technological schemes and operating modes.
CONCLUSION

Geothermal energy is the most environmentally friendly and practically transition to green energy, it is necessary to solve the following key crucial tasks.

- Developing and providing large-scale application of geothermal heat pumps.
- Ensuring preferential development of binary cycles, including those for energy-saving problems.
- Developing deep heat, based on EGS as the most promising type of geothermal energy.
- Extracting valuable chemicals, especially rare earth elements from thermal water.
- Developing advanced efficient drilling technologies that can have revolutionary significance not only for geothermal energy but also for many other industries.
- Developing and applying geophysical diagnostic methods.

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EXTRA: MODERN METHODS AND TECHNOLOGIES TO ENHANCE SAFETY AND EFFICIENCY OF HYDROCARBON ENERGY

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INTRODUCTION

The main task of the energy industry development is to improve safety and efficiency of the already existing technologies, as well as to develop and introduce new ones. Thus, energy transition and the fourth industrial revolution are already a reality. This chapter looks at certain promising technologies for the storage and use of hydrogen along with the smart gas pipeline project in terms of their implementation feasibility, advantages and disadvantages.

SCOPE OF APPLICATION OF THE PROMISING ENERGY CARRIER

Hydrogen is a special, universal type of energy resource: it is used in various technological processes, both as fuel feedstock and as independent environmentally friendly fuel. When hydrogen is burned, it yields only water; thus, hydrogen energy might be the most advantageous way to solve the global environmental issues. That is why investments in the development of this industry should be encouraged.

One of the most promising segments of hydrogen application is road transport. The present-day trend of reduction of CO₂ and other atmospheric emissions makes using hydrogen as an alternative source of automotive energy highly relevant.

In transport industry, hydrogen is primarily used in fuel cells. Those are devices that efficiently decompose hydrogen-rich fuel into direct current and heat through an electrochemical reaction. Cars with fuel cells have higher efficiency compared to cars with internal combustion engines: 39 to 43% and 23 to 27%, respectively [1].

Rail transport is expected to be the next segment in terms of demand for hydrogen and fuel cells.

In the meantime, the “marine transport” branch has started developing engines that run on hydrogen and ammonia. Thus, the International Maritime Organization (IMO) aims to reduce the carbon intensity of shipping emissions by at least 40% by 2030, and 70% by 2050. The annual energy requirement in shipping is about 12 EJ (3333 TWh). It is clear that cryogenic hydrogen and ammonia are the two most promising maritime fuels. The internal combustion technology is the basic one available in the short term; however, fuel cells look more attractive in the long term.

In addition to the promotion of fuel cells on transport, their use at facilities that require uninterrupted supply of electricity for continuous functioning (for example, medical institutions) seems very promising and relevant.

Hydrogen might be used for fuel in those sectors where process technologies require combustion of hydrocarbon fuel. This alternative fuel will be eagerly demanded by such branches as power industry (thermal, electric and combined plants) and metallurgy.

In the energy sector, hydrogen is used for fuel in boiler rooms, turbine equipment or high-temperature steam generators. However, for the equipment already in use, preliminary assessment of the suitability of heat-loaded surfaces will be required due to the physicochemical characteristics of hydrogen. Hydrogen can be mixed with natural gas to form methane-hydrogen mixtures in various proportions, or used in pure form. Air or oxygen can be used as oxidisers in oxygen production plants.

Steam generators can also be used without hydrogen, by way of combustion of methane-oxygen mixture to increase the steam qualities [2-5]; however, the use of hydrogen-oxygen mixture, according to estimates [5], will increase electric power of the plant more than twofold. The benefit of hydrogen is manifested in an increase in the operating parameters (transition to supercritical steam parameters for steam cycles) of the plant, and in lower greenhouse gas emissions.

Metallurgical companies use hydrogen for fuel in high temperature furnaces. Technologically, the process of supplying hydrogen is similar to that of the energy sector. In addition to use in furnaces, hydrogen could possibly be used as raw material, namely, as reducing agent mixed with oxygen. This will make it possible to obtain temperatures of 2500 to 3000°C, which will allow returning metals to their original properties and obtaining refractory alloys. Thus, hydrogen is mainly used in tungsten production and in the production of cold-rolled products, at the heat treatment stage.

In the petrochemical branch, hydrogen is used at the stage of heavy feedstock purification, in hydrosulphurisation and distillate hydrocracking units, and for manufacture of lubricants.
COMPETITIVE METHODS OF HYDROGEN STORAGE AND TRANSPORTATION

Due to the upcoming transition to carbon-free energy, hydrogen technologies are becoming increasingly important. Methane-hydrogen mixture (MHM) is considered as one of the options for a gradual transition to hydrogen fuel. However, fast transition to widespread use of hydrogen may be hampered due to the lack of hydrogen production, storage and transportation infrastructure. The obvious solution for the transportation of MHM, pipeline transport, is handicapped by a number of restrictions. Those are hydrogen absorption of metal, steel brittleness and as stress corrosion of the pipeline, which increases the risk of destruction of existing pipelines and infrastructure, which will further entail additional costs [6]. This method of transporting methane-hydrogen mixture can be deemed unprofitable, together with the very mixing processes. Individual hydrogen is a reliable and versatile source of clean energy, as well as a potential tool for implementing the transition to a sustainable low-carbon economy. There are various approaches to its storage: for example, in a compressed state (however, there exist cost and safety concerns), in liquid form (cryogenic hydrogen has high density, and is acceptable when stored in large storage facilities), in the form of metal hydrides (there exist thermodynamics reaction issues such as low reaction rate and low hydrogen capacity), ionic liquids (those have very low vapor pressure, high density and thermal stability). A common, very significant, disadvantage of all these hydrogen carriers is their high cost.

Therefore, organic hydrogen carriers are promising accumulators for this energy source; they are capable of accumulating 8 to 12 percent by weight, participating in reversible hydrogenation-dehydrogenation reactions at moderate temperatures. The required heterogeneous catalysts are readily available and well studied, relatively inexpensive and have a long-term working cycle. The energy carriers themselves are compatible with the existing infrastructure for the storage and distribution of hydrocarbon fuels. The most relevant method for storing hydrogen is the use of pairs of organic compounds, for example, toluene-methylcyclohexane [6], which can reversibly transform into each other in the presence of catalysts by the hydrogenation-dehydrogenation reaction, as well as the competitive individual substance dibenzyltoluene, 1 m² of which can store up to 57 kg hydrogen.

In addition to chemical storage methods, physical methods are also actively developing. The novel carbon nanotube (CNT) storage and transportation technology has a number of advantages [7]. Such materials are light enough, have a hollow structure, and can be used as hydrogen storage containers, maintaining the density of gaseous hydrogen and minimising losses. The main distinguishing features of CNT technology are its operational reliability, high manufacturability, economic efficiency and safety.

Table 1 shows the characteristics of hydrogen and methane accumulated in a type 4 composite cylinder and in a CNT storage cell at different pressures.

<table>
<thead>
<tr>
<th>Cylinder type</th>
<th>Cylinder weight, kg</th>
<th>Operational pressure, MPa</th>
<th>Geometric volume, l</th>
<th>Hydrogen weight</th>
<th>Methane weight, kg</th>
<th>Daily loss of H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite type 4</td>
<td>85</td>
<td>70</td>
<td>104</td>
<td>≈4.1</td>
<td>≈31.7</td>
<td>1 to 3%</td>
</tr>
<tr>
<td>CNT cell</td>
<td>5.6</td>
<td>100</td>
<td></td>
<td>≈5.1</td>
<td>≈35.9</td>
<td></td>
</tr>
</tbody>
</table>

As a result of the analysis of the market of potential consumers, the volumes of production and consumption, together with the logistic issues, we can say that it is reasonably more profitable to produce hydrogen in the near proximity of the consumer, sometimes at the customer’s territory, thereby significantly reducing hydrogen transportation and storage costs. Taking into account the technical and economic parameters, the optimum solution to this problem might be transportation of natural gas with further production of hydrogen. Many experts believe that the hydrogen economy is the future of the world economy, where hydrogen will be a more efficient energy source than hydrocarbons. However, in order to achieve this, many tasks will have to be solved.

CREATION OF A “SMART GAS PIPELINE” USING FIBER-OPTIC MONITORING SYSTEMS

In today’s world, the prefix “smart” (smart home, smart phone) is often added to many innovative products. As a rule, in such cases, it is assumed that a “smart” product will perform some functions that were previously performed by people acting themselves or with the help of some ancillary devices. This terminology is also used in gas transmission industry. One of the focus areas for creating a “smart gas pipeline” is the implementation of a system for remote continuous monitoring of its technical condition in real time [9].

The main task of a “smart gas pipeline” using fiber-optic monitoring systems (FOMS) is to improve gas transportation safety and to prevent emergencies.

Let us highlight the main tasks to be solved by the “smart gas pipeline”. Those are:

- Assessment of the gas pipeline endurance and stability;
- Analysis of the impact of accumulated damage on the bearing capacity and life span of the main pipeline section;
- Monitoring of leaks and of access to restricted areas;
- Development of recommendations for the prevention and minimisation of the consequences of sudden failures.

The need for such diagnostics fully applies to potentially dangerous areas located in terrain with specific natural features, such as:

- Permafrost soils;
- Areas with high seismic activity;
- Active tectonic faults;
- Landslide areas;
- Karsts;
- Heterogeneous relief with significant level variations, including river crossings.
These features may generate extra loads and impacts on the gas pipeline. The introduction of a “smart gas pipeline” outfitted with FOMS is a promising innovative solution that could improve gas transportation safety.

It should be noted that fiber-optic monitoring systems may be employed not only for gas transportation, but also at other extended infrastructure facilities, for example, bridges, facilities located in potentially hazardous natural areas, as well as for protecting the territory of important enterprises.

The fiber-optic monitoring system intended for “smart gas pipelines” consists of optical signal sources, distributed fiber-optic sensors (deformation, temperature and vibroacoustic), an optical signal analyser, a computer and special-purpose software (SW), connecting gear and fasteners. The optical signal from the sources passes through the sensors (SW), connecting gear and fasteners. The optical signal from the sources passes through the sensors and then goes to the analyser, where it is converted into digital form and transmitted to the computer. With the help of the special-purpose software, this data is processed and displayed on screen in real time.

Fiber-optic strain sensors are mounted on the pipe at 12, 3, and 9 o’clock positions, and the temperature sensor can be mounted separately anywhere on the pipe.

The cable for ground movement detection is laid in a trench next to the pipeline [10]. It contains temperature and deformation sensors. Its special-purpose design allows it to transmit information about the movements of the surrounding soil more accurately.

A standard buried fiber optic communication cable also plays an important role in the “smart gas pipeline”. It is used for vibroacoustic monitoring of the facility, which allows obtaining information about the presence of strangers and the nature of the impact in the security zone, as well as for gas leak alarm [10].

“Smart gas pipeline” FOMS’s have a number of advantages:

- One such system can monitor a section up to 100 km long without any “blind spots”, that is, each part of the distributed sensor is a sensitive element.
- Fiber optic sensors can be used at temperatures from -60ºC to +80ºC.
- The sensors themselves are lightweight, flexible and reliable. Their estimated service life exceeds 25 years.
- The systems provide for high measurement accuracy. The absolute error of deformation measurement is less than 0.01%, and of temperature measurement, less than 1ºC.
- FOMS are capable of continuous monitoring of the required parameters. They can automatically process the obtained values and draw up decision-making structures.

The few disadvantages of the system are:

Firstly, it is the complexity of installation under field conditions and the low stability of the sensors to external influences.

Secondly, it is a relatively high cost. In the event of an emergency on the gas pipeline, say, formation of a dent due to ground movements, or a gas leak with further ignition, replacement or repair of such a section will require extra costs. If there was a fiber-optic monitoring system on the gas pipeline, we would have received information about negative impacts in advance and would have prevented emergencies.

To solve this problem, methods are being developed to automate the laying and gluing of sensors.

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