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Advanced (photo)electrocatalytic approaches to substitute the use of fossil fuels in chemical production†‡

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Electrification of the chemical industry for carbon-neutral production requires innovative (photo)-electrocatalysis. This study highlights the contribution and discusses recent research projects in this area, which are relevant case examples to explore new directions but characterised by a little background research effort. It is organised into two main sections, where selected examples of innovative directions for electrocatalysis and photoelectrocatalysis are presented. The areas discussed include (i) new approaches to green energy or H_2 vectors, (ii) the production of fertilisers directly from the air, (iii) the decoupling of the anodic and cathodic reactions in electrocatalytic or photoelectrocatalytic devices, (iv) the possibilities given by tandem/paired reactions in electrocatalytic devices, including the possibility to form the same product on both cathodic and anodic sides to "double" the efficiency, and (v) exploiting electrocatalytic cells to produce green H_2 from biomass. The examples offer hits to expand current areas in electrocatalysis to accelerate the transformation to fossil-free chemical production.

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1. Introduction

Defossilization of chemical production to meet targets, such as net-zero emissions by the year 2050, is a challenge influencing research directions.[1–5] Catalysis is affected by this radical transformation for its crucial role in chemical processes with the electrification of the chemical processes being a central area of investigation today.[6–9] Future chemical production will critically depend on developing new catalytic processes using directly renewable energy and alternative carbon raw materials to achieve an ultra-low carbon footprint.[10,11]

Electrocatalysis has better perspectives for industrial implementation among the emerging areas of catalysis.[12–15] In comparison to alternative catalytic technologies using directly renewable energy sources, such as photo- and plasma-catalysis, the main benefits are (i) knowledge for scaling-up and industrialisation of the processes, (ii) better process intensification by developing stacked electrocatalytic cells, and (iii) larger productivities by volume.[14] The latter can be up to two orders of magnitude greater in electrocatalytic processes than in photo-catalytic approaches. Nevertheless, using solar energy directly makes the photoelectrocatalytic approach an attractive option. Plasma catalysis for applications, such as converting CO_2 to CO, N_2 to NO_x, and CO_2 reformation, is also a valuable option. Except for established areas, such as water and air treatment, photocatalysis still needs to overcome the productivity gap for industrial uses. We thus focus attention here on (photo)electrocatalytic technologies.

(Photo)electrocatalysis takes benefits from the developments in the area of electrochemistry. However, a difference with respect to electrolysers and fuel cells is the issue of selectivity.[16–20]

1.1 New catalysis for fossil-free chemical production

Electrochemistry has been known for over a century. Still, the interest in (photo)electrocatalysis has increased recently, with exponential growth over the last two decades reaching over 600 publications and 25 000 citations per year.

Notwithstanding this impressive number of publications and reviews, the reactions investigated are mostly restricted to the conversion of small molecules (CO_2, N_2, and H_2O) and a few biomass intermediates. Regarding reactors and experimental conditions, literature studies are often quite far from those necessary for possible industrial exploitation. Addressing the challenges of creating new fossil-free chemistry requires exploring novel solutions and approaches by identifying the limiting factors for exploitability and studying how to overcome them.[10,11]

Relevant progress has been made in understanding and improving the performance of the (photo)electrocatalysts.[12–15] Still, we suggest that a primary limiting factor in the transition to fossil-free chemical production is the scarce effort to innovate through novel concepts and ideas for (photo)electrocatalytic devices and operations that explore new solutions, opportunities, challenges and value chains.

1.2 Aims and limits

A distinctive aspect of (photo)electrocatalysis is the presence of separate zones for oxidation and reduction reactions, offering creative clues to design innovative solutions and process intensification. Still, most literature studies focus on a single electrode. They do not consider the whole device enough and how to best use both cell sides. In addition, (photo)electrocatalytic devices are often studied as independent elements from their integration in the value chain. An electrolyte is necessary to close the ionic circuit, but electrocatalytic cell design can overcome the need for a liquid electrolyte. This different design also influences the selection of the electrode.

These are some areas in which intensified research in (photo)electrocatalysis is necessary. In addition, we will show here that a lack of background studies exists in several relevant areas of application of (photo)electrocatalysis inspired by the analysis of the value chain, despite a large number of studies in the area.

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Rosa Arrigo

The main feature of (photo)electrocatalysis is process intensification, *e.g.*, producing in a single step the final product. Today, attention is given to power-to-X processes,[21–26] where only the first step is electrified (the production of H_2). The transition to a carbon-neutral emission would instead require accelerating the development of process intensification solutions based on the full electrification, such as the direct electrocatalytic synthesis of the final target products.[10,11] An extension of the concept of process intensification is integrating the photoactive element (photoelectrocatalytic – PEC – devices).

These are the aspects discussed in this highlights contribution. As case examples, we use EU running or proposed research projects to provide a glimpse of the emerging directions. The examples discussed refer to novel directions based on limited background results. They are thus challenging, but partly speculative. Full feasibility cannot be demonstrated, nor extensive scientific detail and/or literature-supporting data be provided.

The aim is to foster exploring new opportunities driven by the value-chain analysis, rather than only developing disruptive catalysis.[27] It is not a "traditional" review summarising the state-of-the-art innovations, but a perspective to stimulate readers' creativity. It is organised into two main topics: innovate in (i) electrocatalysis and (ii) photo-electrocatalysis. The selected examples show emerging possibilities, but with limited background research. The background and motivations for exploring these directions will thus be presented, in addition to the possible novel (photo)electrocatalytic technology with a discussion of the (few) literature results as the basis to provide indications of the research opportunities.

2. Innovation in electrocatalytic devices

2.1 New approaches to green H_2 vectors

The first selected example involves the direct electrocatalytic synthesis of green H_2 vectors to foster the creation of an H_2 economy. The transition to carbon-neutral chemical production requires the electrification of the processes.[28] Still, it suffers from the limits of (i) discontinuity and variability of electrical energy production from renewable resources, and (ii) insufficient local production by accounting for the multiple uses from mobility and building to applications in the process industry.

It is thus necessary to develop technologies to store and transport long-distance renewable energy sources in a chemical form (chemical energy storage).[29] These molecules, which mediate the production/availability of renewable energy and the requirements for industrial utilisation, are indicated as green energy vectors. In many process industries, mainly those that are energy-intensive, hydrogen is the candidate as an energy vector.[2,4] Still, it suffers from storage and transport to long-distance issues. Direct onsite hydrogen production is considerably influenced by the limited time and availability (at low cost) of the renewable energy necessary to produce H_2 with the continuity and amount required by energy-intensive processes.[30] Still, onsite storage solutions for H_2 are not very effective. Thus, green hydrogen vectors are a necessary element of an H_2 economy panorama.[10,28,31,32] An active research area is

thus related to developing liquid hydrogen vectors, which facilitate transport and storage.[32–35]

The production of hydrogen vectors currently involves multistep technologies.[28,31,32] H_2 is typically produced by electrolysis, and then used to produce the hydrogen vectors in consecutive catalytic step(s). Among the limitations of this approach:

1. The presence of multiple steps, operating at different conditions and with different dynamics, makes the integration complex by impacting costs and energy efficiency.

2. The production of molecular H_2 determines the presence of reversible reactions in consecutive steps, limiting the process efficiency (for example, when H_2 is then used to produce NH_3 catalytically).

The development of 2nd generation technologies, where the direct production of the hydrogen vectors is realised, overcomes the above drawbacks, potentially reducing costs and intensifying the process.[10]

**2.1.1 Electrocatalytic synthesis of LOHCs as H_2 vectors.** The cost of producing the H_2 vectors, a critical issue, could be reduced by (i) integrating their production in the electrocatalytic step of H_2 production, and (ii) valorising the anodic reactions. The latter aspect offers the possibility to link different sectors in the area of renewable energy and create further added value. Both of these aspects are at the core of the EPOCH EU project that is just starting (electrocatalytic production of liquid organic hydrogen carriers and chemicals from lignin, Project 101070976).

Motivations. Various hydrogen vectors have been proposed in the literature. Among them, liquid organic hydrogen carriers (LOHCs) have received considerable attention. LOHCs are organic molecules, typically polycyclic aromatics, which are catalytically hydrogenated or dehydrogenated.[36–40] They are stable under multiple conversion cycles, have a good storage capacity (typically around 6–7% by weight), and are relatively safe to store and transport. This redox conversion allows the transport of H_2 through this cycle.

LOHCs are liquid at ambient conditions, and have properties similar to diesel and gasoline. Therefore, their use allows a stepwise adaptation of the existing crude oil-based infrastructure. Avoiding extensive and costly changes in the energy infrastructure is mandatory to enable a smooth transition.

LOHCs are synthesised as a downstream process after the generation of green H_2. Their production is an additional cost to be compensated only by the decrease in H_2 transport and storage costs. Using LOHCs is generally advantageous for long-term storage/long-distance transport applications.[39] Fig. 1 schematically summarises the concept of LOHC, with an example of them.

The capital and operative expense costs are lowered by hydrogenating LOHC directly in an electrocatalytic device. This unit couples the two separate units of water electrolysis and catalytic hydrogenation in the conventional process (process intensification). A further advantage (explained later) is that the hydrogenation occurs *via* H^+/e^-, which jointly represent the equivalent of molecular H_2.
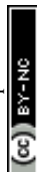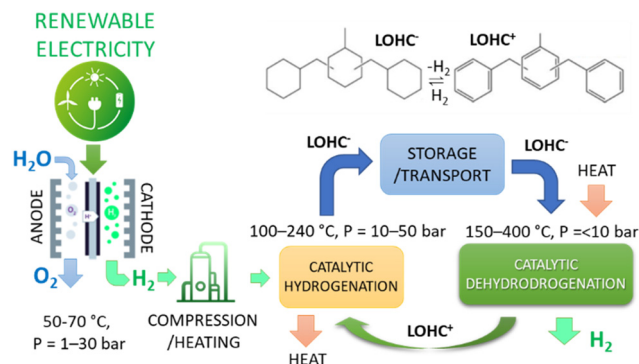
Fig. 1 Illustration of the LOHC concept with an example of them and the operative conditions used (polymer electrolyte membrane technology for electrolyser). LOHC$^-$ indicates the fully hydrogenated molecule, and LOHC$^+$ is the dehydrogenated molecule that is transported back.

Water electrolysers require high voltages (typically 1.8–2.6 V) for the reaction to proceed with sufficient current densities.[41] The part that exceeds 1.23 V is the process overpotential. It represents the energy loss and nonideality in the electrochemical process. The main part of this overpotential is related to OER. Still, the cell aspects (resistance, bubble formation, *etc.*) and the reaction of H$_2$ evolution (HER) significantly contribute.[41] These energy losses can be reduced using (i) an alternative anodic reaction to OER, and (ii) H$^+$/e$^-$ directly to hydrogenate LOHC$^+$, as in the cited EPOCH project.

In addition, the catalytic hydrogenation of LOHC$^+$ requires heat and pressurising the reactants (Fig. 1), requiring further energy. Furthermore, most hydrogenation reactions (relevant to forming H$_2$ vectors) are reversible. They determine, for example, the need for high-pressure operations and large recycling, as exemplified in ammonia synthesis. These limitations are not present in the case of electrocatalytic hydrogenation *via* H$^+$/e$^-$, avoiding related limitations.

The direct LOHC$^+$ hydrogenation led to process intensification and potential increased energy efficiency with respect to the conventional multistep process. The quantification of these aspects and impact on costs (capital and operative costs, *e.g.*, CAPEX and OPEX, respectively) is still premature, being that the direct process is still to be developed. Nevertheless, it may be stated that a direct process offers advantages beyond process intensification. The cost of the integrated device is expected to be comparable to those of the H$_2$ electrolysers (polymer electrolyte membrane type).

Challenges. Several challenges exist beyond identifying an appropriate selective electrocatalyst that combines high productivity (current density) and faradaic efficiency. The latter requires avoiding both side reactions of H$^+$/e$^-$ recombination to H$_2$ and other side hydrogenation reactions aside from the target to form LOHC$^+$.

Cathodic reaction. There are still only limited studies on the electrocatalytic hydrogenation of LOHC$^+$.[42] One of the few studies that refers specifically to LOHC is a recent paper by Shiraz *et al.*[43] They studied the proton-coupled electron transfer (PCET) reaction

of 9-fluorenone/fluorenol as a model for the hydrogenation of LOHC. However, the latter involves the hydrogenation of the aromatic ring rather than the C=O to CH–OH reaction. In general, different reversible LOHCs have been proposed:[42] (i) homocyclic compounds (to which belong the dibenzyltoluene illustrated in Fig. 1), (ii) nitrogen-containing compounds as *N*-heterocyclic compounds, amides or imides, urea/carbamates and nitriles, and (iii) oxygen-containing compounds as ketones, silane/alcohol or ester/alcohol pairs. However, the first class, particularly the molecules analogous to that presented in Fig. 1, show that the best LOHCs possess stability, cost, H$_2$ storage capability, toxicity, and eco-toxicity, physical properties.

The catalytic hydrogenation of dibenzyltoluene to perhydrodi-benzyl-toluene is realised typically at 30–50 bar and 150–200 °C on Ru- or Ni-based catalysts.[44] RANEY® nickel is an effective catalyst.[45] However, there are no studies on the electrocatalytic hydrogenation of dibenzyltoluene. However, the electrocatalytic hydrogenation of toluene using Ni-RANEY®-based electrodes has been reported.[46] Noble-metal-based cathodes such as the Ru–Ir alloy show excellent properties.[47] However, using Ni-RANEY® electrodes would be preferable over the noble-metal-based electrocatalysts for sustainability and cost motivations.

Even if the specific electrocatalytic hydrogenation of diben-zyltoluene has not yet been reported in the literature, it may be thus considered feasible.

Anodic reaction. As mentioned above, the valorisation of the anodic reaction over the conventional OER is crucial for cost and energy intensity reduction. It is a primary advantage of the solution explored in EPOCH technology (Fig. 1). In water electrolysers, the O$_2$ produced has a low, often negligible, value. In addition, OER requires a high overpotential and shows sluggish kinetics.[48,49] Producing a higher-value chemical instead of O$_2$ can make the overall process a competitive one. In addition, the selected reaction should improve the kinetics of the process and reduce the overpotential. Again, changing the anodic reaction combines multiple advantages.

The EPOCH-proposed technology offers additional benefits deriving from the synergic joining of multiple areas of renewable energy panorama. Selecting the target anodic reaction to have comparable production volumes to the cathodic reaction and compatible markets is a crucial factor of success. Many alternatives to OER have been proposed, from wastewater treatment to the oxidation of different organic compounds, such as glycerol, ethanol, and others.[50,51]

Coupling with the biorefinery, especially with the valorisation of lignin derivatives, is a valuable option. A high volume of waste lignin is potentially available, and high-added-value products can be produced.[52–54] In addition, often in biorefineries, green electricity by biowaste combustion or gasification is available.[55,56]

Limitations. Notwithstanding the potential relevance of the electrocatalytic selective oxidation of lignin and its derivatives, there are limited studies reported in the literature in this direction. Yang *et al.*[57] reviewed recent achievements in

electrocatalytic lignin oxidation, and compared them with enzymatic oxidation and the mediated oxidation by molecules, such as TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) and PINO (phthalimide-N-oxyl). The authors commented on a few studies using heterogeneous electrocatalysts, mainly based on noble metals such as Pt, Au, and Ir. Among the non-noble-based electrocatalysts, the best results were obtained with lead/lead-oxide-based anodes. Even if these anodes are active in oxidative lignin conversion, a broad range of products is usually obtained. A further general issue is the electrode fouling caused by the polymerisation of the reactants and/or products.

Garedew et al.[58] also discussed lignin valorisation and the use of electrochemistry as a greener route for the process. In addition to noble metal and lead-based electrocatalysts, they also discussed nickel-, cobalt-, and nickel–cobalt-based electrodes. A specific section was also dedicated to the electrochemical degradation of lignin for hydrogen co-production. Among the challenges indicated are the complexity of the lignin polymer and its resistance to degradation, the limited choice in the electrolytes that can be used, and the difficulty in obtaining both selective products or complete mineralisation, as well as anode degradation.

Du et al.,[59] Movil-Cabrera et al.,[60] Bateni et al.,[61] and Wijaya et al.[62] also reviewed the electrochemical lignin conversion, but the analyses were not significantly different from those discussed above. However, the analysis of these results does not allow for identifying a proper target anodic reaction for coupling with the LOHC electrocatalytic hydrogenation, which meets the criteria indicated before.

The LOHC$^+$ hydrogenation was also not extensively investigated in the literature.[63–66] The need to overcome limitations by the reaction equilibrium was discussed in the literature, but electrocatalysis was not considered among the possible solutions.[67] There are no reports in the literature on attempts to integrate LOHC hydrogenation and lignin or lignin derivatives electrocatalytic oxidation into a single device, nor examples of coupling the LOHC electrocatalytic hydrogenation with other biorefinery waste conversions. The simplified scheme of the integrated device is illustrated in Fig. 2.

The concept presented in Fig. 2 is an example of the possible new directions for electrocatalysis, in which there is a lack of studies. It couples different sectors of applications for a sustainable future (green hydrogen vectors and biorefinery). It exemplifies a new valuable research direction to expand the current studies in electrocatalysis, mainly focused on water electrolysis and CO_2 or N_2 electroreduction.

However, many studies have been reported on the electro-oxidation of biobased chemicals. As examples, the electrochemical oxidation of 5-hydroxymethylfurfural (HMF),[68–70] furfural,[71–74] and glycerol[75–77] may be cited. However, they never arrived at developing a process for the mismatch between volumes required by H_2 carriers and the chemicals produced by these biobased chemicals, as well as the limited synergies between the two value chains and sectors.

While these examples provide valuable inspiration for electrocatalysts to be used and optimal operation conditions, the main
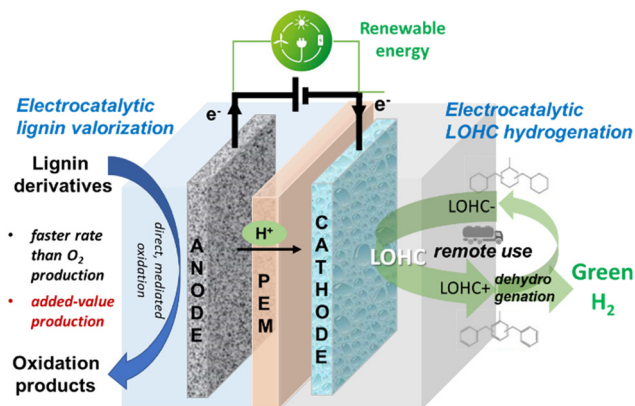

Fig. 2 Simplified scheme of the electrocatalytic integrated device of LOHC hydrogenation coupled with lignin valorisation. Based on the device concept presented in the cited EPOCH EU project (HE, project 101070976).

issue in developing an industrial-relevant case for the direct electrocatalytic production of LOHC is the identification of a proper target anodic reaction that brings the cited benefits of reduction in costs and energy intensity, but have a value chain that integrates well with that of the LOHC sector and brings effective synergies.

2.1.2 Electrocatalytic direct synthesis of ammonia as H_2 vector. There are also other exciting possibilities in the area of green hydrogen vectors. Among them, ammonia is a preferential choice, (i) for the high H_2 capacity by weight (around twice that of LOHC), (ii) for being a liquid under mild conditions (around 7 bar at room temperature), and (iii) for not requiring transport back the carrier. The N_2 formed from NH_3 decomposition to generate H_2 can be released into the atmosphere.

Ammonia is considered a preferential hydrogen vector for applications in marine transport,[78,79] despite some limitations.[80] Several companies (Alfa Laval, Hafnia, Haldor Topsoe, Vestas, and Siemens Gamesa) recently prepared a report with a comprehensive and up-to-date overview of the applicability, scalability, cost, and sustainability of NH_3 as a marine fuel.[81]

The current technology to produce green ammonia is a three-step process: (1) produce H_2 by electrolysis, (2) separate N_2 from the air, and (3) thermo-catalytically convert $H_2 + N_2$ to ammonia. The latter stage is similar to the conventional Haber–Bosch (HB) unit for industrial ammonia production, but with the catalysts and operative conditions adapted to operate under milder conditions due to coupling with the electrolyser. The catalyst under these milder operative conditions shows a higher sensitivity to deactivation.

Several companies, including Stamicarbon, Kapsom, Harold Topsoe, Thyssenkrupp, and Siemens Energy, propose this green ammonia process. Several large projects in Saudi Arabia, Australia, Germany and Japan have started.[82] However, costs are still high. Nazemi and El-Sayed[83] indicated that the green ammonia synthesis would be cost-competitive with the conventional HB process, having an estimated production cost of around 143 ± 14 USD. To be competitive, green H_2 production should have an energy input lower than 6 MW h per ton$_{NH3}$ (now

around 7.7 MW h) and a price of renewable electricity below 0.025 USD per kW h (now higher, but depends on many aspects).

Thus, an increase in the process energy efficiency would be required, together with a reduction in renewable electricity costs. This reduction is difficult to achieve in green ammonia synthesis *via* electrolysis, followed by HB catalytic synthesis. The degree of improving energy efficiency in the two separate steps is limited, and energy is required to compress H_2 from the electrolyser to the pressure required for HB operations. The HB catalytic step is an exothermic reversible reaction between molecular H_2 and N_2. The related thermodynamic constraints determine high-pressure operations and large recycling. Furthermore, energy efficiency in the HB step largely depends on the possibility of an efficient heat recovery, which is less effective in small-medium scale plants as would be necessary for a distributed production of ammonia as a hydrogen vector.

In a direct electrocatalytic synthesis of NH_3, the hydrogen-equivalent (H^+/e^-) rather than molecular H_2 is involved in the hydrogenation of N_2, and the reaction mechanism is different from heterogeneous catalysis.[84] Operations proceed under mild conditions, and a single unit, whose cost could be comparable in principle to that of the electrolyser, allows for direct ammonia synthesis rather than having a downstream catalytic step operating at higher pressure and temperatures. For these reasons, various authors consider it necessary to move to the 2nd generation technologies of direct electrocatalytic synthesis of ammonia from N_2.[11,28,83,85] Fig. 3 shows the concept of a direct electrocatalytic device to produce ammonia from the air at ambient conditions.

Direct electrocatalytic synthesis of ammonia. The direct electrocatalytic synthesis of ammonia from N_2 is an area of fast-rising research. Over 600 papers on this topic have been published in the last two years. The studies focus on the electrocatalysts and conditions to minimise the side formation of H_2, which reduces the faradaic efficiency,[86–91] even if questions still exist about the reliability of the results, *e.g.*, if the N in ammonia is derived from N_2 rather than N-impurities.[92] Among the remarkable developments, Xue *et al.*[93] showed about 68% faradaic efficiency in Au electrocatalyst nanoparticles by increasing their electron density through donor–acceptor couples.

On the other hand, the current densities at the maximum faradaic efficiency (FE) are about 0.1 mA cm^{-2}, while current densities should be three orders of magnitude higher to

consider exploitability. This result exemplifies, among others, that a large gap to reaching the conditions for industrialisation exists even within the relevant scientific progress. Industrial targets can be roughly indicated in FE above 80% at current densities of at least 80–100 mA cm^{-2}.[94] The cell design should allow for scalability, and avoid the use of electrolytes unsuitable for industrial operations to guarantee stable operations in continuous mode.

Most current studies and electrocatalyst design criteria focus on mechanistic aspects as the tool to obtain the targets. We showed[94] that despite the great range of proposed reaction mechanisms, the electrocatalytic results fail within a limited range of faradaic efficiency *versus* current density values. This observation suggests that the existing methodological approaches do not allow the correct identification of the crucial aspects to boost performance.

In addition, many other aspects have to be improved in parallel: (i) realise high stability in extended operations, (ii) design of efficacious continuous-flow reactors with a configuration suitable for scale-up, (iii) an easy, low-cost ammonia recovery, (iv) the use of non-critical and not-costly raw materials, (v) avoiding the use of electrolytes, which may cause problems of corrosion and long-term stability, *etc.*

Despite many literature studies, only a few studies address these aspects. Tuning the current approach and extending the concepts and methodologies used, including reactor design and the direct coupling with air, is required to accelerate the implementation of a distributed production of H_2 vectors.

Producing ammonia directly from the air. Fig. 3 illustrates a device to make NH_3 directly from the air rather than from N_2 produced by air separation. There are still no studies in this direction. However, conceptually, it can be a direction to create artificial-leaf-type devices (coupled with a photovoltaic panel) to produce ammonia. We can thus imagine having future artificial trees that directly produce H_2 in remote areas in the form of an easily storable and transportable vector (ammonia). For such a device, it is mandatory to integrate the N_2 separation from the air in the device.

It may be questioned whether this is feasible or even necessary. All current studies in direct electrocatalytic NH_3 synthesis use rather pure N_2, and the effect of oxygen impurities has not been analysed. Although membrane units for up to 99.9% or over are commercially available, they require multistep separation stages, making the process costly in energetic terms.[95] In addition, in a model of artificial-leaf devices, it is necessary to integrate the N_2 separation component in the unit. However, in a different approach, where the decentralised ammonia production unit still has a larger capacity than a single artificial-leaf type device, it is likely preferable to have a separate air separation unit. Thus, the need to integrate the N_2 separation component from the air in the device depends on the target.

Conceptually, the air-separation unit is different from the membrane-like element indicated in Fig. 3. In commercial membrane units, the separation factor is related to the rate of
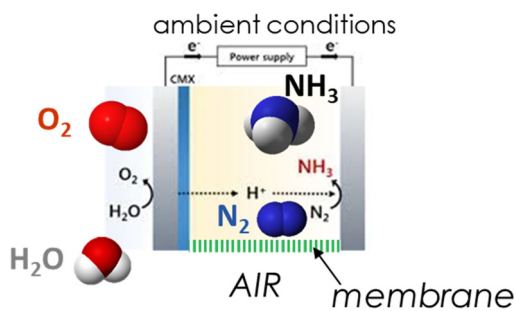

Fig. 3 Concept of a direct electrocatalytic device to produce ammonia from the air at ambient conditions.

transport of N_2 and O_2 through the membrane, with oxygen diffusing faster through the membrane (typically 5–10 times more quickly).[95] Pressure is the driving force. A single-stage unit typically allows an N_2 flow (retentate side) having around 90% concentration in N_2. In the membrane-like element integrated into the electrocatalytic device (Fig. 3), it is necessary to diffuse N_2 selectively and block O_2 transport. Thus, a different transport mechanism is essential via, for example, metal-complexes binding N_2 selectively rather than O_2.[96,97]

This topic of functional elements for the selective transport of N_2 in membranes is a novel development area. Some preliminary studies, however, indicate the feasibility. Yoon et al.[96] showed that mesoporous metal–organic framework materials containing accessible Cr(III) sites could capture N_2 over O_2.

On the other hand, N_2-selective group V metallic membranes are known.[97] Thus, from a conceptual perspective, it is feasible to indicate the device scheme reported in Fig. 3, although the membrane-like elements are still unavailable.

Out of the membrane availability, some O_2 will still be present together with N_2. It is thus necessary to explore whether it could be feasible for the ammonia synthesis catalyst to have some oxygen in the N_2 feed, and determine the oxygen-limiting concentration. Despite over 600 papers on this topic in the last two years, none has analysed the crucial question of the impact of the presence of O_2 in the N_2 flow. O_2 has likely stronger binding than N_2 and higher reducibility.

On the other hand, there is a rich dinitrogen coordination chemistry,[98] although the possibility of selective binding and activation of N_2 rather than O_2 was never systematically explored.

Nitrite/nitrate can be electrocatalytically reduced to ammonia faster than N_2.[99,100] Therefore, the oxygen in nitrite/nitrate does not poison the electrocatalysts for ammonia reduction. It may also be possible to consider an oxygen-assisted mechanism, in which N_2 first converts to the NO_x species, and successively reduced onsite to ammonia. This is a less efficient redox mechanism because it requires more electrons/protons. On the other hand, the electrocatalyst reduction of NO_x to NH_3 is faster and more selective than the direct reduction of N_2 to ammonia.[101] Long et al.[101] reported experimental and theoretical results showing that on copper foams, reaction rates of over 500 μmol h^{-1} cm^{-2} and FE over 90% are possible at the low potential of −0.9 V vs. RHE. In addition, long-term stability (over 100 h) was shown. Ko et al.[102] also showed that >80% FE is obtained in the electrocatalytic reduction of NO on copper. N_2 oxidation to nitrogen oxides is also a faster process than the N_2 reduction,[103,104] as also discussed later.

Thus, it is not unfeasible to develop an electrocatalyst for direct ammonia production in the presence of some oxygen in the feed. However, this is a topic largely unexplored, even if crucial from an application perspective.

2.2 Fertilisers directly from the air

The concept presented in Fig. 3 could be extended to directly produce fertilisers. The separation of N_2 from the air could be in a separate unit or integrated into the device.

Background. Ammonium nitrate is the most common fertiliser. It is produced commercially by the oxidation of ammonia of NO (then oxidised and adsorbed in water to form nitric acid), rather than by direct N_2 oxidation for both thermodynamic and kinetic aspects. The nitric acid is then neutralised with ammonia to form ammonium nitrate, the most common fertiliser produced worldwide at over 50 Mt per year.

Nitrate ions are highly mobile/soluble in soil water, and can be assimilated directly by the root system of plants. The ammonium ion is the counter-ion and acts as a reservoir, then transformed to nitrate by the enzymes present in the soil. Its role is thus to double the nitrogen content of the fertiliser.

Commercially, ammonium nitrate is produced as an aqueous solution. Still, to transport, it is necessary to make a solid first by concentrating the ammonium nitrate solution in an evaporator or concentrator, and then spraying the concentrated melt into the top of a prilling tower. Besides safety aspects (ammonium nitrate is an explosive), this prilling (or alternative granulating) process is energy intensive (around 8500 MJ per ton N) and costly.

Motivations for a novel electrocatalytic process. A technology for the direct electrocatalytic production of ammonium nitrate is well suited for distributed (farmer) production using locally available renewable electricity sources. It can produce an ammonium nitrate aqueous solution for local use as a fertiliser with multiple advantages: (i) a low-carbon technology, (ii) relevant process intensification, (iii) a potentially better energy efficiency avoiding losses of multiple unit operations, (iv) eliminates the energy losses, costs and safety issues of producing a solid ammonium nitrate, (iv) avoids the costs and energy losses for long-distance transport, and (v) use directly locally available renewable energy sources. Thus, there are many motivations to develop such a device for directly producing fertilisers (ammonium nitrate aqueous solution) from the air. Fig. 4 illustrates this concept concisely.

Challenges. Abundant literature exists on the electrocatalytic reduction of N_2 (often indicated as NRR – nitrogen reduction reaction), but the reaction of nitrogen oxidation (NOR) has been investigated much less.[103,104]

Dai et al.[105] showed the possibility of preparation by direct electrochemical oxidation of nitrogen on $ZnFe_xCo_{2-x}O_4$ spinel oxides in an alkaline electrolyte. They reported a nitrate production rate of ∼130 μmol h^{-1} g_{MO}^{-1} at an applied potential of 1.6 V versus the reversible hydrogen electrode (RHE). The faradaic efficiency, however, is only a few percentages, attributed to low N_2 solubility. Spinel $ZnFe_{0.4}Co_{1.6}O_4$ exhibits the highest nitrate yield.

Guo et al.[106] used atomically dispersed Fe-based catalysts on N-doped carbon nanosheets. They reported a nitrate yield of 6.12 μmol mg^{-1} h^{-1} (2.45 μmol cm^{-2} h^{-1}) and Faraday efficiency of 35.6%. The proposed reaction mechanism indicates Fe atoms as active centres for NOR, able to elongate the N≡N bond through hybridisation between the Fe 3d orbitals and N 2p orbitals. This hybridisation activates N_2 molecules and triggers the subsequent NOR.

Limited additional results on direct N_2 to nitrate electro-oxidation have been reported, but are based on noble-metal
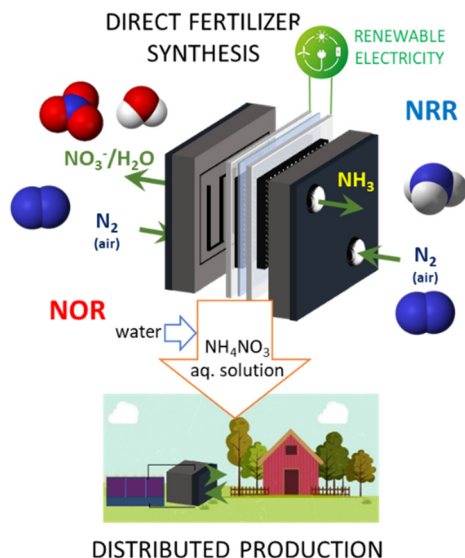
Fig. 4 Concept of a direct electrocatalytic device for a distributed production of fertilisers (ammonium nitrate aqueous solution). For clarity, the integration of a membrane for the direct use of air is omitted. NOR: nitrogen oxidation reaction. NRR: nitrogen reduction reaction.

Fig. 5 Selection of representative electrocatalytic results in the nitrogen reaction and oxidation reactions (NRR and NOR, respectively): faradaic efficiency *versus* the rate of ammonia or nitrate formation at ambient conditions. The dashed arrow indicates the gap in the electrocatalytic results to meet requirements for industrial exploitability. M−N−C: nitrogen/metal-doped carbons.

electrocatalysts. A theoretical study[107] indicates a noble metal, such as IrO_2 (110), as an excellent catalyst because it limits the side oxygen evolution reaction. Avoiding this side reaction is undoubtedly a challenge. However, the results of Guo *et al.*[106] evidence that alternative designing characteristics for the electrocatalyst exist aside from the oxide electrocatalysts considered by Anand *et al.*[107]
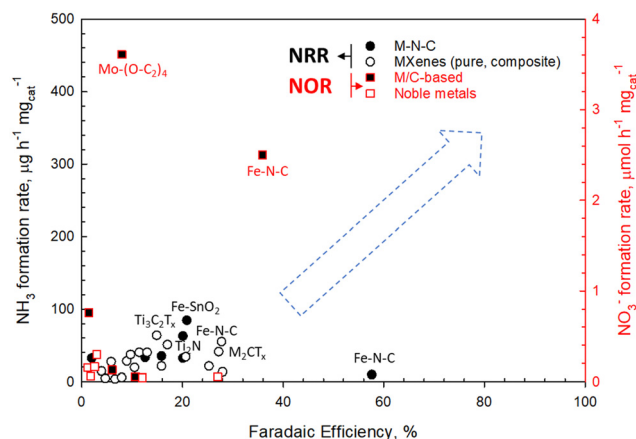
Therefore, even if very limited studies exist on the NOR reaction, they indicate a promising direction to explore, and the feasibility of combining NOR and NRR reactions in a single device (Fig. 4).

Fig. 5 reports selected examples of literature results in nitrogen reduction and oxidation reactions (NRR and NOR, respectively). The dashed arrow indicates the gap in the electrocatalytic results to meet conditions for industrial exploitability.

Two main classes of materials are emerging: (i) double transition metal MXene (a class of two-dimensional carbides, nitrides, and carbonitrides), and (ii) nitrogen-doped carbon materials (single-atom catalysts). However, Fig. 5 shows that significant improvements are still necessary. In addition, some results need further studies to verify reproducibility and stability.

Fig. 5 shows the feasibility of coupling NRR and NOR in a single device for producing fertilisers directly from N_2 and, in the future, directly from the air. The last challenge has still not been attempted in the literature. Some EU projects, for example, the Horizon Europe FERTIGEN (CL4-2022-TWIN-TRANSITION) proposal from which Fig. 4 and 5 are derived, attempt to investigate this novel route. However, the disruptive character of this approach with respect to more conventional ones fails to be adequately understood. Nevertheless, we discuss the need to explore these novel directions by electrocatalysis to expand the range of possibilities.

2.2.1 Plasma-catalytic direct N_2 oxidation. Exciting developments have been recently proposed in producing fertilisers

from the air by non-thermal plasma. However, they are limited to nitrate production,[108–110] while producing ammonia by non-thermal plasma is harder. Still, plasma-activated electrochemical ammonia synthesis from nitrogen and water has been reported.[111] Protons produced by water oxidation at the anode are transported through a proton-conducting ceramic membrane ($BaCe_{0.2}Zr_{0.7}$-$Y_{0.1}O_{3-\delta}$) to the cathode, where they react with the plasma-activated nitrogen toward ammonia. Ammonia production rates and faradaic efficiencies over 25 nmol of NH_3 s^{-1} cm^{-2} and 85%, respectively, were achieved at 500 °C. The approach is interesting, but it remains unclear whether the total energy efficiency was achieved (a crucial question).

N_2 fixation with non-thermal plasma can be divided into (i) ammonia synthesis reaction by nitrogen reduction, and (ii) the direct production of NO_x or NO_3^-/NO_2^- by oxidation.[112] In both cases, the energy utilisation rate is still very low. However, the second path is better in terms of energy efficiency than the first.[109] It is preferable to produce fertilisers directly in a distributed approach. However, coupling with a tailored catalyst would be necessary.

In direct plasma oxidation to nitrogen oxides, some main issues to solve to exploit this route could be identified: (i) coupling effectively with a catalyst to improve the performances, particularly the formation of NO_2 with respect to NO, (ii) increasing the energy efficiency under relevant reaction conditions (atmospheric pressure), and (iii) scalability of the results considerably, depending on the plasma reactor. Intensification of research is necessary to solve these many challenges. The research in this direction is at a low technology readiness level.

2.3 Tandem/paired electrocatalytic reactions

Background. Electrocatalytic devices, having separate oxidation and reduction reactions, offer many valuable options for process intensification and develop low-carbon processes. Further advantages are:

– Use of renewable electricity to drive the process.

– Presence of an *in situ* generation of the redox reactants (hydrogen equivalents, active oxygen species).

– Process intensification; a single unit allows for realising complex multistep processes.

Electrocatalytic devices are thus truly crucial technologies for future chemical production. However, their potentialities are still underestimated, and most literature studies do not attempt to study them.
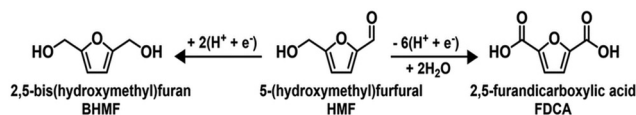
The challenge of coupling reactions at the anodic and cathodic sides. Both electrochemical half-reactions must produce value-added chemicals to maximise the economic viability of an electrosynthesis method. This concept has been explored primarily in biomass electrocatalytic reactions.[113] It is beginning to be investigated for other cases, but studies are still limited.

The main issue in pairing reactions at the cathodic and anodic sides of the electrocatalytic cell is to identify good examples from an industrial perspective, which overcome limitations from different markets and market dynamics of the products. An example is the coupling of cathodic reactions such as CO_2RR with the anodic degradation of organics in wastewater.[114–116]

Notwithstanding this possibility being known and investigated for many years, it never reached commercial use, except in niche cases. This choice of relevant reactions and industrial sectors to be coupled must be addressed, in addition to the technical issues. It is similar to what was discussed before for the LOHC case.

The other relevant challenge is developing electrocatalysts and operative conditions that match the requirements of anodic and cathodic reactions and their optimal coupling (*e.g.*, balance in terms of reaction rates, electron and H^+/OH^- flow, *etc.*). It is often assumed that anodic and cathodic reactions can be independently developed. The optimal electrocatalysts could be significantly different when both reactions are simultaneously studied, instead of using another reaction or sacrificial agents at the counter electrode. Literature results on this crucial question, however, are scarce.

2.3.1 Tandem/paired electrocatalytic production of monomers for polymers. Developing novel electrocatalytic solutions to produce monomers for polymerisation is a challenging area offering many exciting possibilities, and some are mentioned below.

Synthesis of monomers for PEF. An example is the production of the two monomers used in the production poly(ethylene 2,5-furanoate) (PEF), a biobased polymer to substitute the fossil-based polyethylene terephthalate.[117,118] The latter is synthesised from furan dicarboxylic acid (FDCA) and mono ethylene glycol. The electrocatalytic oxidation and reduction of sugars can lead to these chemicals.

The electrosynthesis of FDCA was reported in many studies.[119–122] Differently, the electrocatalytic reductive cleavage of sugars to obtain ethylene glycol has been rarely investigated. Even less studied is the tandem process of producing FDCA and ethylene glycol at the two sides of the electrocatalytic cell. Studying these reactions and the related electrocatalytic reactor was the objective of the EU H2020 project TERRA (Tandem Electrocatalytic reactor for energy/resource efficiency and process intensification, project no. 677471).[123]

The alternative is the production of 2,5-bis(hydroxymethyl) furan (BHMF) instead of ethylene glycol:[124,125]

5-(Hydroxymethyl)furfural (HMF) can be obtained from glucose (a primary C6 sugar obtained by cellulose depolymerisation) by isomerisation to fructose. The latter is then dehydrated to HMF.

HMF can then be transformed by electro-oxidation to FDCA in a paired electrocatalytic reactor with BHMF production by electroreduction.[125] At the anode side, the electro-oxidation is realised using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as an organic redox mediator to enhance the performance. A combined faradaic efficiency (FE) as high as 139% to BHMF and FDCA was obtained,[125] or even higher up to nearly 190%.[124] The FE higher than 100% is derived from the fact that the same reactant is converted at both the cathodic and anodic sides.

Although BHMF could be considered an equivalent ethylene glycol diol for polyester production, aliphatic diols such as ethylene glycol or more rigid diols such as isosorbide are necessary to obtain good polymer characteristics.[126] BHMF needs to be converted to products, such as 1,6-hexanediol or 1,2,6-hexanetriol, or polymerised with chemicals other than FDCA to produce bio-based polymers.[127] Therefore, the benefit of making the monomers simultaneously at the two electrocatalytic cell sides for the same polymer is not present in the case of BHMF coproduction with FDCA.

Electrocatalytic synthesis of adipic acid. Other industrial-relevant examples of paired/tandem electrocatalytic reactions exist. One of them is the production of bio-adipic acid, one of the most relevant dicarboxylic acids from an industrial point of view. Among the different possible routes,[128,129] the direct electrocatalytic synthesis summarised in Fig. 6 is one of the challenging possibilities. It is explored in the frame of the EU H2020 PERFORM project (PowerPlatform: establishment of platform infrastructure for highly selective electrochemical conversions, project 820723). Limited literature data are available on the target electrocatalytic reactions,[130–132] particularly
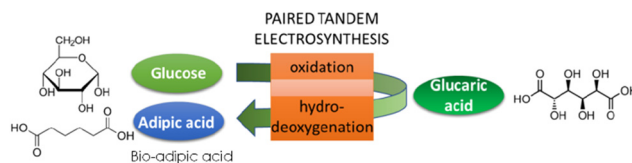

Fig. 6 Scheme of the direct electrocatalytic synthesis of adipic acid from glucose in a paired/tandem electrocatalytic cell.

the cathodic reaction. The PERFORM project aims to develop a pilot plan unit to demonstrate process feasibility.

Among the developments realised in this project are (i) NiFe oxide supported on Ni-foam as an anodic material for the electrocatalytic oxidation of glucose to glucaric acid, and (ii) supported PbO_2 electrocatalysts for the oxidation of furfural to maleic acid, as documented in the project web site (**https://www.performproject.eu**). In contrast, other developments are still maintained as confidential. A general review on the electrosynthesis of biobased chemicals using carbohydrates as a feedstock was published by Vedovato et al.[133] This review, besides discussing state of the art innovations, gives recommendations of the research needs, choice of electrocatalyst and electrolyte, and for upscaling the technology from an industrial perspective.

Tandem-paired electrocatalytic conversion of xylose into δ-valerolactone. There are different electrocatalytic cell design possibilities to pair two electrocatalytic reactions.[134] The conventional is when the two reactions occur in different reactor compartments, separated by a membrane. The latter could be bipolar to allow different electrolyte conditions (for example, pH). The two reactions are only coupled through the protons or hydroxyl ions passing the membrane to close the cycle and the flow of electrons connecting the two electrodes.

When the membrane is not present, reactions between the products formed at the two electrodes are eventually mediated by other redox chemicals in the electrolyte. The intermediate products can react with each other, generating a coupling product, or the product generated at one electrode can then be further converted at the other electrode.

This possibility is exemplified in the tandem paired electrolysis of xylose into δ-valerolactone in an undivided cell (Fig. 7). James et al.[135] reported the electro-deoxygenation of xylose to δ-valerolactone on porous Pb electrodes, but with HCl conversion to Cl_2 as a counter-reaction on the RuO_x–TiO_2 anode. The latter, for safety concerns, cannot be used industrially.

Lucas et al.[134] discussed several other examples of the electrochemical conversion of biobased molecules: polyols, carbohydrates, heterocyclic, and other chemicals.

Although excellent performances have been obtained in some cases at the laboratory scale, several challenges were still identified

Fig. 7 Tandem-paired electrocatalytic conversion of xylose into δ-valerolactone.

by Lucas et al.[134] for the industrialisation of these electrocatalytic processes. The main issues are summarised below:

– Low faradaic efficiency and presence of competitive HER/OER reactions.

– Cost in downstream processing due to low product concentrations and complex product streams; needs to recycle the electrolyte.

– Slow conversion rates compared to non-electrochemical techniques.

– Low selectivity in targeting specific chemicals within real mixtures; the role of impurities.

– Electrode stability due to fouling; electrocatalyst stability.

– Reactor scale-up and moving from half-cell to continuous whole-cell processes.

– Membrane crossover of chemical species.

– Calibrating simultaneous tandem electrocatalysis on the anode and cathode in terms of rates, market sizes, technical variables.

– Establishment of compatibility with intermittent power.

2.3.2 Pairing reactions in an electrocatalytic cell. Pairing two electrocatalytic reactions require matching reaction rates, and mass and electron balance. It is a closed circuit with both reactions mutually influencing. Therefore, the study of separate reactions is a good starting point. Still, the optimal electrocatalysts in the paired or tandem electrocatalytic cell will likely differ from those determined for the individual studies.

In addition, in studies of single reactions, the counter-reaction is typically water oxidation or reduction. The overpotential for these reactions and electron/proton exchanges are likely different from when the pairing with the other target reaction is made. The electrolyte could also be different, and this also drastically influences the behaviour.

Thus, the assumption that an electrocatalytic cell's cathodic and anodic reactions can be independently developed is an oversimplification, even if typically made.

It should also be noted that most of the studies in electrocatalytic reactions operate at room temperature, and the effect of the temperature is often not investigated. There are material stability issues both on the electrocatalysts side and especially on the membrane, but operations above room temperature may often offer a key to enhancing performance.

Finally, it is usually assumed that the same temperature should be used at both the cathodic and anodic sides. The possibility of having different temperatures at the anodic and cathodic sides, up to a 50–100 °C gradient, is a technically feasible option. It has scarcely been investigated in the literature, but offers a novel key to optimising the two reactions at the anodic and cathodic sides. The cited EU TERRA project explored this possibility.

2.3.3 Pairing CO_2RR with biobased platform molecules. Another valuable possibility is to pair CO_2RR with the electrooxidation of biomass-derived platform molecules. Na et al.[136] reported a techno-economic analysis for the electrochemical coupling of CO_2 reduction with organic oxidation. They developed a framework approach to guide process simulations. Then, they used it to predict levelized costs of chemicals and
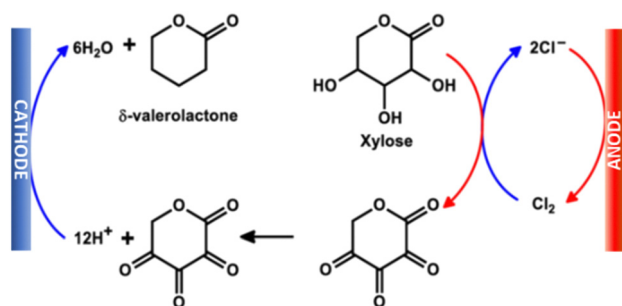
critical parameters for evaluation, such as the sensitivity to current density, Faraday efficiency, and overpotential.

These examples illustrate the possibilities of pairing electrocatalytic reactions, but often industrial applicability and use within an advanced biorefinery value chain have not yet been convincingly proven.[137] Besides the technical challenges above, a top-down approach would be necessary to identify the proper targets in integration within biorefinery schemes, such as the volume produced, feeds available and product quality demand, costs and availability of renewable energy sources, and competitive alternatives. On the contrary, research has been mainly driven from a bottom-up approach. Even with recent advances, mechanistic data are still limited to designing *ad-doc* electrocatalysts given a target reaction. A general toolbox of electrocatalysts to use is not available.

In addition, a new framework of electrocatalytically based reactions is required to develop a new chemistry based on renewable resources alternative to fossil fuel use.[10–12] Rather than just coupling the conversion of biobased molecules with reactions such as HER, OER or CO2RR, new electrocatalytic methods should be developed to use the active intermediates generated in the electrocatalytic conversion of small molecules. Examples are (i) H* and OH* from H_2O conversion, (ii) CO* and $*C_xH_y$ from CO_2 reduction, (iii) $*NH_y$ by N_2 reduction or *NO by N_2 oxidation; the asterisk indicates active surface intermediates produced during the electrocatalytic conversion.

Reactions to explore include (i) direct coupling of *in situ* generated intermediates, (ii) tandem reactions using *in situ* generated chemicals, and (iii) the eventual coupling between electro- and heterogeneous catalysis.

A full set of novel possibilities exists beyond the actual studies in electrocatalysis. Exploring these routes is the grand challenge to innovate electrocatalysis, not just scaling up and exploiting the current approaches.

2.4 Electrodriven production of green H_2 from biomass

The previous discussion focused on pairing reactions for products derived from biomass transformation. Other alternatives to exploit the potentialities of electrocatalytic devices were scarcely investigated.

Interesting is the dehydrogenation of organic chemicals to produce in an electrocatalytic cell both H_2 and electricity together with the dehydrogenated (added-value) organic. Different from endothermic catalytic dehydrogenation, this electro-driven process produces protons and electrons, which migrate on the other side of the electrocatalytic cell, forming pure H_2 on the cathode (Fig. 8). Ding *et al.*[138] demonstrated that ethane could be selectively converted to ethylene with the coproduction of electricity and H_2 using $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ as a solid-oxide electrolyte, Ni on the anodic side, and a perovskite as the cathode.

The ethylene selectivity was close to 100%, but the hydrogen generation rate was low, around 0.45 mol cm^{-2} per day at 400 °C. The reason is the low ionic conductivity of the electrolyte. However, the concept could be extended to other reactions using better conductive protonic membranes, which need more reactive substrates than alkanes.
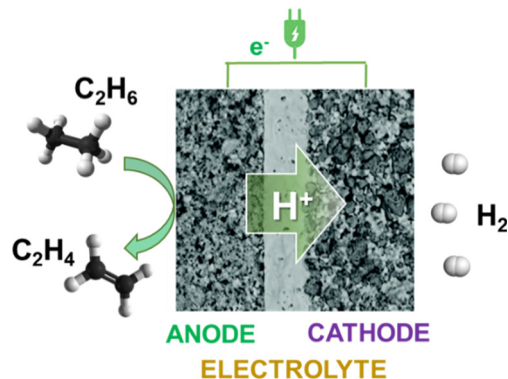

Fig. 8 Schematic illustration of the ethane to ethylene + H_2 coproduction on solid proton-conductive membranes in an electrochemical cell.

This concept was explored by Zhang *et al.*,[139] who studied the electrocatalytic oxidation of glycerol on Pt/C in an anion-exchange membrane electrocatalytic cell, with the production of H_2 on the cathodic side and the cogeneration of electricity (Fig. 9).

Zhang *et al.*[139] used an anion-exchange membrane electrocatalytic cell and a Pt/C anode catalyst for glycerol dehydrogenation with cogenerating electricity and green H_2. The anode overpotential determines the oxidation product distribution. Higher anode overpotentials favour bond breaking, thus lowering the C3 acids' selectivity. The highest selectivity of C3 acids (glyceric acid + tartronic acid) reaches 91%. Higher current densities require operating above room temperature, up to 80 °C, which lowers the selectivity.

Fig. 9 indicates that the methanol-to-formaldehyde conversion is a valuable possible alternative. Formaldehyde is commercially produced from methanol on a Mton scale by catalytic oxidative dehydrogenation or dehydrogenation. The electrocatalytic process thus offers an alternative possibility for a low-carbon process. However, very few literature studies have reported this possibility,[140,141] and they were two-three decades old.
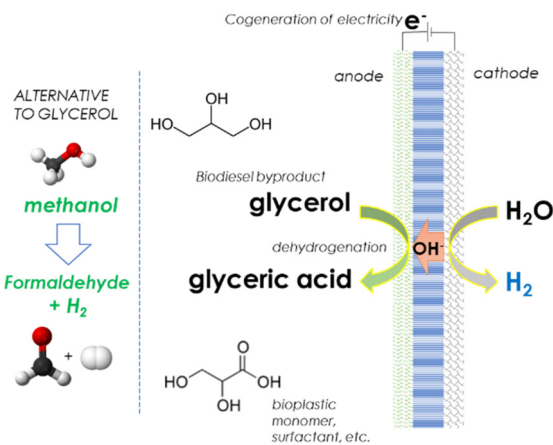

Fig. 9 Concept of using an electrocatalytic cell for dehydrogenating chemicals combined with the coproduction of H_2 and electricity in an anion-exchange membrane electrocatalytic cell.

3. Innovation in photo-electrocatalytic devices

Integrating a photo-active element in the electrocatalytic (EC) cell offers the possibility to develop devices that do not depend on the external availability of renewable energy, and thus on their large variability. They thus allow the development of artificial-leaf devices and artificial trees for a distributed production of chemicals and fuels.[142–147]

While attention is typically focused only on solar-to-fuel efficiency, many other challenges are present, from the possibility of extending the limited range of uses explored today (essentially water splitting, CO_2 reduction and more recently ammonia production from N_2)[146] to developing compact and efficient devices,[148] extending the time of operations beyond the period of illumination and overcoming limitations by OER. Some of the possibilities will be discussed in the following sections.

3.1 Extending the time of operations and improving efficiency by decoupling anodic and cathodic reactions

Background. The main factor influencing the capital cost in electrocatalytic devices is the limited availability of renewable electrical energy when produced onsite. This aspect is valid in general for all devices using renewable electricity. On the other hand, transporting renewable energy from far regions is not feasible.

On average, depending on the mix of sources used to produce the renewable electricity, from 4 to 8 h is the daytime when renewable electricity could be considered available. Thus, the device has to be amortised annually for a time ranging from 1000 to 2000 h, instead of the conventional 8000 h considered in chemical processes. On the other hand, storage of renewable electricity is still costly, and not efficient on a large scale and seasonally.

As an example, the following factors mainly determine the production cost of green H_2 by electrolysis:

(i) The amortisation time (the cost of electrolytic H_2 increases very steeply for insufficient electrolyser up-time, *e.g.*, <2000 h per year);[149]

(ii) The cost of renewable electricity.[150]

The second aspect depends on the energy market rather than on technology solutions. Integrating a photo-active element in the device, such as a photovoltaic (PV) module, can overcome this dependence on strong fluctuations. This is the main motivation to develop photoelectrocatalytic (PEC) devices, and also called artificial leaf or photosynthesis. We use here the extended concept of artificial leaf devices as those that use solar light to produce chemicals or fuels without external bias or use sacrificial agents.[151] The definition is thus independent of the device's configuration, whether wireless or not, or the use of a PV module to drive the process rather than photo-electrode.

A technological challenge is to explore solutions to overcome the first limitations, *e.g.*, the operations only when solar light is present. The combination of a battery with the PV module to operate also during the dark period is not effective for an artificial tree (or analogous) solution due to the still inadequate energy density capacities of the batteries. A flow battery[152] should be integrated into a PEC cell, realizing a solar flow battery design.[153] However, this integration is highly challenging and alternative solutions should be identified.

Decoupling anodic and cathodic reactions. A prerequisite for advanced design in PEC devices is to decouple the anodic and cathodic reactions. In a conventional PEC cell, the anodic and cathodic reactions are coupled, with the slowest reaction (for example, the oxygen evolution in water electrolysis) determining the overall productivity. By substituting the anodic reaction of oxygen evolution with a solid-state redox reaction as the $Ni(OH)_2$ to NiOOH reaction, it is possible to spatiotemporally decouple the two reactions of H_2 and O_2 production in water electrolysis. This decoupling is possible because $Ni(OH)_2$ can be regenerated periodically at a slightly higher temperature (95 °C) by passing an aqueous solution of NaOH with the generation of O_2 in a separate stage.[154] This solution shows several advantages:

(i) Introduces a redox function that allows a temporal decoupling of the anodic and cathodic processes.

(ii) The kinetics of the $Ni(OH)_2$ to NiOOH reaction is faster than that of OER, and shows a lower overpotential because it is a one-electron reaction rather than a $4e^-$ as OER; the result is better productivity and energy efficiency.

(iii) it avoids using a membrane to separate the anodic and cathodic zones, resulting in cost reduction.

Such a type of configuration also facilitates electrocatalytic operations under pressure. Several studies have explored this possibility,[155–160] although limited mainly to water electrolysis as the application. An Israelian company (H_2Pro) is also trying to commercialise the device.

However, these studies focus on taking advantage of the latter two aspects (the increased energy efficiency of the electrolysis, from less than 75% to over 90%), and not the potential benefit of the change in electrochemical cell architecture offered by this spatio-temporal decoupling. In addition, limited studies are present in the literature on the following aspects:

– To use the concept of spatiotemporal decoupling in PEC devices.[155,161]

– Applying it to reactions other than water electrolysis, such as the direct conversion of N_2 to ammonia.[162]

Using this solid-state redox approach for the anode could improve the energy efficiency, reaction rate and flexibility of operations also in PEC devices for chemical energy storage. An example is the PEC device to produce methane from CO_2 (solar-to-fuel), presented in Fig. 10.

Several studies have been reported in the literature on the photoelectrochemical conversion of CO_2 into fuels, including methane, as reviewed, for example, by Kumaravel *et al.*[163] However, a specific configuration such as that presented in Fig. 10 has not been reported insofar. It reduces the potential necessary to drive the CO_2 methanation, and thus increases energy and solar-to-fuel efficiency. Among the best electrocatalysts for CO_2 to methane are modified copper nanoparticles, with FE above 70%.[164]

Ideally, the anode capacity should allow the PEC cell to operate at all daytime hours, with the regeneration occurring at
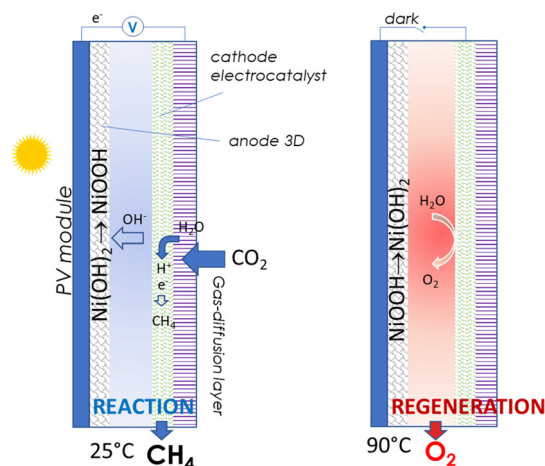
Fig. 10 Concept of an integrated PEC device for the solar-to-fuel (CO_2 to CH_4) conversion.

Fig. 11 The general design scheme for an integrated SFB device.

night. The determining factor is the amount of Ni-hydroxide available for the reaction at the anode. 3D High-capacity anodes should be thus developed.[165–167] Still, the operation times are of the order of a few hours.

It should be noted that the possibility of spatial decoupling of the cathodic and anodic reactions through the electrolyte circulation makes it possible to consider a design where the solid anodic state anodic component is in one place (for example, on the roof), and the cathodic part of the cell is in a different (dark) location.

Redox mediators can be present instead in the liquid phase (the electrolyte),[168] overcoming the capacity limits of the solid-state redox anode. There is an increasing interest in this approach for spatiotemporal decoupling, although still focused on water electrolysis and not applied to the promotion of devices for solar-to-fuel energy storage.

Wang et al.[169] used sodium nickel hexacyanoferrate as a redox reservoir to produce electrochemically strong oxidants. Frey et al.[170] demonstrated the possibility of a Ce-mediated dual-use (energy storage and H_2 production) cell. The high reduction potential of the Ce^{III}/Ce^{IV} redox couple allows the decoupling of the water-splitting reaction into a charging cell that produces H_2 and a discharging cell that produces electricity. Ho et al.[171] reported a PEC cell where a Ni-electrode generates O_2 from OH^- at the anode, and the cathode V^{3+} is reduced to V^{2+}. Then, the V-containing electrolyte is transported to a different reactor, where a MoC_x-based catalyst produces H_2 and forms V^{3+} again for subsequent reduction. Although the averaged diurnal solar-to-hydrogen (STH) energy conversion efficiency was limited (3.7%), this solution represents an interesting advancement towards realising PEC devices with continuous operations.

The concept of solar flow batteries should now be introduced to further understand these possibilities.

Integration of the PEC design into solar flow battery. In PEC cells, solar energy is stored as chemical energy in the fuel or chemical produced. In solar flow batteries (SFBs),[172–174] the solar semiconductor is combined with a redox flow battery (RFB)[175] for the reversible storage of electrical energy in the form
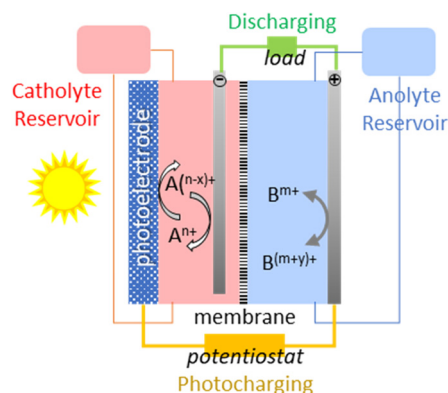
typically of redox changes in inorganic ions such as vanadium. These devices thus integrate the functionalities of solar energy conversion and electrochemical energy storage devices, allowing a more compact and cost-effective approach for off-grid electrification.

The principle of operations of SFB is summarised in Fig. 11. Solar energy is absorbed by a photoelectrode, and the photoexcited carriers convert the redox couples, i.e., store the solar energy in the electrolytes. When electricity is needed, the charged-up redox couples will be discharged on the electrodes, as in normal RFB, to generate the electricity. Catholite and anolyte reservoirs will allow for modulating the storage capacity to the needs.

Integration of this approach directly into that of a PEC device, where the aim is to produce chemicals/fuels rather than a reversible redox change in an inorganic ion, is not straight. It should be noted that organic redox batteries are also possible.[176] However, this does not markedly change the issue of integrating SFB and PEC devices.

The examples presented in the previous section evidence some possible direction, but an optimal solution still has not been clearly identified. Research in this direction should be intensified because it offers significant relevant possibilities to exploit PEC devices.

Spatiotemporal decoupling thus offers a range of exciting solutions for innovation in electro- and photo-electro catalytic devices integrating redox mediators. These concepts will allow for the design of next-generation PEC devices for distributed production of fuels/chemicals. They offer many innovation opportunities that are still largely unexplored. However, the study of all these possibilities is just starting.

Alternative approach to enable continuous PEC operations. An alternative possibility for a PEC device with a continuous (24 h) production of H_2 is presented in Fig. 12. It represents a scheme for an artificial leaf device built with earth-abundant materials for combined H_2 production and storage as formate with solar-to-fuel efficiency > 10%.[177] The PEC unit, schematically shown in Fig. 12(b), has a highly compact design, amenable to scale-up, and is integrated with gas diffusion electrodes based on Cu–S for CO_2 reduction and Ni–Fe–Zn oxide for water oxidation. The PV module is a low-cost PV four-cell module with shingled
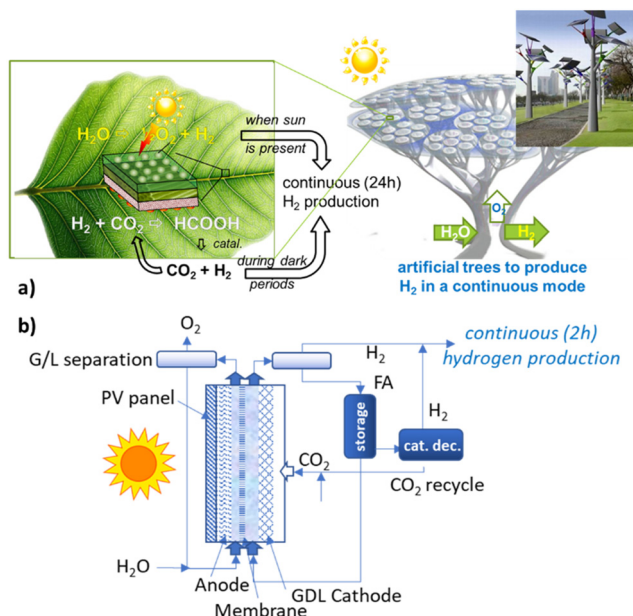
Fig. 12 (a) A pictorial illustration of the concept of artificial leaves and trees to produce H_2 in a continuous mode, and (b) a schematic diagram of the PEC device to realise such a possibility.

Fig. 13 Simplified scheme of the electrocatalytic approach to producing ethyl acetate at both sides of the electrocatalytic cell.

interconnection based on silicon heterojunction technology. It is wire-connected, and not in contact with the electrolyte. An overall 10% solar-to-fuel efficiency also considered hydrogen production was reached at high current densities (about 17 mA cm^{-2} at one Sun), making record performances. The chemical storage of H_2 as formic acid (FA) is realised. Its catalytic decomposition during dark periods allows for the continuous production of H_2 or, alternatively, hydrogen production on demand, as required in various industrial applications. However, the operations of the full unit presented in Fig. 12 have not yet been reported.

3.2 Doubling the efficiency by producing the same product on both electrocatalytic sides

Another challenge scarcely explored for PEC devices is the possibility of producing the same product at both the anode and cathode sides to formally "double" the efficiency. In addition, downstream separation costs often determine the overall process's feasibility. Thus, producing the same chemical in an electrocatalytic cell on both sides and avoiding the need for downstream operations may appear to be an impossible challenge. However, this is the objective of the EU H2020 DECADE project (distributed chemicals and fuels production from CO_2 in photoelectrocatalytic devices, project 862030).

Synthesis of ethylacetate at both electrocatalytic sides. The cited DECADE project aims to maximise efficiency and reduce downstream costs. The device produces the same chemical on both sides of the electrocatalytic cell. It uses streams from a biorefinery, and the product can be used as such with minimal downstream processing. The effluent from the electrocatalytic cell is an ethyl acetate solution with some side ethyl formate in ethanol (the reactant, together with CO_2). It can be used directly
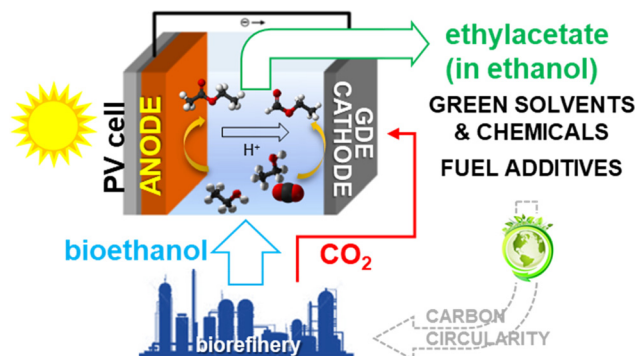
as a green solvent or gasoline additive. The concept is summarised in Fig. 13.

On the anode side, bioethanol from biorefinery is oxidised to acetate, which further reacts with ethanol to form ethyl acetate. On the cathode side, CO_2 emitted in the biorefinery is fed to a gas diffusion cathodic electrode (GDE) to be converted to acetate, which reacts with ethanol to produce ethyl acetate. Ethyl formate forms as a side product. For the target uses, the additional presence of ethyl formate is not critical. In this way, carbon circularity is also enhanced.

A photovoltaic module is integrated into the device to use direct solar energy. Thus, this concept of a PEC device combines the two challenges of synthesising a single product at both the anode and cathode sides, which can be directly used without downstream separation. Both these aspects are critical for process economics.

The same concept can be used for the valorisation of methanol production rather than for biorefinery streams. The device can synthesise methyl formate from methanol by adapting the electrocatalysts. This way, CO_2 from methanol plants is reused to produce a higher-added-value chemical.

There are limited studies on the electrocatalytic conversion of ethanol to ethyl acetate,[178,179] while there several studies on CO_2 reduction to acetate and/or formate.[180–183] In addition to the low conductivity of ethanol, the main issue is that the same electrocatalysts change behaviour in an ethanol environment rather than an aqueous solution. This change is possibly related to the absence of the equilibria of CO_2 with mono- and bi-carbonate present in water. However, this is another missing aspect of the literature. Thus, new electrocatalytic chemistry and materials have to be discovered. On the other hand, there are still insufficient scientific bases to design tailored electrocatalysts for operations under less conventional conditions and electrolytes.

Producing glycolic acid at both electrocatalytic sides. One question is whether the previously discussed example is unique, or whether a similar approach can be applied to other cases. Another possibility is taken from another project proposal (GALACTIC, CL4-2022-TWIN-TRANSITION) aimed at producing the same chemical (glycolic acid) on the two sides of the electrocatalytic cell.

At the anode, glycerol (a byproduct of biodiesel production) is electro-oxidised to glycolic acid (GC), while at the cathode side, GC is produced by oxalic acid reduction. The latter is made in a bio-reactor by biowaste fermentation, followed by electrochemical oxalate to oxalic acid extraction. GC is a monomer for green poly-glycolic acid production, a high-value polymer. GC is also widely used (i) in the textile industry as a dyeing and tanning agent, (ii) in food processing as a flavouring agent and a preservative, and (iii) in the pharmaceutical industry as a skin care agent. It is a high-added-value chemical produced from biowaste, according to this process scheme.

However, few studies have been reported in this direction. No one addressed the tandem electrolyser with glycerol to GC on the anode side and oxalic acid to GC on the cathodic side. However, separate studies on these two reactions have been reported on glycerol to GC electro-oxidation,[184–187] and oxalic acid to GC electro-reduction.[188–191]

It may be argued that in organic chemistry, the stable product of glycerol oxidation is glyceraldehyde, which quickly isomerises to dihydroxyacetone. The next two-electron oxidation does not form the acid, but the pyruvaldehyde, as observed in most biochemical enzyme cycles. However, various authors demonstrate the feasibility of the electro-oxidation of glycerol to GC.[184–187] Kim et al.[184] used nanostructured Au catalysts at the anode of an electrochemical cell, reporting a glycerol conversion of ∼51% and GC selectivity ∼47% at 1.0 V (vs. RHE). The selectivity to GC was attributed to the enhanced facet-dependent OH adsorption, especially at the (100) and (110) sites. Lee et al.[185] reported a selectivity to GC up to 72% with a yield of 66% using an anode based on carbon-black and Amberlyst-15. Brix et al.[186] used a nickel boride electrocatalyst, forming GC and other products. At a potential of 0.4–45 V vs. Ag/AgCl/KCl (3 M), GC is the main product. Santiago et al.[187] used $LaNiO_3$ and $LaCoO_3$ perovskite as anodes, forming nearly equimolar amounts of formate and glycolate. Thus, different performances have been shown depending on the electrode, but up to high selectivities to GC have been demonstrated in glycerol electro-oxidation.

The reasons for the differences to that observed in organic and enzymatic chemistry are still unclear, but likely related to the different reaction mechanisms. On the other hand, this aspect demonstrates how different and novel reaction mechanisms could be present in electrocatalysis.

Oxalic electrocatalytic reduction to GC has also been demonstrated. Abramo et al.[188] used as electrocatalysts an ordered array of vertically aligned TiO_2 nanotubes, on top of which some small partially-reduced titania nanoparticles are present. The synergy between these two elements is necessary.

GC with faradaic selectivities up to about 60% was observed. Masaaki et al.[189] used TiO_2 on Ti mesh or Ti felt as a cathode to obtain similar faradaic selectivities. Zhao et al.[190] used roughened TiO_2 film electrodes, forming mainly glyoxylic acid. This molecule is an intermediate in the hydrogenation of oxalic acid to GC. De Luca et al.[191] used g-C_3N_4 decorated TiO_2 nanotube thin films as cathodic electrodes for the selective reduction of oxalic acid. They found that g-C_3N_4 promotes the behaviour with FE to GC up to 76%.

Although the tandem electrocatalytic approach was not reported in the literature, the independent cathodic and anodic reactions were proven feasible.

Oxalic acid, rather than being produced by fermentation of biowaste, can also be made from CO_2.[192] This way offers the possibility of developing a new value chain for C2 products from CO_2 by using electrocatalysis. This was the objective of the EU H2020 project OCEAN (Oxalic acid from CO_2 using electrochemistry at demonstration scale, project no. 767798; **https://www.aspire2050.eu/ocean**). The electrocatalytic process was demonstrated up to a pilot unit scale. It is a prototype electrochemical reactor with a stack of electrochemical cells of about 0.4 m^2 working at current densities of at least 1.5 kA m^{-2} to convert 250 g of CO_2 into formate per hour. The formate is then thermally converted to oxalic acid, being that this solution is preferable over the direct electrocatalytic synthesis of oxalic acid. Sn-based electrodes convert CO_2 to formate with high FE at high current densities.

4. Conclusions

We have provided some examples, without being exhaustive of all the possibilities, of novel valuable directions for innovation in (photo)electrocatalysis by starting from the analysis of the needs in some relevant value chains.

These examples and approaches highlight the demand to expand the current area of studies, mainly focused on a restricted range of options. We focused on running or proposed EU projects in which we were involved because it is often difficult to have precise insights into them otherwise. However, for confidentiality, only published data were discussed here.

These projects indicate the innovative effort to realise the challenge of electrifying chemical production. However, as discussed in this manuscript, the fundamental studies to support these novel, industrially-valuable directions are often lacking, despite the impressive number of publications on electrocatalysis and related aspects.

Often, this determines an inadequate recognition of the potential of these novel directions because there is a lack of fundamental background studies. This is an egg and chick problem. The aim of this feature article was thus to remark on the need for a scientific effort to open the horizons in (photo)-electrocatalysis to new directions. On the other hand, the example of GC from glycerol demonstrates how electrocatalysis could produce chemicals that are otherwise difficult to synthesise by organic or enzymatic chemistry.

Other relevant research areas were discussed earlier[11] in outlining the feasibility of fossil-free chemical production. The new areas of development indicated were the following: (i) benzene direct electrocatalytic hydroxylation to phenol, (ii) novel electrocatalytic routes by coupling the products of the conversion of small molecules (CO_2, N_2, H_2O) with the in situ functionalisation of biobased molecules, (iii) electrocarboxylation of olefins, diolefins or aromatics, (iv) use of the reactive intermediates formed in the electrocatalytic conversion

of small molecules to make new paths, and (v) the electrocatalytic conversion of biomethane.

These developments and those discussed here require improving the fundamental bases for (photo)electrocatalysis. Among the different necessary aspects: (i) the design of advanced (photo)electrocatalytic reactors, (ii) the study of multiphasic (photo)electrocatalytic reactors, (iii) understanding of the differences, including in mechanistic aspects, between (photo)electrocatalysis and conventional heterogeneous catalysis, (iv) develop new approaches and explore novel (complex) pathways, and (v) analyse the complex interplay determining behaviour (rational design of three-phase boundary address the selectivity challenges of electrocatalysts).

Creating a new value chain for chemical production to substitute fossil fuels requires advances in the (photo)electrocatalysis approach and exploring new possibilities, some of which are discussed here as an example. It is necessary to accelerate the progress in this area by exploring new solutions, reactions and topics rather than focusing only on mechanistic aspects and developing new catalysts.

Notwithstanding the many studies in electrocatalysis, there is still too limited research on creative directions. The most research effort is restricted to a few areas, such as CO_2 or N_2 electrocatalytic reduction. Meeting the ambitious net-zero emissions target by 2050 requires accelerating research in the directions outlined in this highlight manuscript.

Abbreviation

BHMF	Bis(hydroxymethyl)furan
CAPEX	Capital expenditures
CO$_2$RR	CO$_2$ reduction reaction
EU	European Union
FA	Formic acid
FDCA	Furan dicarboxylic acid
FE	Faradaic efficiency
GC	Glycolic acid
HB	Haber–Bosch (process)
HER	Hydrogen evolution reaction
HMF	5-(Hydroxymethyl)furfural
LOHC	Liquid organic hydrogen carriers
NOR	Nitrogen oxidation reaction
NRR	Nitrogen reduction reaction
OER	Oxygen evolution reaction
PCET	Proton-coupled electron transfer
PEC	Photoelectrocatalytic
PEF	Poly(ethylene 2,5-furanoate)
OPEX	Operative expenditures
RFB	Redox flow battery
RHE	Reverse hydrogen electrode
SFB	Solar flow battery

Author contributions

All authors equally contributed to the realisation of this manuscript.

Conflicts of interest

There are no conflicts to declare.

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