

Emerging opportunities for electrochemical processing to enable sustainable chemical manufacturing

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Electrochemical processes are poised to play a critical role in the future energy economy by supporting widespread decarbonization efforts and providing new avenues for sustainable energy use including the electrification of industry. Opportunities exist for the development and integration of novel electrochemical processes that offer carbon-neutral or even carbon-negative synthetic routes to important products by exploiting new reactivities that enable molecular transformations difficult to realize via thermochemical methods. This mini-review highlights these opportunities by first considering the factors that have enabled electrochemical technologies to flourish in certain industrial sectors and then contemplating how those attributes may be leveraged to enable broader adoption. Hydrogen production, carbon dioxide fixation, and organic hydrogenation are discussed as promising electrochemical processes that may find industrial use in the near future.

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Current Opinion in Chemical Engineering 2018, 20:xx–yy

This review comes from a themed issue on **Nanotechnology: nanocatalysis**

Edited by **Hua Chun Zeng** and **Hong Yang**

<https://doi.org/10.1016/j.coche.2018.05.002>

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Introduction

The abundance, availability, and affordability of fossil fuels has been a key driver of societal progress over the past two centuries. However, with global energy demand projected to increase 48% by 2040 [1], there is an increasingly urgent need to decouple carbon emissions from economic activity without stifling growth. This necessitates the development and deployment of sustainable and reliable energy solutions [2,3]. Electrochemical processes are poised to play a pivotal role in the evolving global

power system as the efficient interconversion of electrical and chemical energy can enable the deployment of green technologies that support the decarbonization of the electric grid, power the automotive fleet, and offer new opportunities for chemical manufacturing. While the grid and transportation sectors are the subject of intensive research and development efforts worldwide, there has been considerably less focus on the electrification of non-energy-related industries. Yet, the industrial sector currently accounts for 40% of the total global energy demand, of which 26% is used for basic chemicals and refining [1], while also accounting for 32% of the global greenhouse gas emissions [4]. Thus, the identification and implementation of sustainable operating principles will be key to improving energy efficiency and reducing environmental impact.

Historically, fossil fuels have been more heavily utilized than electrical energy in the chemical industry due to their low cost and the dominant role of fossil fuel combustion in electricity generation. For example, the present cost of natural gas is about $0.005 \text{ \$ kWh}^{-1}$ (estimated from the lower heating value) as compared to about $0.066 \text{ \$ kWh}^{-1}$ for industrial electricity [5,6]. However, this paradigm is being disrupted by the rapidly decreasing cost of wind and solar electricity generation coupled with the growing global consensus on the importance of climate change. Over the past eight years, the cost of electricity generated from wind and solar photovoltaic has fallen 67% (to $0.045 \text{ \$ kWh}^{-1}$) and 86% (to $0.050 \text{ \$ kWh}^{-1}$), respectively, and is now competitive with fossil fuel based electricity generation technologies ($0.055 \text{ \$ kWh}^{-1}$) [7]. Future cost reductions to $0.03 \text{ \$ kWh}^{-1}$ are anticipated from materials advances, economies of scale, and manufacturing improvements although issues with intermittency are likely to persist without the incorporation of energy storage [8]. Simultaneously, mounting concerns about the impact of carbon emissions on the environment are driving policy decisions at the local, national, and international levels, notably the recent Paris Agreements, which seek to drive tangible action in carbon management across the globe [2,9].

The development of efficient electrochemical processes, which leverage renewable electrons, would enable decarbonization of the industrial sector and spur innovations including reducing plant costs through modularity and process intensification, improving safety and decreasing

reactor costs through mild reaction conditions, and increasing flexibility through tunable product generation. Moreover, electrochemistry may allow new molecular transformations, unlocking previously inaccessible or unimaginable synthetic routes. However, current understanding of the catalyst science and reaction engineering of electrochemical transformations is limited to a narrow set of reactions, largely influenced by historical interest in fuel cells and batteries. Consequently, electrochemical engineering faces several rectifiable knowledge gaps in materials, device, and process design.

This mini-review aims to highlight opportunities for electrochemical processing as a means of sustainable chemical manufacturing by first considering the factors that have enabled electrochemical technologies to flourish in certain industrial sectors and then contemplating how those attributes may be leveraged to enable broader adoption.

A brief history of the chemical industry

Before envisioning the future role of electrochemical processing in the chemical industry, it is instructive to consider the advent and growth of modern chemical processes. While society has harnessed chemical reactivity for centuries, the technological innovations of the Industrial Revolution enabled manufacturing at previously unprecedented rates, scales, and costs. Common themes of successfully adopted processes are product demand, availability of inexpensive reactants, minimal toxic by-products, and ease of implementation and scale up. To illustrate these points, we provide a brief review of chemical process development and improvement since the 1790s (Figure 1). For the interested reader, comprehensive treatments of the subject can be found in references [10,11].

Among the first chemical manufacturing processes, the Leblanc process arose to meet the growing demands for sodium carbonate from the fledgling European glass- and soap-making industries by developing a route using coal, limestone, brine, and sulfuric acid [11,12]. The increased sulfuric acid demand was met using lead-coated reactors, previously developed by Roebuck, that could produce sulfuric acid at a rate of hundreds of pounds per day, a two orders of magnitude improvement over the prior glass jar technology, as well as using a nitrate catalyst that Ward developed for sulfur oxidation [10,13]. Though effective in producing sodium carbonate, the Leblanc process also generated significant amounts of hydrogen chloride and calcium sulfide as toxic and environmentally hazardous by-products, which ultimately motivated the need for process improvements in the mid-1800s.

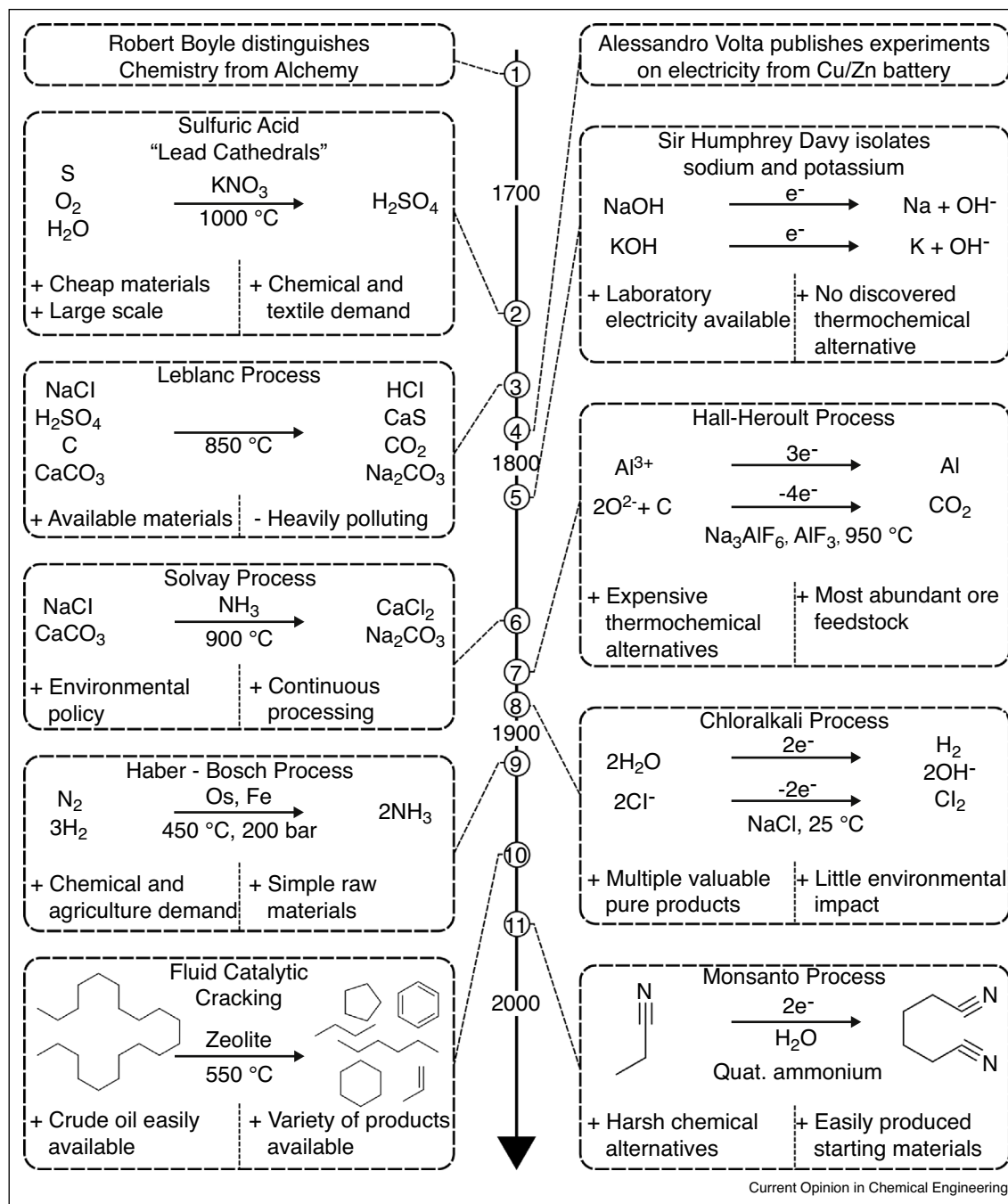
In the 1860s, the Solvay process arose as an alternative means of producing sodium carbonate. In this process, ammonia is bubbled through a brine column and the resulting ammoniated mixture is passed through a

separate column where carbon dioxide (CO_2) is bubbled to precipitate sodium bicarbonate [14]. Finally, the sodium bicarbonate is heated in air to form sodium carbonate and release CO_2 and water. In addition to being more environmentally friendly than the Leblanc process, the Solvay process was continuous thus enabling greater production rates and improved product consistency. However, at the time of the Solvay process, ammonia was only obtained through distillation of natural wastes. With the important need for ammonia as an industrial feedstock, as well as for explosives and fertilizers, Haber and Bosch developed a process in 1913 for combining nitrogen and hydrogen at 150–250 bar and 400–500 °C over a variety of metal catalysts (*e.g.*, promoted iron, osmium, uranium) [15–18]. To this day, the Haber-Bosch remains the dominant ammonia synthesis method.

While knowledge of electricity existed for centuries, the development of reliable sources of electrical energy, such as Volta's pile, enabled Sir Humphry Davy and others to establish electrolysis in the early 1800s as a means of generating previously unobtainable metals, including sodium and potassium, from salt solutions [19,20]. The invention of dynamos and formative work on electromagnetism in the 1860s allowed broader access to electricity further opening the door to electrochemical processing. In some cases, thermochemical routes existed for generating important metals but they were expensive and inefficient. Notably, aluminum was produced via the Deville process in which the double salt sodium chloride-aluminum chloride was reduced at high temperatures by metallic sodium [21]. This process relied on the chloride salts of aluminum as the more common bauxite ore, containing primarily alumina, could not be reduced to metallic aluminum due to the strong bond between the aluminum and oxygen. In 1886, Hall and Héroult independently developed a method for direct electrolytic reduction of alumina to aluminum. Alumina from bauxite via the Bayer process could be reduced electrochemically: by dissolving alumina in a bath of molten cryolite (sodium hexafluoroaluminate) and passing a direct current through the bath, aluminum would be deposited at the negative electrode. From these developments, aluminum could be produced at large scales from abundantly available bauxite, direct current electricity, and carbon which is used as a sacrificial anode material. As electricity prices fell, so too did the direct cost of producing aluminum [22] but, it is important to note that the energy required for aluminum production from bauxite necessitates recycling as much of its high embodied energy can be recovered.

Another early success was the electrolytic co-production of chlorine and sodium hydroxide from brine solutions, now known as the chlor-alkali process. Indeed, an early method to both increase the revenue and decrease the environmental impact of a Leblanc plant was to convert the waste hydrogen chloride to more valuable chlorine gas

Figure 1



A chronological diagram of several important industrial processes based on thermochemical (left) and electrochemical routes (right).

through the Deacon process, a high temperature oxidation on a copper, chromium, or ruthenium-based catalyst. Electrolysis of inexpensive brines offered the opportunity to generate valuable products on each electrode at ambient temperatures but required a means of separating the products within the reactor to prevent parasitic reactions curtailing efficiency and yield. In 1886 Matthes and

Weber developed and patented porous membranes to separate each electrode compartment in an electrolysis cell, enhancing product recovery rates and enabling the industrial dominance of the electrolytic chlorine production [11]. In 2011, the chlor-alkali process accounted for 97% of 77 million metric tons of chlorine produced globally [18,19].

The early 1900s saw the rise of oil and gas industry, largely based on the refinement of crude oil to fuels, to support the emerging transportation sector. This led to the development of complex high-temperature processes which produced a significant number of useful intermediates that, in turn, enabled the generation of a range of valuable organic products such as plastics and polymers. Despite these advances, electrochemical processing continued to be valuable as it enabled unique reactivities. Most notably, in the 1960s Monsanto developed an electrochemical route to adiponitrile, a key precursor for nylon, which is an important synthetic polymer, particularly in modern textiles, based on monomer amides. A popular early pathway to nylon was through oxidation of cyclohexanol and cyclohexanone (*i.e.*, KA oil) using harsh chemical oxidants resulting in NO_x pollutants [23]. In contrast, adiponitrile can be obtained through the single-step hydrodimerization of acrylonitrile, obtained from the ammoxidation of propylene, which relies on abundant feedstocks. As such, Monsanto developed a relatively mild electro-hydrodimerization process for generating adiponitrile which, to date, remains the largest organic electrochemical production method, accounting for about 31% of the US production of adiponitrile in 2011 (930,000 metric tons) [24,25].

Though brief, two lessons can be drawn from the historical review: (1) cost is a significant driver for process development and (2) electrochemical processes have thrived in the absence of thermochemical alternatives.

Advantages of electrochemical processing

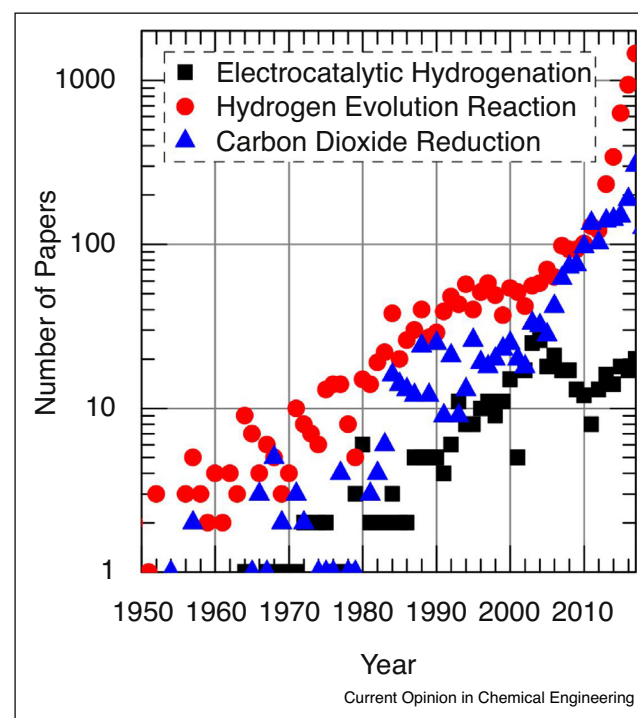
Electrochemical processing holds several advantages over traditional thermochemical processing that may promote industrial use, despite generally higher input energy costs. First, electrochemical processes directly utilize electrons, which are increasingly being derived from renewable sources, rather than relying on potentially harmful chemical reductants and oxidants [26,27,28**]. Second, electrochemical processes are separated into distinct half-reactions, specifically reduction at the cathode and oxidation at the anode, enabling independent optimization of each reaction. In contrast, thermochemical processes rely on intimately coupled redox events that cannot be separately tailored. Furthermore, while typical methods for tuning surface energies in traditional catalytic applications rely on synthetic approaches (*e.g.*, composition, nanostructure) or operating conditions (*e.g.*, temperature, pressure) to achieve desired performance, electrocatalytic systems offer the added benefit of direct control over the surface free energy via electrode potential [29,30]. This, in turn, may allow real-time tuning of catalyst activity and selectivity, which, in principle, can be leveraged for flexible manufacturing processes. While traditional electrochemical systems have focused on the conversion of simple compounds with limited reaction complexity, the shift towards selective transformations of

organic compounds (*e.g.*, partial oxidation / reduction of specific moieties) requires a deeper understanding of catalysis for suppressing undesired reaction pathways and enhancing the desired ones, while maintaining activity and selectivity in compositionally-diverse and often poorly-defined feeds.

Possibilities for industrial electrification

Recent advances in electrocatalyst design and cell engineering are inspiring industrial implementation of certain electrochemical processing. Figure 2 highlights growing interest, as evidenced by increased publication rates, for three major electrochemical processes: hydrogen formation, CO_2 valorization, and organic hydrogenation. Materials development is an area of intensive research as improving electrocatalyst activity, selectivity, and stability is paramount to achieving the high production rates and energy efficiencies necessary for economic viability. Beyond electrocatalysis, there is a need to transition performance nanomaterials to appropriate high surface area electrode structures and integrate those electrodes into reactor configurations that do not hinder catalyst improvements. This section is not intended to provide a detailed literature review but rather a short overview of each topic highlighting both the promise and the current

Figure 2



A representation of increasing interest in electrochemical processes relevant to the chemical industry based on a March 2018 Scopus search for keywords “Electrocatalytic Hydrogenation”, “Hydrogen Evolution Reaction”, and “Carbon Dioxide Reduction”.

state-of-the-art. For the interested reader, detailed reviews on these topics can be found in the following references [27^{*},28^{**},31^{**},32,33^{*},34,35^{*},36,37].

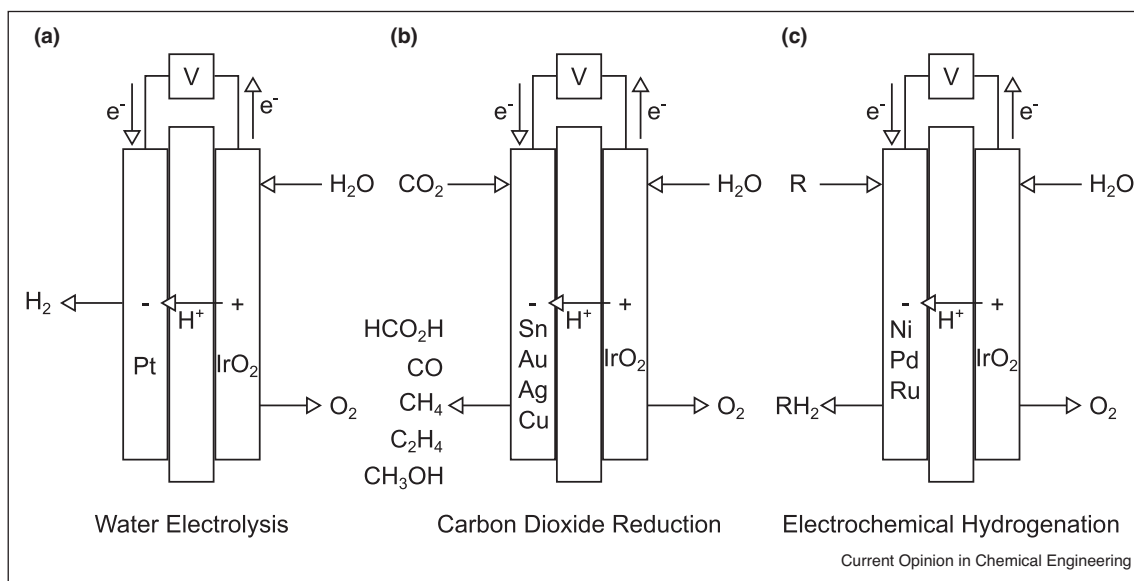
Hydrogen production

Hydrogen is a widely-used reagent that enables hydrocracking, saturation of olefins, hydrogenation in the food industry, and further increases in demand are expected should fuel cell technology become more widespread. As of 2010, more than 52 million metric tons of hydrogen were produced worldwide [38], primarily through steam methane reforming (SMR) (48% of global production and 95% of U.S. production [39,40]) which converts natural gas and steam to hydrogen and CO₂ (with carbon monoxide co-generation), in a 4 to 1 ratio, at 800 and 900 °C over a variety of catalysts (nickel, ruthenium, rhodium, iridium) [41]. The co-generation of CO₂ challenges the sustainability of hydrocarbon reforming processes, and requires costly downstream separations which impact process scalability. While high electricity costs limit the cost-competitiveness of present electrolysis technology, projected reductions to as low as 0.03 \$ kWh⁻¹ provide a pathway to hydrogen generation at similar costs to SMR (1.20–1.80 \$ kg⁻¹) [40].

The electrochemical reduction of protons to hydrogen is a facile reaction, especially on platinum, but the high cost of these materials continues to spur research and development towards reducing or eliminating precious metal content. Recent examples include core-shell catalysts with noble metal shells and earth-abundant core materials

[42^{*}] as well as molybdenum sulfide nanoparticles which mimic hydrogenases used to generate hydrogen in biological systems [43]. The hydrogen evolution reaction proceeds via a three step process where protons are first reductively bound to the catalyst surface as atomic hydrogen (Volmer step), then either two surface bound hydrogens combine (Tafel step) or one surface bound hydrogen reacts with a proton and electron (Heyrovsky step) to produce molecular hydrogen. Any of these three steps can be rate determining depending on reaction conditions and catalyst surface, but the Volmer step is always necessary for catalyst activity [44–47]. Significant advances in density functional theory at electrified solid-liquid interfaces have enabled detailed descriptions of optimum electrocatalytic surfaces in the complex electrochemical environment required for hydrogen evolution [48–50] by tailoring the energetic interactions between protons in solution and the catalytic surface through electronic structure modifications. While hydrogen evolution under acidic conditions is facile to the point that the reaction is typically mass-transfer limited, hydrogen evolution under alkaline conditions is more sluggish motivating research into new electrocatalysts [51]. However, traditional water electrolysis cells (Figure 3a) are limited by other factors including slow oxygen evolution kinetics, material stability issues particularly on the anode, and expensive membranes (typically Nafion) [52]. These challenges have inspired investigations into novel catalyst materials and associated reaction mechanisms for the oxygen evolution reaction

Figure 3



Representative electrochemical cells for (a) water electrolysis to generate hydrogen, (b) carbon dioxide reduction to a range of valuable products, and (c) electrochemical hydrogenation of organic materials. For simplicity, the oxygen evolution reaction is shown as the anode reaction in all cells but other oxidation reactions may be considered. Representative catalyst materials are shown for each reaction which draw from the current state-of-the-art.

especially in alkaline media [53–55], as well as into the design of novel cell architectures that utilize cheaper membranes, or eliminate the membrane altogether [56*].

Carbon dioxide utilization

Carbon dioxide (CO₂) fixation has been a process of increasing interest as anthropogenic emissions of CO₂ have nearly doubled from 27 GtCO₂-eq to 49 GtCO₂-eq, motivating the development of carbon-neutral or -negative processes [4]. While it has been posited that electrochemical CO₂ reduction alone is unlikely to significantly impact atmospheric concentrations of the greenhouse gases, the potential exists to valorize CO₂-concentrated industrial waste streams by forming useful products (*e.g.*, hydrocarbons and oxygenates) [57]. Traditional thermochemical methods for CO₂ processing are limited outside of the reverse water gas shift reaction which converts CO₂ and hydrogen to carbon monoxide and water but requires high operating temperatures (above 900 °C) to achieve high equilibrium conversions.

Electrochemical reduction of CO₂ can be achieved at, or near, ambient conditions, which minimizes environmental impact and safety hazards. Electrocatalysts for CO₂ reduction are typically grouped by favored majority product and can be broadly defined as formate- (HCOO⁻) producing (tin, lead), carbon monoxide- (CO) producing (silver, gold, zinc), or hydrocarbon-producing (copper) [58]. The focus of recent efforts in CO₂ reduction catalysts have been three-fold: (1) increasing energy efficiency by decreasing the overpotential required to achieve a given reaction rate, (2) increasing the durability under realistic operating conditions and (3) improving the selectivity towards a single (or few) desired product(s) [31**,32,59,60,61**]. The proposed rate determining step for CO₂ reduction involves formation of the radical anion, CO₂^{-•}, on the catalyst surface [32], thus materials that stabilize this high-energy intermediate are expected to show improved rates of reaction. For example, nanoporous silver achieves current densities up to 3000 times greater than polycrystalline silver while maintaining high selectivity (92% CO), metal-free carbon nanofibers exhibit similar overpotentials to metal-based catalysts and high selectivities (98% CO), and nanostructured tin reduces CO₂ at overpotentials as low as 340 mV (93% HCOO⁻) which can be heavily impacted by metal facet [62–65]. Additional complications arise from poorly defined catalytic sites and active surface area, which conflate intrinsic catalyst improvements with increased active area. While these systems have demonstrated significant improvements in activity and selectivity, there are still precious few demonstrations of electrocatalysts for CO₂ reduction that have been tested for longer than 24-hour periods due to challenges in reactor design leading to mass-transfer limitations (*e.g.* flooding) [60]. Although the production of CO and HCOO⁻ are well studied due to the relative simplicity of the two electron reduction reactions, more deeply reduced products,

especially larger hydrocarbons and oxygenates, are much harder to obtain due to the greater number of electron transfer events that must occur and the diverse set of potential reaction pathways. While improvements in energy efficiency apply to all CO₂ reduction catalysts, selectivity improvements are particularly relevant for copper-based catalysts which appear unique in their ability to generate an array of hydrocarbon products. This distribution can be narrowed through nanostructuring, for example, copper nanocubes which favor ethylene formation over other hydrocarbons [66]. While significant improvements have been made in CO₂ reduction electrocatalysts, cell designs that support these active, selective, and stable catalysts will be critical to realizing economically-feasible electrochemical CO₂ reduction.

Organic hydrogenation

As the use of fossil fuel decreases, biomass will become increasingly important as a feedstock for hydrocarbons. However, the high cost of transporting these resources to traditional centralized refining centers (0.12 \$ ton⁻¹ km⁻¹ [67]) motivates the development of smaller distributed processing facilities. High temperature catalytic hydrogenation is the most common means of saturating the carbon-carbon bonds of organic species but requires pressurized hydrogen to saturate the reaction media necessitating either a nearby source of high-pressure hydrogen or significant capital investment to install compressors upstream of the reaction vessel.

Electrocatalytic hydrogenation unlocks this reactivity at milder conditions by generating surface-bound hydrogen species *in-situ*, which can then react with the unsaturated organic molecules of interest. However, electrocatalyst development has lagged behind thermocatalyst development and, as a result, remains a nascent technology concept. Consequently, the electrocatalytic hydrogenation literature is limited and largely focused on qualitative catalyst and reaction screening rather than systematic quantification. Ruthenium, platinum, and nickel electrocatalysts have demonstrated the ability to hydrogenate bio-oil model compounds as well as pyrolysis bio-oil due to their affinity for generating surface-bound hydrogens (Volmer step) [68–70]. Several materials have been investigated for the electrocatalytic hydrogenation of furanic compounds including nickel, iron, palladium, and platinum which all show significant activity towards reducing the aldehyde of furfural to furfuryl alcohol [71–73]. Bimetallic catalysts have been investigated for the electrocatalytic hydrogenation of ketones finding that while copper itself demonstrates poor selectivity to reducing the ketone, copper-nickel catalysts show comparable selectivity to pure nickel at higher turnover frequencies [74**]. Finally, palladium and Raney-nickel have also been shown to electrolytically cleave lignin model β-O-4 bonds [75]. Although these examples identify promise in individual areas, they rely primarily on

phenomenological results without demonstrating fundamental catalyst understanding. Recent research has begun to focus on developing insights into the electrocatalytic hydrogenation mechanism using site titration studies with organic thiols on copper catalysts in the electrocatalytic hydrogenation of furfural [76**]. Establishing rigorous structure-activity relations for reactions of interest is paramount to advancing the approaches and identifying competitive electrochemical routes.

Future directions

Electrochemical processes are poised to play a critical role in the future global power system supporting decarbonization efforts and providing new avenues for sustainable energy use. While extensive efforts have focused on the transportation and grid sectors, there has been considerably less focus on the electrification of the chemical industry. Opportunities exist for the development and integration of novel electrochemical processes that offer carbon-neutral or even carbon-negative synthetic routes, assuming the use of renewable electricity, to important products by exploiting new reactivities that enable molecular transformations difficult to realize via thermochemical methods. While this mini-review seeks to highlight a few representative reactions of general interest, many others may be considered. A key challenge will be accelerating the development of electrochemical technologies to compete with thermochemical technologies which have benefitted from over a century of intensive fundamental and applied catalyst research spurred by the petrochemical and, more recently, the pharmaceutical industry. Leveraging knowledge in adjacent and more advanced electrochemical technologies (*e.g.*, fuel cells) as well as employing cutting-edge experimental techniques and imaging tools may expedite the actualization of suitable electrocatalysts and reactors.

Acknowledgements

This work was funded by the Massachusetts Institute of Technology. The authors thank Steven Brown and John Barton for insightful discussion and constructive feedback. MJO gratefully acknowledges the National Science Foundation Graduate Research Fellowship Program for additional financial support. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1122374. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Conflict of interest statement

Nothing declared.

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