

# Emerging Opportunities for Electrochemical Processing to Enable Sustainable Chemical Manufacturing

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## Abstract:

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. Immense 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 aims to highlight 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 in the future. Hydrogen production, carbon dioxide fixation, and organic hydrogenation are discussed as promising electrochemical processes that may find industrial use in the near future.

**Keywords:** electrochemical processing, electrocatalysis, hydrogen evolution, carbon dioxide reduction, electrochemical hydrogenation, industry

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## 1. 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 by 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, at present, the cost of natural gas is about 0.005 \$ kWh<sup>-1</sup> (estimated from the lower heating value) as compared to about 0.066 \$ kWh<sup>-1</sup> 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 \$ kWh<sup>-1</sup>) and 86% (to 0.050 \$ kWh<sup>-1</sup>) respectively and is now competitive with fossil fuel based electricity generation technologies (0.055 \$ kWh<sup>-1</sup>) [7]. Future cost reductions to 0.03 \$ kWh<sup>-1</sup> 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 the decarbonization of the industrial sector and spur innovations including reducing plant costs through modularity and process intensification, improving safety and decreasing reactor costs through ambient reaction conditions, and increasing flexibility through tunable product generation. Moreover, electrochemistry may allow new molecular transformations, unlocking previously inaccessible or unimaginable synthetic routes. However, our 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.

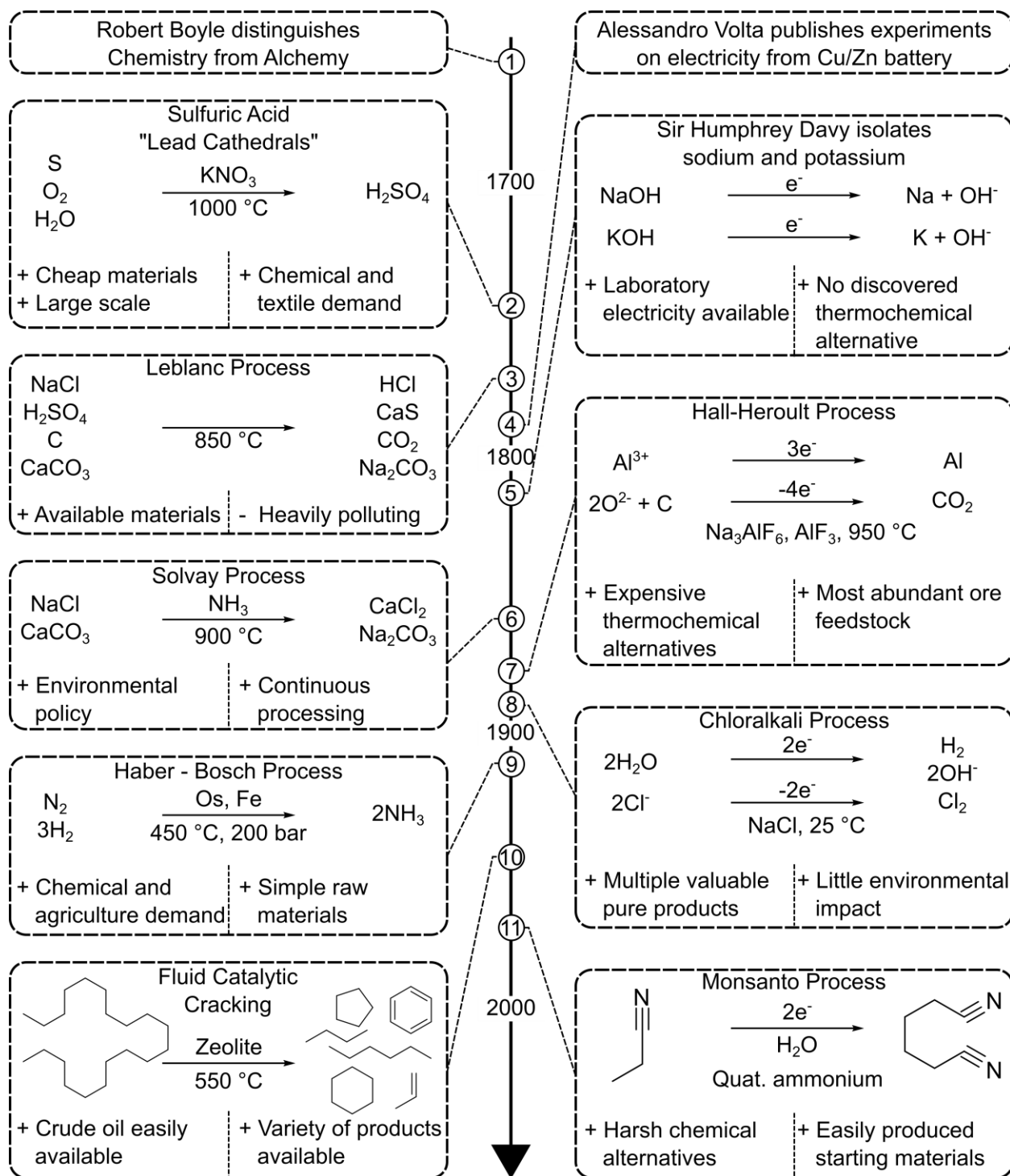
## 2. A Brief History of the Chemical Industry

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, which was 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 byproducts, 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 ( $\text{CO}_2$ ) is bubbled

to precipitate sodium bicarbonate [14]. Finally, the sodium bicarbonate is heated in air to form sodium carbonate and release  $\text{CO}_2$  and water. In addition to being more environmentally friendly than the Leblanc process, the Solvay process was inherently 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 to 250 bar and 400 to 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.



**Figure 1.** A chronological diagram of several important industrial processes based on thermochemical (left) and electrochemical routes (right).

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 pioneer 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 pioneering 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 now 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. Now, aluminum could be produced at large scales from bauxite, which is abundantly available, 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 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 production of chlorine [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 supply the emerging transportation sector leading to the development of complex high-temperature processes which produced a significant number of useful intermediates that, in turn, enabled 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 the adiponitrile, a key precursor for nylon, which is one of the most important synthetic polymers for its use 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  $\text{NO}_x$  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 electrohydrodimerization 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 when limited thermochemical alternatives have existed.

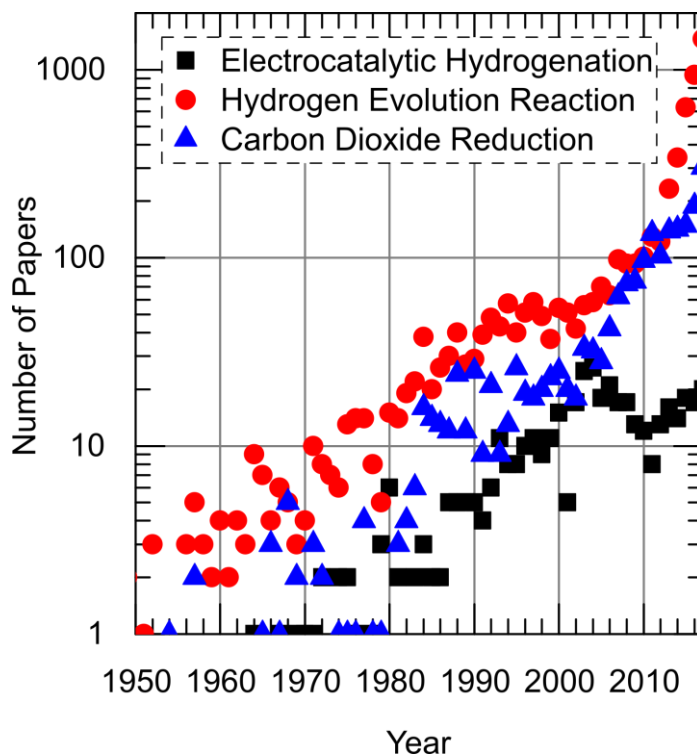
### **3. Advantages of Electrochemical Processing**

Electrochemical processing holds several advantages over traditional thermochemical processing that may promote industrial use, despite the 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 [26–28]. 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 catalyst 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 focus 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

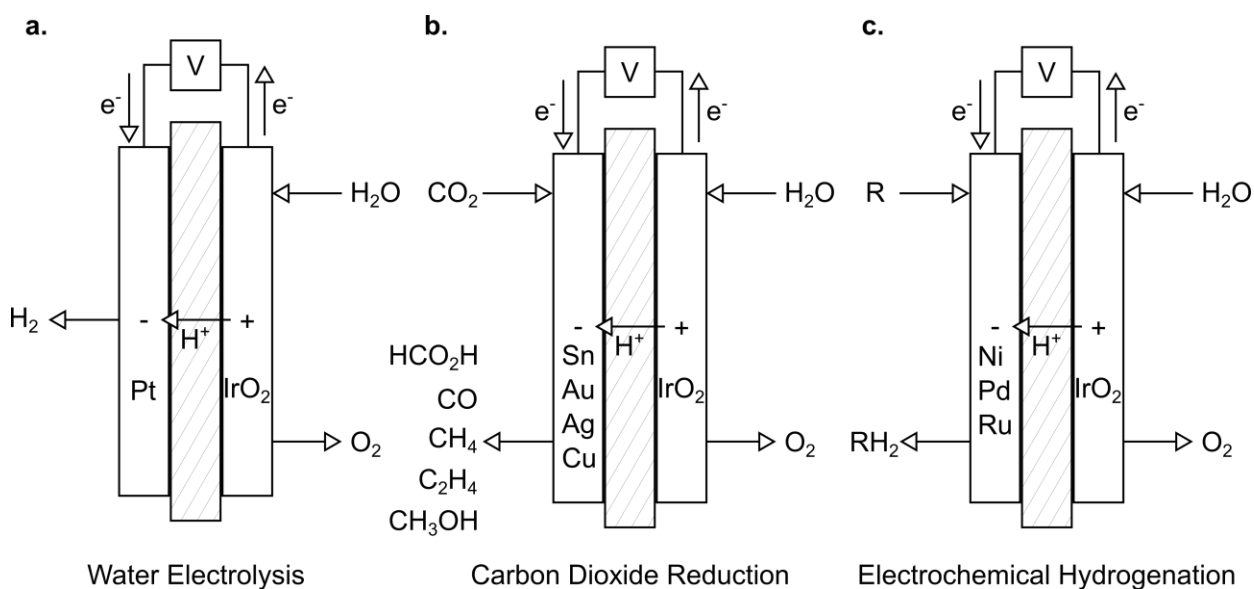
suppressing undesired reaction pathways and enhancing the desired ones, while maintaining activity and selectivity in compositionally-diverse and often poorly-defined feeds.

#### **4. 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 reactions: hydrogen formation, CO<sub>2</sub> valorization, and organic hydrogenation. Materials development is an area of intensive research as improving electrocatalyst activity, selectivity, and stability is paramount for achieving the high production rates and energy efficiencies necessary for economic viability. Beyond electrocatalysis is the 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 attempting to highlight both the promise and the current state of the art. For the interested reader, detailed reviews on these topics can be found in the following references [27,28,31–37].



**Figure 2.** A representation of increasing interest in electrochemical processes relevant to the chemical industry based on a Scopus search for keywords “Electrocatalytic Hydrogenation”, “Hydrogen Evolution Reaction”, and “Carbon Dioxide Reduction.”



**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.

#### 4.1 Hydrogen Production

Hydrogen is a widely-used reagent that enables hydrocracking, saturation of olefins, hydrogenation in the food industry, and others, and, should fuel cell technology become more widespread, further increases in demand are expected. 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 CO<sub>2</sub>, 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 CO<sub>2</sub> challenges the sustainability of hydrocarbon reforming processes, and requires costly downstream separations which impact the process scalability. While high electricity costs limit the cost-competitiveness of present electrolysis technology, projected reductions to as low as 0.02-0.03 \$ kWh<sup>-1</sup> provide a pathway to hydrogen generation at similar costs to SMR (1.20 – 1.80 \$ kg<sup>-1</sup>) [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 the above three steps can be rate determining depending on reaction conditions and catalyst surface, but the Volmer step is always critical 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 especially in alkaline media [53–55], as well as designing novel cell architectures that utilize cheaper membranes, or eliminate the membrane altogether [56].

## **4.2 Carbon Dioxide Utilization**

Carbon dioxide (CO<sub>2</sub>) fixation has been a process of increasing interest as anthropogenic emissions of CO<sub>2</sub> have nearly doubled from 27 GtCO<sub>2</sub>-eq to 49 GtCO<sub>2</sub>-eq, motivating the development of carbon-neutral or -negative processes [4]. While it has been posited that electrochemical CO<sub>2</sub> reduction alone is unlikely to significantly impact atmospheric concentrations of the greenhouse gases, the potential exists to valorize CO<sub>2</sub>-concentrated industrial waste streams by forming useful products (e.g., hydrocarbons and oxygenates) [57]. Traditional thermochemical methods for CO<sub>2</sub> processing are limited outside of the reverse water

gas shift reaction which converts CO<sub>2</sub> and hydrogen to carbon monoxide and water but requires high operating temperatures (above 900°C) to achieve appreciable equilibrium conversions.

Electrochemical reduction of CO<sub>2</sub> can be achieved at, or near, ambient conditions, which minimize environmental impact and safety hazards. Electrocatalysts for CO<sub>2</sub> reduction are typically grouped by favored majority product and can be broadly defined as formate- (HCOO<sup>-</sup>) producing (tin, lead), carbon monoxide- (CO) producing (silver, gold, zinc), or hydrocarbon-producing (copper) [58]. The focus of recent efforts in CO<sub>2</sub> 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 of the electrocatalysts and (3) improving the selectivity towards a single (or few) desired product(s) [31,32,59–61]. The proposed rate determining step for CO<sub>2</sub> reduction involves formation of the radical anion CO<sub>2</sub><sup>-</sup> on the surface [32]. Catalysts that stabilize this high-energy intermediate will 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 CO<sub>2</sub> at overpotentials as low as 340 mV (93% HCOO<sup>-</sup>) and 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 CO<sub>2</sub> 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<sup>-</sup> 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 available reaction pathways. While improvements in energy efficiency apply to all CO<sub>2</sub> reduction catalysts, selectivity improvements are particularly relevant for copper-based catalysts which appear unique in their generation of an array of products. This distribution can be narrowed by using copper nanocubes which favor ethylene formation over other hydrocarbons [66]. With the improvements that have been realized in CO<sub>2</sub> reduction electrocatalysts, cell designs that support these active, selective, and stable catalysts will be critical to realizing economically-feasible electrochemical CO<sub>2</sub> reduction.

### 4.3 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<sup>-1</sup> km<sup>-1</sup> [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 much 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 significantly behind thermocatalyst development and, as a result, remains a nascent technology concept. As such, 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  $\beta$ -O-4 bonds [75]. Although these examples identify promise in individual areas, they rely primarily on phenomenological results without demonstrating fundamental catalyst understanding. As such, 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]. Developing rigorous structure-activity relations for reactions of interest is paramount to advancing the approaches and identifying competitive electrochemical routes.

## **5. 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. Immense 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 sought 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 accelerate the development of suitable electrocatalysts and reactors.

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## References

1. Conti J, Holtberg P, Diefenderfer J, LaRose A, Turnure JT, Westfall L: *International Energy Outlook*. US Energy Information Administration; 2016.
2. Horowitz CA: **Paris agreement**. *Int. Leg. Mater.* 2016, **55**:740–755.
3. Deutch J: **Decoupling Economic Growth and Carbon Emissions**. *Joule* 2017, **1**:3–5.
4. Pachauri RK, Mayer L (Eds): *Climate change 2014: synthesis report*. Intergovernmental Panel on Climate Change; 2015.
5. Hankey R: *Electric Power Monthly*. Energy Information Administration; 2018.
6. *Monthly Energy Review February 2018*. Energy Information Administration; 2018.
7. • *Lazard's Levelized Cost of Energy Analysis - Version 11.0*. Lazard; 2017.  
  
Detailed analysis of electricity costs from a variety of sources that presents reasonable estimates and historical data.
8. • Haegel NM, Margolis R, Buonassisi T, Feldman D, Froitzheim A, Garabedian R, Green M, Glunz S, Henning H-M, Holder B, et al.: **Terawatt-scale photovoltaics: Trajectories and challenges**. *Science* 2017, **356**:141–143.  
  
A broad reflection on the state of solar photovoltaic (PV) technology and what needs to be accomplished to allow PV to make up a significant share of the energy landscape. The authors focus on reduced costs of PV, faster manufacturing and installation, flexible grids, increased electrification of transportation, heating, and cooling, and complementary technologies such as energy storage or chemical production.
9. Hood C, Janoska P, Lee C, Hafner A, Kamiya G, Le Marois J-B, Mark L, Moarif S: *Real-world policy packages for sustainable energy transitions*. International Energy Association; 2017.
10. Derry TK, Williams TI: *A short history of technology from the earliest times to A.D. 1900*. Oxford University Press; 1960.
11. Aftalion F: *A history of the international chemical industry*. Chemical Heritage Press; 2001.
12. Kiefer DM: **It was all about alkali**. *Today's Chem. Work* 2002, **11**:45–46,49.
13. Kiefer DM: **Sulfuric acid: Pumping up the volume**. *Today's Chem. Work* 2001, **10**:57–58.
14. Kiefer DM: **Soda ash, Solvay style**. *Today's Chem. Work* 2002, **11**:87–88, 90.
15. Haber F, Le Rossignol R: Haber F, Le Rossignol R: **Production of ammonia**. 971,501. Grant. United States Patent Office. 1910.

16. Haber F, Bosch C, Mittasch A: Haber F, Bosch C, Mittasch A: **Producing Ammonia**. 1,149,510. Grant. United States Patent Office. 1915.
17. Bosch C, Mittasch A: Bosch C, Mittasch A: **Process of producing ammonia**. 993,144. Grant. United States Patent Office. 1911.
18. Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W: **How a century of ammonia synthesis changed the world**. *Nat. Geosci.* 2008, **1**:636–639.
19. **Sir Humphry Davy**. *J. Chem. Educ.* 1928, **5**:1664.
20. McEvoy AJ: **Fundamentals and applications of electrochemistry**. In *New Strategies for Energy Generation, Conversion and Storage*. Edited by Cifarelli L, Wagner F, Wiersma DS. E D P Sciences; 2013:01018.
21. Deville HS-C: *Aluminum (its manufacture, properties and uses)*. The Sherwood Press; 1933.
22. Prasad S: **Studies on the Hall-Heroult aluminum electrowinning process**. *J. Braz. Chem. Soc.* 2000, **11**:245–251.
23. Vyver SV de, Román-Leshkov Y: **Emerging catalytic processes for the production of adipic acid**. *Catal. Sci. Technol.* 2013, **3**:1465–1479.
24. Pletcher D, Walsh FC: **Organic electrosynthesis**. In *Industrial Electrochemistry*. . Springer Netherlands; 1993:294–330.
25. Davis S, Mori H: *Chemical Economics Handbook: Hexamethylenediamine (HMDA)/Adiponitrile (ADN)*. SRI Consulting; 2010.
26. Frontana-Uribe BA, Little RD, Ibanez JG, Palma A, Vasquez-Medrano R: **Organic electrosynthesis: a promising green methodology in organic chemistry**. *Green Chem.* 2010, **12**:2099.
27. • Horn EJ, Rosen BR, Baran PS: **Synthetic Organic Electrochemistry: An Enabling and Innately Sustainable Method**. *ACS Cent. Sci.* 2016, doi:10.1021/acscentsci.6b00091.  
  
A succinct demonstration of the advantages of electrochemical organic synthesis and discussion of the apparatus necessary to conduct experiments.
28. •• Yan M, Kawamata Y, Baran PS: **Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance**. *Chem. Rev.* 2017, doi:10.1021/acs.chemrev.7b00397.  
  
Comprehensive review of demonstrated electrochemical organic syntheses along with the requisite reaction conditions and catalysts.
29. Jüttner K: **Technical Scale of Electrochemistry**. In *Encyclopedia of Electrochemistry*. . Wiley-VCH Verlag GmbH & Co. KGaA; 2007.

30. Pletcher D, Walsh FC: **Electrochemical engineering**. In *Industrial Electrochemistry*. . Springer Netherlands; 1993:60–172.

31. •• Endrődi B, Bencsik G, Darvas F, Jones R, Rajeshwar K, Janáky C: **Continuous-flow electroreduction of carbon dioxide**. *Prog. Energy Combust. Sci.* 2017, **62**:133–154.

Compelling review discussing the existing need for translation of carbon dioxide reduction technology to flow systems as this will likely be the method necessary for industrial adaption. The authors highlight two scientific research directions as most promising for CO<sub>2</sub> reduction improvements: optimization of electrode materials and development of economically favorable anodic half reactions beyond oxygen evolution.

32. Lu Q, Jiao F: **Electrochemical CO<sub>2</sub> reduction: Electrocatalyst, reaction mechanism, and process engineering**. *Nano Energy* 2016, **29**:439–456.

33. • Cave ER, Montoya JH, Kuhl KP, Abram DN, Hatsukade T, Shi C, Hahn C, Nørskov JK, Jaramillo TF: **Electrochemical CO<sub>2</sub> reduction on Au surfaces: mechanistic aspects regarding the formation of major and minor products**. *Phys. Chem. Chem. Phys.* 2017, **19**:15856–15863.

The authors propose a mechanism for the electroreduction of carbon dioxide based on computational methods that provide a rationalization for the trace amounts of methanol that were experimentally detected on gold surfaces.

34. Kuhl KP, Hatsukade T, Cave ER, Abram DN, Kibsgaard J, Jaramillo TF: **Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces**. *J. Am. Chem. Soc.* 2014, **136**:14107–14113.

35. • Yan M, Kawamata Y, Baran PS: **Synthetic Organic Electrochemistry: Calling All Engineers**. *Angew. Chem. Int. Ed.* [date unknown], doi:10.1002/anie.201707584.

An insightful call to the development of new electrochemistry instrumentation that will enable the widespread adoption of electrochemical organic synthesis on the laboratory scale. Namely, instruments must be standardized, modular, cost efficient, have user-friendly interfaces, designed with industrial application in mind, have electroanalytical capabilities, and easily updated.

36. Conway BE, Tilak BV: **Interfacial processes involving electrocatalytic evolution and oxidation of H<sub>2</sub>, and the role of chemisorbed H**. *Electrochimica Acta* 2002, **47**:3571–3594.

37. Carmo M, Fritz DL, Mergel J, Stolten D: **A comprehensive review on PEM water electrolysis**. *Int. J. Hydrog. Energy* 2013, **38**:4901–4934.

38. Suresh B, Schlag S, Kumamoto T, Ping Y: *Chemical Economics Handbook: Hydrogen*. SRI Consulting; 2010.

39. Ogden JM: **Prospects for building a hydrogen energy infrastructure**. *Annu. Rev. Energy Environ.* 1999, **24**:227–279.

40. *IEA Energy Technology Essentials*. International Energy Association; 2007.
41. Armor JN: **The multiple roles for catalysis in the production of H<sub>2</sub>**. *Appl. Catal. Gen.* 1999, **176**:159–176.
42. • Hunt ST, Milina M, Wang Z, Román-Leshkov Y: **Activating earth-abundant electrocatalysts for efficient, low-cost hydrogen evolution/oxidation: sub-monolayer platinum coatings on titanium tungsten carbide nanoparticles**. *Energy Environ. Sci.* 2016, **9**:3290–3301.  
  
Novel material design and synthesis protocol for platinum on titanium tungsten carbide core-shell nanoparticles with hydrogen evolution activity measured by the exchange current density surpassing that of a standard platinum supported on carbon.
43. Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H: **MoS<sub>2</sub> Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction**. *J. Am. Chem. Soc.* 2011, **133**:7296–7299.
44. Bockris JO, Potter EC: **The Mechanism of the Cathodic Hydrogen Evolution Reaction**. *J. Electrochem. Soc.* 1952, **99**:169–186.
45. Kahyarian A, Brown B, Nesic S: **Mechanism of the Hydrogen Evolution Reaction in Mildly Acidic Environments on Gold**. *J. Electrochem. Soc.* 2017, **164**:H365–H374.
46. Pentland N, Bockris JO, Sheldon E: **Hydrogen Evolution Reaction on Copper, Gold, Molybdenum, Palladium, Rhodium, and Iron Mechanism and Measurement Technique under High Purity Conditions**. *J. Electrochem. Soc.* 1957, **104**:182–194.
47. Eftekhari A: **Electrocatalysts for hydrogen evolution reaction**. *Int. J. Hydrog. Energy* 2017, **42**:11053–11077.
48. Nørskov JK, Bligaard T, Logadottir A, Kitchin JR, Chen JG, Pandelov S, Stimming U: **Trends in the Exchange Current for Hydrogen Evolution**. *J. Electrochem. Soc.* 2005, **152**:J23–J26.
49. Greeley J, Jaramillo TF, Bonde J, Chorkendorff I, Nørskov JK: **Computational high-throughput screening of electrocatalytic materials for hydrogen evolution**. *Nat. Mater.* 2006, **5**:909.
50. Hinnemann B, Moses PG, Bonde J, Jørgensen KP, Nielsen JH, Horch S, Chorkendorff I, Nørskov JK: **Biomimetic Hydrogen Evolution: MoS<sub>2</sub> Nanoparticles as Catalyst for Hydrogen Evolution**. *J. Am. Chem. Soc.* 2005, **127**:5308–5309.
51. Alia SM, Pivovar BS: **Evaluating Hydrogen Evolution and Oxidation in Alkaline Media to Establish Baselines**. *J. Electrochem. Soc.* 2018, **165**:F441–F455.
52. Suen N-T, Hung S-F, Quan Q, Zhang N, Xu Y-J, Ming Chen H: **Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives**. *Chem. Soc. Rev.* 2017, **46**:337–365.

53. Suntivich J, May KJ, Gasteiger HA, Goodenough JB, Shao-Horn Y: **A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles.** *Science* 2011, **334**:1383–1385.
54. Lee Y, Suntivich J, May KJ, Perry EE, Shao-Horn Y: **Synthesis and Activities of Rutile IrO<sub>2</sub> and RuO<sub>2</sub> Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions.** *J. Phys. Chem. Lett.* 2012, **3**:399–404.
55. McCrory CCL, Jung S, Peters JC, Jaramillo TF: **Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction.** *J. Am. Chem. Soc.* 2013, **135**:16977–16987.
56. • Esposito DV: **Membraneless Electrolyzers for Low-Cost Hydrogen Production in a Renewable Energy Future.** *Joule* 2017, **1**:651–658.  
  
Describes the economic advantages that exist in membraneless electrolyzers, primarily from the point of view of economical production of hydrogen, while highlighting the many technical hurdles that need to be overcome such as significant Ohmic losses and downstream separations.
57. Pletcher D: **The cathodic reduction of carbon dioxide—What can it realistically achieve? A mini review.** *Electrochem. Commun.* 2015, **61**:97–101.
58. Hori Y, Wakebe H, Tsukamoto T, Koga O: **Electrocatalytic process of CO selectivity in electrochemical reduction of CO<sub>2</sub> at metal electrodes in aqueous media.** *Electrochimica Acta* 1994, **39**:1833–1839.
59. Kenis PJA, Dibenedetto A, Zhang T: **Carbon Dioxide Utilization Coming of Age.** *ChemPhysChem* 2017, **18**:3091–3093.
60. Jhong H-R “Molly,” Ma S, Kenis PJ: **Electrochemical conversion of CO<sub>2</sub> to useful chemicals: current status, remaining challenges, and future opportunities.** *Curr. Opin. Chem. Eng.* 2013, **2**:191–199.
61. •• Verma S, Hamasaki Y, Kim C, Huang W, Lu S, Jhong H-RM, Gewirth AA, Fujigaya T, Nakashima N, Kenis PJA: **Insights into the Low Overpotential Electroreduction of CO<sub>2</sub> to CO on a Supported Gold Catalyst in an Alkaline Flow Electrolyzer.** *ACS Energy Lett.* 2018, **3**:193–198.  
  
The authors demonstrate an alkaline electrolysis cell with supported gold catalyst particles that is able to achieve partial current densities towards carbon monoxide near the range for economic feasibility while maintaining high faradaic efficiency at low overpotential.
62. Lu Q, Rosen J, Zhou Y, Hutchings GS, Kimmel YC, Chen JG, Jiao F: **A selective and efficient electrocatalyst for carbon dioxide reduction.** *Nat. Commun.* 2014, **5**:3242.
63. Zhang S, Kang P, Meyer TJ: **Nanostructured Tin Catalysts for Selective Electrochemical Reduction of Carbon Dioxide to Formate.** *J. Am. Chem. Soc.* 2014, **136**:1734–1737.

64. Back S, Yeom MS, Jung Y: **Active Sites of Au and Ag Nanoparticle Catalysts for CO<sub>2</sub> Electroreduction to CO.** *ACS Catal.* 2015, **5**:5089–5096.
  65. Kumar B, Asadi M, Pisasale D, Sinha-Ray S, Rosen BA, Haasch R, Abiade J, Yarin AL, Salehi-Khojin A: **Renewable and metal-free carbon nanofibre catalysts for carbon dioxide reduction.** *Nat. Commun.* 2013, **4**:2819.
  66. Roberts FS, Kuhl KP, Nilsson A: **High Selectivity for Ethylene from Carbon Dioxide Reduction over Copper Nanocube Electrocatalysts.** *Angew. Chem.* 2015, **127**:5268–5271.
  67. Searcy E, Flynn P, Ghafoori E, Kumar A: **The relative cost of biomass energy transport.** *Appl. Biochem. Biotechnol.* 2007, **137**:639–652.
  68. Li Z, Garedew M, Lam CH, Jackson JE, Miller DJ, Saffron CM: **Mild electrocatalytic hydrogenation and hydrodeoxygenation of bio-oil derived phenolic compounds using ruthenium supported on activated carbon cloth.** *Green Chem.* 2012, **14**:2540–2549.
  69. Li Z, Kelkar S, Raycraft L, Garedew M, Jackson JE, Miller DJ, Saffron CM: **A mild approach for bio-oil stabilization and upgrading: electrocatalytic hydrogenation using ruthenium supported on activated carbon cloth.** *Green Chem* 2014, **16**:844–852.
  70. Lam CH, Lowe CB, Li Z, Longe KN, Rayburn JT, Caldwell MA, Houdek CE, Maguire JB, Saffron CM, Miller DJ, et al.: **Electrocatalytic upgrading of model lignin monomers with earth abundant metal electrodes.** *Green Chem.* 2015, **17**:601–609.
  71. Zhao B, Chen M, Guo Q, Fu Y: **Electrocatalytic hydrogenation of furfural to furfuryl alcohol using platinum supported on activated carbon fibers.** *Electrochimica Acta* 2014, **135**:139–146.
  72. Nilges P, Schröder U: **Electrochemistry for biofuel generation: production of furans by electrocatalytic hydrogenation of furfurals.** *Energy Environ. Sci.* 2013, **6**:2925–2931.
  73. Green SK, Lee J, Kim HJ, Tompsett GA, Kim WB, Huber GW: **The electrocatalytic hydrogenation of furanic compounds in a continuous electrocatalytic membrane reactor.** *Green Chem.* 2013, **15**:1869–1879.
  74. •• Carroll KJ, Burger T, Langenegger L, Chavez S, Hunt ST, Román-Leshkov Y, Brushett FR: **Electrocatalytic Hydrogenation of Oxygenates using Earth-Abundant Transition-Metal Nanoparticles under Mild Conditions.** *ChemSusChem* 2016, **9**:1904–1910.
- Detailed study of activity of bimetallic catalysts for the electrocatalytic hydrogenation of ketone functional groups in small molecules.
75. Cyr A, Chiltz F, Jeanson P, Martel A, Brossard L, Lessard J, Ménard H: **Electrocatalytic hydrogenation of lignin models at Raney nickel and palladium-based electrodes.** *Can. J. Chem.* 2000, **78**:307–315.

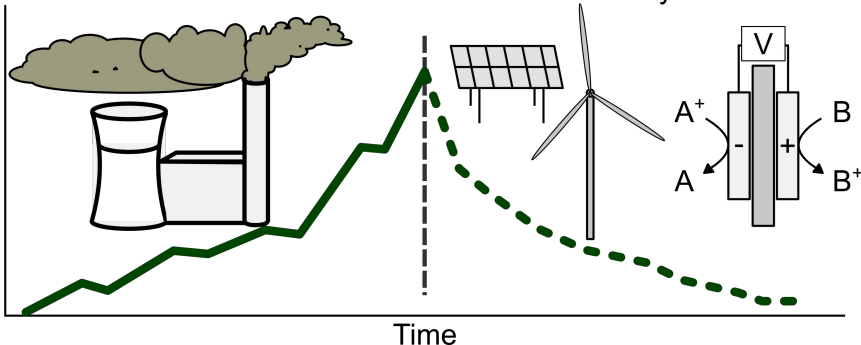


76. •• Chadderdon XH, Chadderdon DJ, Matthiesen JE, Qiu Y, Carraher JM, Tessonnier J-P, Li W: **Mechanisms of Furfural Reduction on Metal Electrodes: Distinguishing Pathways for Selective Hydrogenation of Bioderived Oxygenates.** *J. Am. Chem. Soc.* 2017, **139**:14120–14128.

Provides great mechanistic insight into the relative likelihood of reaction pathways based on selective poisoning of active sites.

# Electrification of the Chemical Industry

GHG Emissions



Time