

Electrocatalytic Approaches to Traditional Thermochemical Processes

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SCOPE

This report describes and provides fresh perspective on the new advanced electrocatalytic approaches to traditional thermochemical processes. It outlines the new trends, and anticipates the new directions, providing an overview of the new possibilities, challenges, and gaps for electrocatalysis.

The topic represents an area getting a lot of scientific attention worldwide, for the crucial role to develop the catalytic technologies necessary for the on-going transition in energy and chemistry and in developing new paths to substitute the use of fossil fuels both as energy and carbon source.

The Report Is Structured In Four Chapters.

- ✓ **Chapter 1 addresses motivations and drivers**, briefly introduces the differences between electrochemistry and electrocatalysis, some key mechanistic aspects, the challenges in the field, including scale-up aspects.
- ✓ **Chapter 2 discusses recent developments on the electrocatalytic synthesis of inorganic chemicals**, analyzing the differences in thermocatalytic routes, the type of electrocatalytic materials used and some key aspects of the reaction mechanism and nature of the active sites, the role of the optimal design of the electrocatalytic cells, and some elements on bioelectrocatalytic and biomimetic approaches.
- ✓ **Chapter 3 focuses on the electrocatalytic synthesis of base and intermediate chemicals**, key elements of the design of electrocatalysis, aspects of the mechanism of action, performances obtained with critical results analysis, production of large-volume chemicals, the electrocatalytic conversion of CO₂ to a range of recent products and emerging possibilities particularly in the area of electro-oxidation.
- ✓ **Chapter 4 analyses the electrocatalytic conversion of biobased platform molecules**, in relation to the opportunities to develop an e-refinery and e-chemistry; highlights the role of electrochemical methods in transforming biomass-derived molecules, as a key technology to move to electrification of chemical production and the substitution of fossil fuels both as energy and carbon source; and new areas of development at the interface between the reactions of small molecules and those of electrocatalytic transformation.

This study provides a critical guide to understand the limits in current approaches. It includes the analysis of about 700 publications thus providing a comprehensive, but critical update of the recent developments in the field.

DRIVERS

The push to decarbonization, together with the opportunity window created by low-cost renewable energy (RE) production, is a main driver to accelerate the development of electrocatalytic processes.

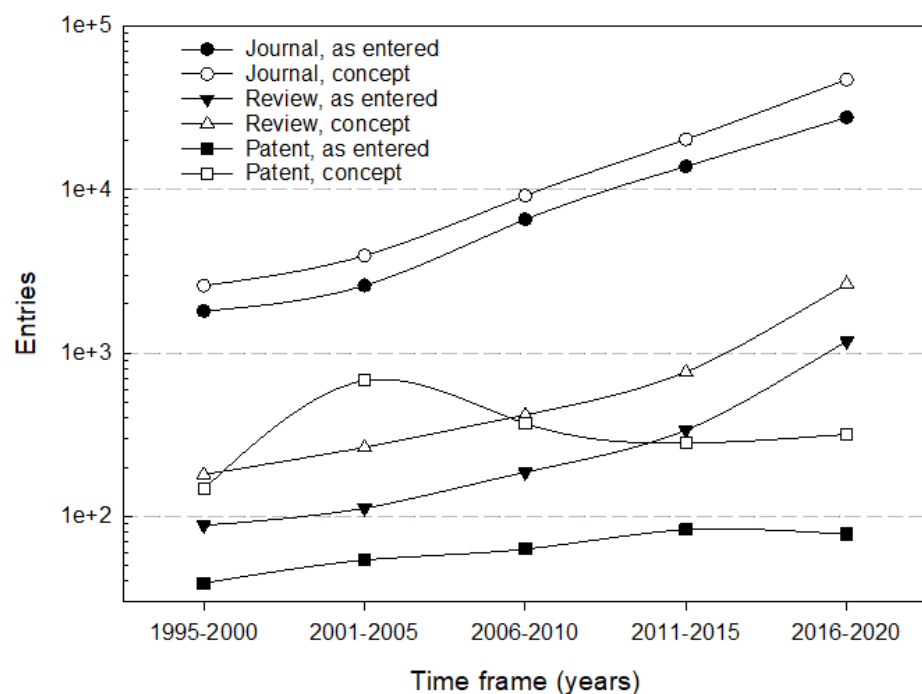


Figure 1: Number of entries versus time frame by SciFinder literature search for the word "electrocatalytic" (as entered, and as a concept) with limits "English" and Journal, Review or Patents.

While an exponential increase in the number of papers and reviews could be observed in the last 25 years, the situation is different for patents.

- ✓ After a fast increase around year 2000, a decrease is expected for the following decade, and the number of patents has nearly stabilized in the last 5 years.
- ✓ While at the beginning of this century, electrocatalysis appears very promising from an industrial perspective, the results were instead still too far from exploitation. Thus, the decline in patents between 2000-2015, has stabilized in the last 5 years.
- ✓ While there is skepticism from an industrial perspective, the rising academic interest has significantly increased the knowledge background. number of patents will soon fast increase.

There are "opportunity windows" for companies to enter this area and establish their business interest and develop their own electrocatalytic processes, but when will companies take advantage of this growing knowledge?

LOW AND HIGH TEMPERATURE ELECTROCATALYSIS

- ❖ In fuel cells or electrolyzers, the pro and cons of operations from low to high temperature cell typologies are well established.
- ❖ For H_2 production (the only well investigated case for electrolyzers), PEM-type are those on which most attention is focused, even if medium-temperature (alkaline electrolysis cell, AEC; 70-90°C temperature of operation) were the first developed and most common commercialized.
- ❖ Thus, there is a current shift from AEC to PEM-type electrolyzers, while SOEC are still considered a longer-term technology for water electrolysis.
- ❖ These cells are suitable for lab initial experiments, but for more realistic configurations it is necessary to switch to continuous type two compartment electrocatalytic reactors, eventually with Gas Diffusion Layer (GDL) type of electrode or the electrocatalyst on the two sides of the membrane separating the two cathodic and anodic parts of the electrocatalytic reactor.
- ❖ The SOEC community speaks in general of CO_2 electrolysis, while for low temperature electrocatalytic community the most diffused terms of CO_2 RR (CO_2 reduction reaction). Possibly associated to this different terminology, many review papers on CO_2 electrocatalytic reduction do not consider high-temperature CO_2 electrolysis technologies

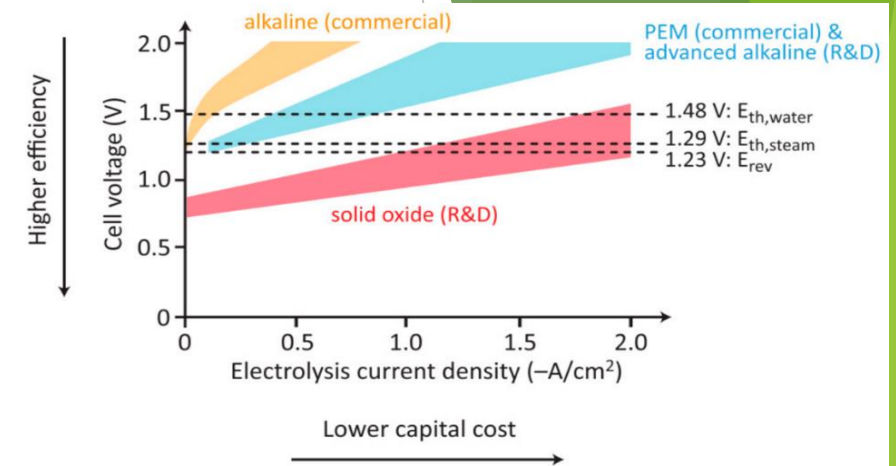


Figure 2: Comparison between alkaline (AEC), polymer electrolyzer membrane (PEM), and solid oxide (SOEC) water electrolyzers in terms of voltage vs. current density Source: Barelli et al, 2017.

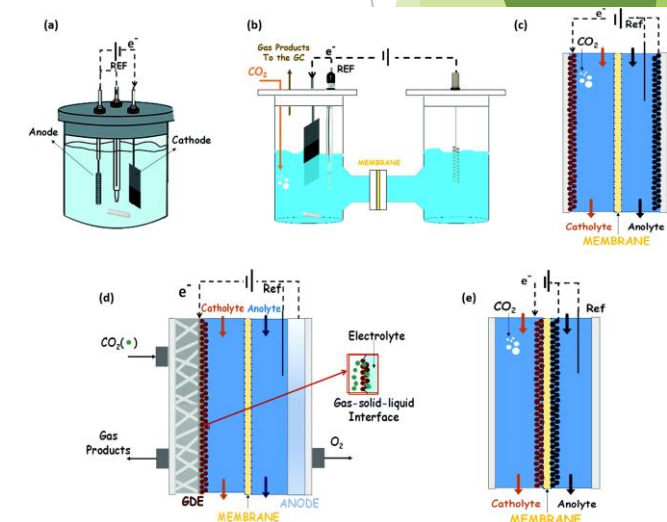


Figure 3: Schematic concepts of (a) Traditional 3-electrode cell, (b) H-type cell, (c) Two Compartment cell, (d) Gas Diffusion Electrode cell and (e) Membrane Electrode Assembly for electrochemical CO_2 reduction reactions. Source: Guzmán et al, 2021.

TEA, LCA AND CO₂ FOOTPRINT, COMPARISON WITH THERMO APPROACHES

A multicriteria approach would be necessary to assess the need of developing electrocatalysis technologies, while techno-economic assessment (TEA), eventually sustained from an environmental impact analysis of the benefits, through methodologies such as Life Cycle Assessment (LCA) and related methods (social life assessment, life cycle costing, life cycle sustainability assessment, etc.), are the typical methods used to decide whether to invest in new technologies.

- ✓ **While these are well established method** for industrial planning of the activities, the problem is that well-established technologies with large industrial experience are compared with early-stage technologies which are not just the extension of the current ones but requires a full change of materials/technologies to become competitive.
- ✓ **The application of conventional assessment methods**, such as TEA, are not well suited for this comparative assessment because when a system change occurs as ongoing, and the technologies which are compared are a key part of the two systems in transition.
- ✓ **The current methodologies are even less valid**, and new methodologies of assessment, which can include the evolution of the whole system, must be developed, and applied. This is one of the reasons why sometimes quite different indications can be found in literature.
- ✓ **This report presents**, analyses and offers perspective on the past, current and future models and how to apply new information to create new model for future success.

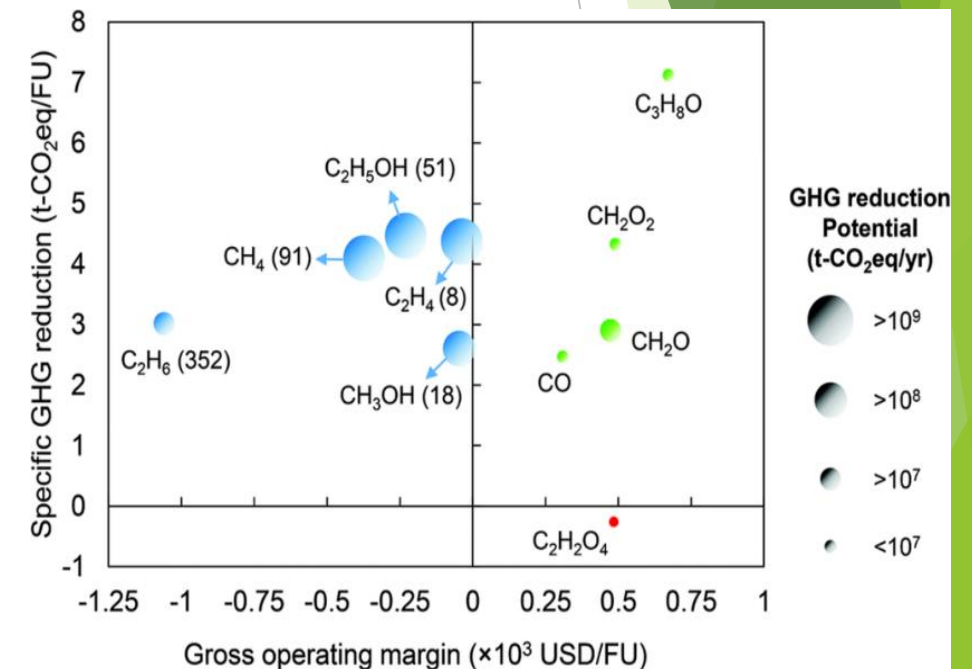


Figure 4: Comparison of ten electrochemical CO₂ conversion technologies. The functional unit is 1 ton of the target product and X ton of oxygen. The numbers inside brackets are GHG avoidance costs (USD per t-CO₂eq). Source: Roh et al., 2020.

SCALE-UP & ENGINEERING CHALLENGES

Most of the studies in electrocatalysis are still at the laboratory scale, with electrodes of few cm^2 , but particularly for CO_2 electrocatalytic reduction, and for green H_2 production scale-up. The development of continuous industrial size electrochemical flow reactors poses several challenges.

- ▶ It requires to optimize the geometry/configuration, to realize a uniform electricity distribution and optimal flow distribution of large electrodes, realizing an efficient heat management, and stable operations.
- ▶ An optimal balance between maximization of selectivity and Faradaic efficiency (FE), as well as of the productivity (i.e., current density - J) is necessary.
- ▶ Realizing conditions of not-costly downstream separation of the products which also imply the type of products formed is another crucial aspect not often considered.
- ▶ In addition to stability of the system, including in relation to the presence of poisoning elements in the feed, an additional challenge is given by transient operations to deal with process fluctuations, pulsed reactions, and the effects of fouling, particularly critical with biobased products conversion.
- ▶ In terms of electrocatalytic reactors, while still most of the studies are on the traditional electrochemical reactors illustrated schematically in Figure 5, for operations such as CO_2 or N_2 electrocatalytic reduction, gas diffusion layer (GDL) flow reactors are typically used, with the next step to move to a compact and electrolyte-less design, where the electrolyte to close the electronic circuit is given by the membrane itself, thus eliminating the presence of liquid catholytes and anolytes.

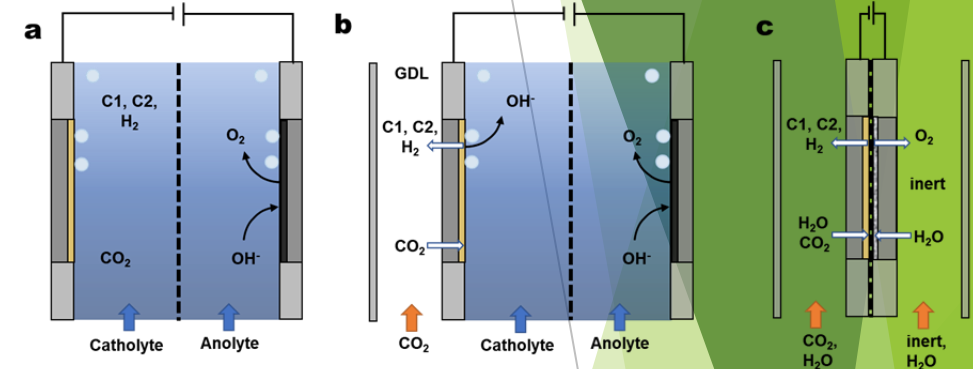


Figure 5: From lab-scale (a) to GDL-type industrial flow reactors for CO_2 and N_2 reduction (b) and to compact, electro-less type of electrocatalytic reactor (c). Source: Perathoner, 2021.

The realization of industrial scale electrocatalytic processes, in addition to a better reactor engineering and to better materials (electrocatalysts, membranes), requires a better understanding (and optimization) of the multiphase interface at the electrocatalyst surface.

ELECTROCATALYTIC SYNTHESIS OF INORGANIC CHEMICALS

FOCUS ON: AMMONIA DIRECT SYNTHESIS FROM N_2

The topic of ammonia direct synthesis from N_2 (also indicated as N_2 fixation or as N_2 reduction reaction, with the acronyms NRR or N_2 RR also often used) is of growing relevance, both from the industrial perspective (to develop an alternative process to Haber-Bosch (HB) thermocatalytic process) and from the scientific one.

Discussion in this report is focused on the direct electrocatalytic conversion of N_2 , by using H_2O as the source of the hydrogen necessary for the synthesis.

A large joint Australia-Japan project on the use of ammonia as an energy vector for hydrogen is beginning. The Green Ammonia Consortium in Japan estimates that the demand for direct use of green ammonia will reach 1.7 Mt/y by 2030 (a \$10 billion/year market).

- ✓ The alternative is a two-step process, with H_2 produced in an electrolyzer and then feed together with N_2 , that should be obtained by air separation, to a thermocatalytic unit.
- ✓ This is the process often indicated as green NH_3 , originally developed by Siemens up to pilot scale, and now explored by various other companies, such as Topsoe with some technology differences, in terms of the electrolyzer.
- ✓ The current RE approach to green NH_3 synthesis entails three-steps:
 - ✓ 1) produce electrical energy from RE sources;
 - ✓ 2) use this output to make H_2 by electrolysis;
 - ✓ 3) combine H_2 and N_2 (after separation from air) in a traditional high temperature/pressure Haber-Bosch catalytic reactor (400-650 °C, 200-400 bar).
- ✓ Integration of these steps, which operate at very different conditions, is not energy efficient, however.

ELECTROCATALYTIC SYNTHESIS OF INORGANIC CHEMICALS

FOCUS ON: ELECTROCATALYTIC PRODUCTION OF H₂ AND O₂

Water electrolysis is the main current industrial option to produce green H₂. Over the past years, interest in water electrolysis technologies has increased, particularly in the area of producing "green" H₂ green" with electricity from renewable sources. This is the only method fulfilling criteria of sustainable, climate-safe energy use or net-zero emissions. Green hydrogen forms a cornerstone of the shift away from fossil fuels. Its uptake will be essential for sectors like aviation, international shipping, and heavy industry, where energy intensity is high, and emissions are hardest to abate. A key issue in this wider introduction of green H₂ is cost reduction. There are various analyses on this aspect, discussed in this report.

It is estimated that a combination of cost reductions in electricity and electrolyzers, combined with increased efficiency and operating lifetime, can deliver 80% reduction in hydrogen cost, as shown in **Figure 6**. **Figure 7** reports the estimates of the potential green hydrogen production cost reduction between 2020 and 2050 for a range of electrolyzers cost and deployment levels.

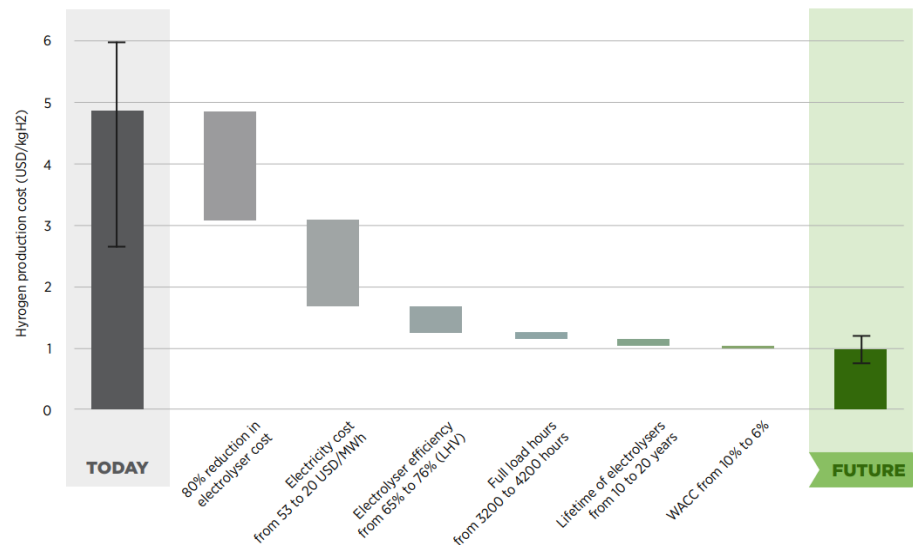


Figure 6: A combination of cost reductions in electricity and electrolyzers, combined with increased efficiency and operating lifetime, can deliver 80% reduction in hydrogen cost. Source: IRENA, 2020.

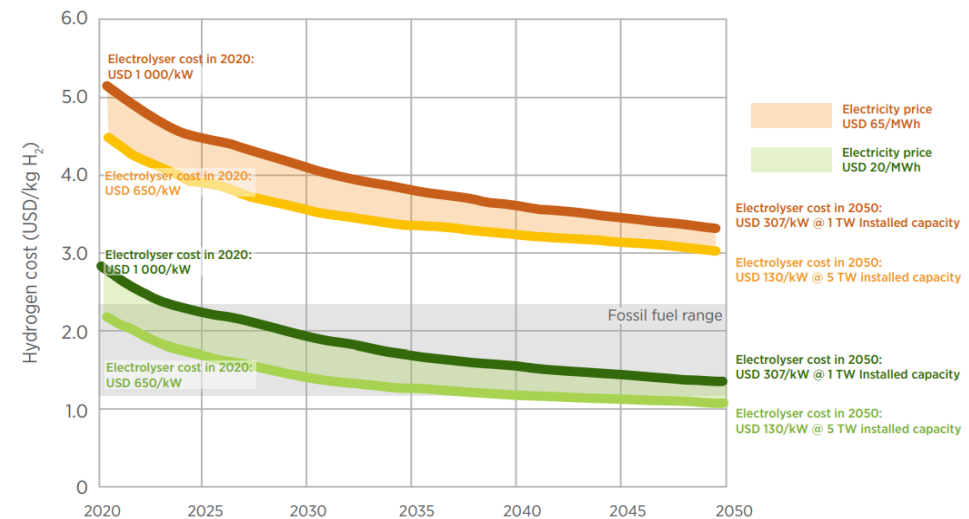


Figure 7: Cost of green hydrogen production as a function of electrolyser deployment, using an average (USD 65/MWh) and a low (USD 20/MWh) electricity price, constant over the period 2020-2050. Source: IRENA, 2020.

ELECTROCATALYTIC SYNTHESIS OF INORGANIC CHEMICALS

FOCUS ON: ELECTROCATALYTIC PRODUCTION OF SYNGAS

There are three possible electrocatalytic approaches to produce syngas:

- i) the coupling of a water electrolysis unit to a CO₂ to CO PEM electrolysis unit (this solution will allow to produce CO/H₂ mixtures in a wide range of ratios, but duplicates CAPEX and OPEX costs)
- ii) the use of a CO₂ to CO PEM-type electrolyzers, where H₂ forms from the side reaction of recombination of H⁺/e⁻ (the CO/H₂ ratio can be changed in a quite limited range in this approach, may vary with time on stream, and limit also effectiveness of the conversion)
- iii) high temperature CO₂/H₂O co-electrolysis (this is actually the preferable solution from an industrial perspective)

The production of syngas from CO₂ and H₂O electrolysis or co-electrolysis is a key step to producing a large variety of efuels and chemicals through established catalytic routes.

ELECTROCATALYTIC SYNTHESIS OF BASE & INTERMEDIATE CHEMICALS

FOCUS ON: ELECTROSYNTHESIS OF LIGHT OLEFINS

The electrosynthesis of light olefins, although a topic studied from several years, has received large attention recently to produce olefins (one of the main base raw materials for chemistry) from (waste) CO₂. In addition to many papers (over 300 in the period 2018-2021 deal on these aspects), the topic of producing ethylene (olefins) from CO₂ by electrocatalysis (electrolysis) was analyzed in many recent reviews.

Different very interesting results have been reported recently which also indicate the possible industrial development, even if the indications are still at lab-scale.

As an example, may be indicated the Faradaic efficiency (FE) for ethylene production of 87% at -0.47 V versus reversible hydrogen electrode obtained on Cu-polyamine hybrid catalyst or a C₂H₄ production rate = 487.9 μmol·m⁻²·s⁻¹ and a FE = 91.1% using CuO/ZnO based electrocatalysts operating in gas-phase CO₂ electroconversion.

Light olefins used as the building blocks of current petrochemistry are ethylene (C₂H₄), propylene (C₃H₆), and butenes and butadiene. They are among the most energy intensive processes of chemical production, accounting for approximately 8% of the sector's total primary energy demand.

ROUTES AND OPTIONS IN BIOBASED PLATFORM MOLECULES

The electrocatalytic reaction can occur between the reactant and the electrode surface directly (direct electrolysis), or by a solution-phase redox mediator (indirect, or mediated electrolysis, as exemplified in Figure 8).

- In direct electrolysis, the reactive species can be formed by catalytic interactions of the electrode that form adsorbates (inner-sphere electron transfer) or by direct charge-transfer to the solution phase, forming solvated radicals (outer-sphere transfer). Indirect electrolyses also generally involve outer-sphere electron transfer to the mediators and allow exploiting highly tailored molecular redox catalysts.
- These can circumvent problems such as electrode deactivation or poor selectivity, though they can add complexity with separations and stability of the mediator. In many cases with large, multistep transformations, electrochemical reactions of all types can also involve both chemical (including organocatalytic) and electrochemical steps.
- Thus, various transformations can be described by kinetic sequences defined by their reaction sequences for example, electrochemical-electrochemical (sequential charge-transfer processes), electrochemical-chemical, chemical-electrochemical, and electrochemical-chemical-electrochemical.

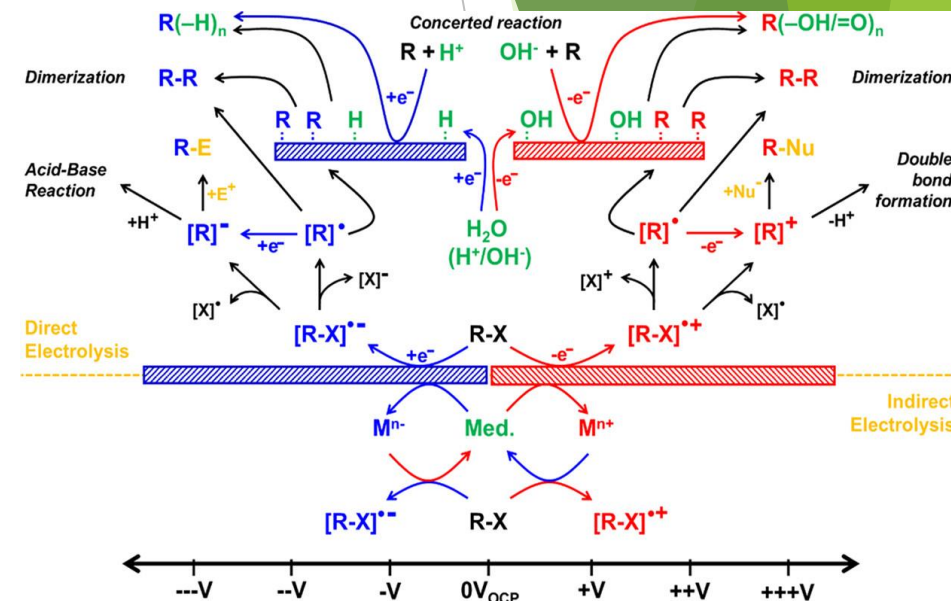


Figure 8: Schematic illustration of some initial steps in generalized electrochemical reactions. Black arrows represent chemical steps, while red and blue arrows represent electrochemical oxidation and reduction steps, respectively; this convention is used in all subsequent figures. “X” represents the more electroactive molecule moiety and its main chain (R), while “E” and “Nu” are electrophile and nucleophile species, and “Med.” is an electrochemical mediator with reduced (Med^{n-}) and oxidized (Med^{n+}) forms, respectively. Source: Lucas et al., 2021.

ELECTROCATALYTIC UPGRADING OF BIOMASS-DERIVED INTERMEDIATES

During the last decade, electrocatalytic upgrading of biomass-derived intermediate compounds to value-added products has started to attract increased attention. Several interesting electrocatalytic systems have been reported with improving performance. However, there are still major aspects which need to be improved before these technologies could become a common industrial approach.

These hurdles are shared in general with the field of electrocatalysis to set-up the future routes for e-chemistry, but they are somewhat amplified in the case of biomass upgrading to produce large-volume chemicals.

- In the case of organic electrosynthesis, being applied to small products of high-added-value chemicals, several of the problems are less critical, and also the use of sophisticated, costly downstream separations is feasible.
- The majority of reported electrocatalytic systems focus on the upgrading transformation of furanics, levulinic acid, glycerol, and sorbital, all of which are among the Top 14 list of biomass-derived platform compounds identified by the US Department of Energy.
- However, as outlined in the previous section, the opportunities of implementation in this area are largely depending on the integration in a creative way with new possibilities.

Thus, it is important to move beyond optimization of reactions being currently emphasized and make new efforts to exploit the vast array of functional transformations biomass can offer.

ELECTROCATALYTIC LIGNIN DEPOLYMERIZATION & DEOXYGENATION

Lignin has the potential to be a renewable source for a plethora of aromatic compounds. However, the production of value-added commodity chemicals via lignin depolymerization remains a major challenge because this biopolymer is by far the most recalcitrant component of biomass.

- Various studies have been reported on the lignin electrocatalytic conversion, finding that overoxidation and repolymerization of monomers are some of the main problems found in lignin oxidative depolymerization.
- Removal of the low-molecular-weight depolymerization products from the reaction medium, integration of polymeric nanofiltration membranes, the use of resins or emulsions to extract the products are some of the strategies used to limit overoxidation and repolymerization.
- Lignin oxidative depolymerization in ionic liquids (ILs) results in better performances, because they have a relatively wide electrochemical stability window and can improve Faradaic efficiency by decreasing parasitic water electrolysis, in addition to have superior capacity to solubilize this biopolymer.
- Electrocatalytic hydrogenation-deoxygenation has been also used to stabilize the bio-oil obtained from many processes of lignin depolymerization.

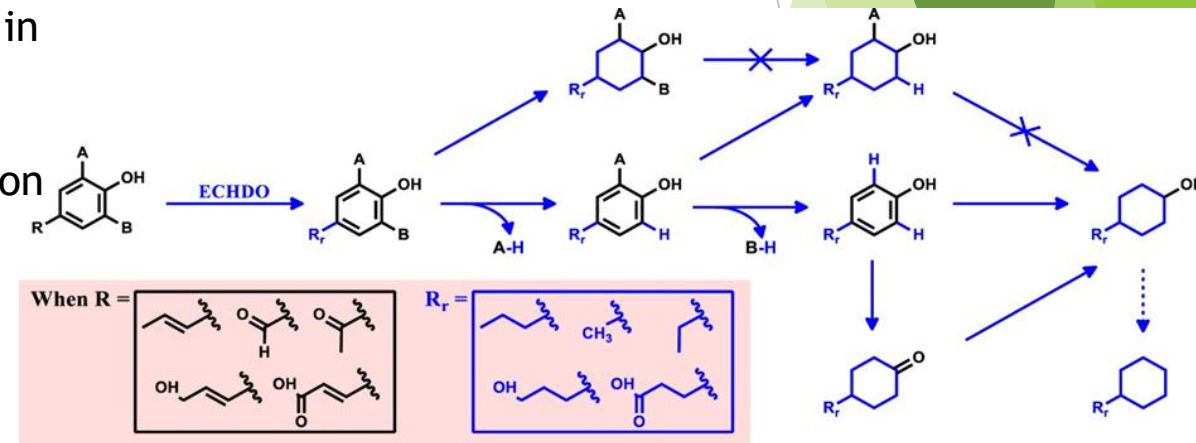


Figure 9 presents a general scheme of the main pathways of electro hydrogenation-deoxygenation of lignin-derived aromatics.

Figure 9: Electro-hydrogenation and deoxygenation of Some Lignin-Derived Aromatics. Source: Lucas et al., 2021.

CONCLUSIONS & FUTURE CHALLENGES

- ✓ Electrocatalysis is a crucial technology to pass from the old chemical (and energy) production system based on fossil fuels to the new system based on renewable energy. Yet, it is evident that this is an ongoing transition which is driven by aspects external to the only technological and impact assessments. Thus, electrocatalysis should be put in this context to be analyzed.
- ✓ The fundamentals of understanding catalysis remain a valid element, as well as theoretical methods, but electrocatalysis cannot be correctly described just by application of (thermal) catalysis methodologies to electrocatalysis.
- ✓ The limit of most current studies relies in not properly understanding this crucial concept. Electrocatalytic reactors should be equally addressed by using new engineering tools for understanding and optimization. However, many studies in electrocatalysis do not properly account the importance of the electrocatalytic configuration and produce results hard to be used in transferring to industrial application.
- ✓ It is thus not only a problem of classical scale-up, but the need to rethink the industrial development of electrocatalysis. Many factors are still not analyzed to allow to accelerate the industrialization of electrocatalytic reactions.
- ✓ There is a wide background on electrolyzer and fuel cells, and in the few industrial electrochemical processes that must be better integrated into the current studies in electrocatalysis to exploit the opportunity windows offered by the lower costs and impact in using renewable energy in contrast with fossil fuels. But there is a gap in these aspects.
- ✓ Even parameters such as the reaction temperature but also requiring a proper redesign of materials and the electrocatalytic cell, are not properly investigated. There are also contradictory indications about the target reactions.

This report provides food for thought on reconsidering contradictory indications present in literature.

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