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Advances in electrosynthesis for a greener chemical industry

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As nations unite to curb anthropogenic greenhouse gas emissions, the decarbonization of the chemical industry has been propelled to the forefront of scientific research. Renewable electricity will play a central role in this effort. In addition to powering chemical plants and allowing for the sustainable production of heat to drive thermocatalytic processes, renewable electricity also provides the chemical industry with opportunities to engage in the sustainability revolution and broadly reduce its environmental footprint through breakthrough innovations in direct electrochemical transformations.

The electrification of chemical synthesis—electrosynthesis—is a promising route to promote sustainability without compromising economic competitiveness. Electrosynthesis uses electrons both as an energy source to drive reactions and as a green reagent for chemical reductions and oxidations under ambient conditions. Therefore, it holds

tremendous potential (pun intended) to increase selectivity to desired products, open green reaction pathways for challenging transformations (e.g., Birch reduction, epoxidations, coupling reactions), and reduce chemical waste.

In addition to a number of intrinsic technological advantages compared to conventional thermocatalytic conversions, electrosynthesis is well-suited for the distributed manufacturing of chemicals due to the modular nature of electrochemical reactors. Electrosynthesis is already being considered for the distributed manufacturing of green hydrogen (H₂), ammonia (NH₃), and hydrogen peroxide (H₂O₂) to overcome challenges with their transportation and storage, as well as for the distributed reduction of carbon dioxide (CO₂) into commodity chemicals. Similar advantages exist when manufacturing chemicals from biomass. Various studies have shown that transportation costs are prohibitive in the case of agricultural waste, e.g., corn stover, due to its low density (~50 kg m⁻³) and high water content (~30 wt%). New technologies that could easily transform regional- and community-scale feedstocks into valuable chemicals using distributed chemical plants, are therefore desired to achieve greener chemical manufacturing practices.

This themed issue sheds light on some of the recent advances in electrosynthesis and electrochemical manufacturing from experimental, computational, and techno-economic/life-cycle analysis perspectives. Bergerson and co-workers studied the environmental

impact and economic trade-offs of the electrochemical reduction of CO₂ to CO for the industrial production of methane, methanol, and diesel fuel (<https://doi.org/10.1039/D2GC01466A>). Life-cycle analysis (LCA) was used to provide guidelines and recommendations for the development of different technologies, and the best use of the products, namely power generation, transportation, and polymer production. In addition to the importance of electricity source and consumption, the study highlights the impact of cell degradation on process economics, an aspect that is often overlooked.

Electrosynthesis also offers unparalleled opportunities for synergies with biocatalysis and the production of chemicals through electrobiomanufacturing. Palkovits and co-workers leveraged these opportunities to design an alternative method for the production of acrylonitrile, a commodity chemical (<https://doi.org/10.1039/D3GC01045G>). The conventional Standard Oil of Ohio (SOHIO) process relies on the use of fossil propylene, ammonia, and air as the necessary substrates, which imposes a significant environmental concern. In contrast, Palkovits and co-workers present an electrochemical pathway using the biogenic amino acid D,L-glutamic acid, proceeding through an electro-oxidative decarbonylation and non-Kolbe electrolytic nitrile formation. Using a similar approach, Tessonier, Roling, and co-workers leveraged biologically-produced *cis,cis*-muconic acid to synthesize C6 diacids that find appli-

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cations in the manufacture of Nylon 6,6 and performance polyamides, namely adipic acid (<https://doi.org/10.1039/D3GC03021K>) and *trans*-3-hexenedioic acid (<https://doi.org/10.1039/D3GC02909C>).

Environmental remediation and waste treatment have also been at the center of intense research in the last few years. Ren and co-authors (<https://doi.org/10.1039/D3GC02252H>) discuss the role of microbial electrosynthesis for the hydrothermal liquefaction (HTL) of wet waste into biocrude and biofuels. HTL produces wastewaters of complex organic composition. The study argues that microbial electrolytic treatment, where electroactive microbes can be incorporated into the anode of microbial electrolysis cells (MECs), can be used for the conversion of the organic contaminants in the wastewater into CO₂ and H₂. Using high-performance liquid chromatography and 2D nuclear magnetic resonance spectroscopy, the authors confirmed the efficient transformation of

short-chain carboxylic acids and organic alcohols through the metabolic action of fermentative and electroactive bacteria for record production of H₂ and high oxygen removal.

Computational methods have become indispensable in the investigation of mechanistic details of chemical transformation, leading to quick and better screening of chemical reagents, catalysts, and descriptors of chemical reactivity. Janik and co-authors (<https://doi.org/10.1039/D3GC01144E>) used density functional methods to investigate the mechanism and rate-determining steps for trinitrotoluene (TNT) electroreduction to 2,4,6-triaminotoluene and guide the design of catalysts for this reaction. While a number of methods have been proposed to treat the toxic wastewater generated during TNT production, electrochemical methods are respectful of the environmental, scalable and efficiency aims, and operate under ambient conditions. The team investigated the rate-determining steps over

multiple metal surfaces (Au, Ag, Cu, Pt, Pd, Ir, and Rh) and compared the outer- vs. inner-sphere reduction of TNT. The energetics suggest that the non-catalyzed outer-sphere pathway is competitive on Fe(110) and Au(111) surfaces. The overall activity when comparing mono- and bi-metallic surfaces is subject to a trade-off in the initial activation of the –NO₂ group and reduction of surface –OH*.

This collection includes contributions on many other topics that are not discussed in this editorial due to space restrictions. We thank all the authors for the high quality of their contributions. We also thank the editorial office of *Green Chemistry*, in particular Dr. Hugh Ryan and Dr. Andrea Carolina Ojeda Porras, for their guidance and support throughout the creation process. It is our hope that this themed issue will bring together researchers from various fields and (electro)catalyze new interdisciplinary collaborations.

