

Introduction to ACS Catalysis' Special Issue on Electrocatalysis

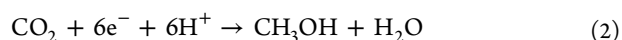
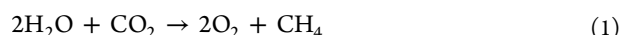
This special issue of ACS Catalysis on "Electrocatalysis" is both timely and to the point. Increasing attention is being paid to electrochemistry and electrocatalysis, driven by their growing importance in energy applications and in helping to define a new energy future. Electrochemistry is of fundamental interest because it provides an understanding of the interconversion of chemical/electrical energy between molecules and an externally applied potential. Chemical conversion occurs to a new state by interfacial electron transfer often associated with proton transfer equilibration driven by the applied potential and resulting current.

- When operated with zero applied current, under conditions of rapid interfacial electron transfer, electrochemical cells and potential measurements provide a measure of the "driving force" of an electrochemical half reaction as a redox (oxidation or reduction) potential relative to a reference. The latter is usually taken to be the $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$ couple under standard conditions. Redox potentials provide a thermodynamic basis for systematizing redox reactions and for understanding electron transfer. Operating the system at zero net driving force (i.e., at the equilibrium potential) gives the exchange current density and information about the kinetic facility of the system.
- The free energy content of a solution or surrounding medium can be increased and a new state of equilibrium reached by the application of an applied potential with current flow. This mode of operation provides the basis for energy storage in batteries and for the electrosynthesis of commodities such as chlorine and aluminum. The existing and future importance of batteries for electrical energy storage in our increasingly electronic society and, in the future, for transportation and for grid applications is evident. At current prices, per mile transportation costs are six times less for electrically powered vehicles than for comparable gasoline-powered vehicles.
- In fuel cells, free energy is extracted continuously as a current driven by a chemical potential by replenishing the reactants. Implementation of practical fuel cell technologies with hydrogen or small organic molecules (SOM) as fuel would revolutionize the transportation economy with increased efficiencies and decreased environmental degradation.

Driven by economic and environmental factors, pressure is mounting and momentum building for creating and implementing a new generation of energy technologies. Advances are needed both in using existing energy sources more efficiently and in enabling the large scale use of renewable energy sources. While the sun is the "ultimate energy source", providing $\sim 10\text{--}000$ times our current energy needs, its energy is diffuse. To meet current U.S. power demands with a 10% efficient device would require a collection area of $\sim 60\,000$ sq miles at a cost of $\sim \$60$ trillion at $\$400/\text{meter}$. In addition, the sun is intermittent, providing, on average, only ~ 6 h of useful energy

per day. If solar energy is to become a primary energy source, it will have to be coupled with energy storage for power consumption at night at unprecedented scales.

The only reasonable way to provide energy storage at this scale is "artificial photosynthesis" in which energy is stored in the chemical bonds of high-energy molecules or "solar fuels". Light absorption and catalysis are integrated to drive solar fuel reactions, such as water splitting, into hydrogen and oxygen or to use water to reduce CO_2 to CO, other oxygenates such as methanol or hydrocarbons (eqs 1 and 2).



Integrating light absorption with the large-scale synthesis of solar fuels is challenging, but photoelectrolysis based on an "inverse" fuel cell design has real promise. Direct band gap excitation of oxide semiconductors in which excitation is followed by separation of electron-hole pairs by internal electric fields with electrons and holes driving surface catalyzed water reduction and oxidation is under investigation. In dye sensitized photoelectrosynthesis cells (DSPEC), molecular level excitation and excited state injection occur into the conduction band of an oxide semiconductor, providing oxidative equivalents for water oxidation at an added catalyst. Electrocatalytic reduction of CO_2 or H_2O occurs at a physically separated cathode.

Success on all fronts could lead to a combined photoelectrochemical-fuel cell with solar fuels produced during the day and power generated at night in the fuel cell. The combination would be an ultimate device, providing a closed, nonpolluting basis for continuous energy production from the sun.

Electrochemistry and photoelectrochemistry may play increasingly important roles in a new energy landscape. However, success hinges on electrocatalysis and overcoming the barriers to electrochemical conversion needed to achieve high rates and unlimited stability at the interfaces of working devices. The challenges arise from the underlying chemistry and the multielectron, multiproton nature of solar fuel half reactions. In working devices, there is a need to minimize overpotentials and maximize free energy electrical efficiencies. There is also a need to create highly stabilized, high-surface-area electrode interfaces and membranes that retain their functions over unlimited redox cycles and turnovers.

For the energy conversion half-reactions for water oxidation and water/carbon dioxide reduction, bare electrode surfaces and interfaces are limited in what they can provide mechanistically. The half reactions are multielectron, multiproton in nature (eqs 1 and 2). Reaction pathways that occur by forming highly unstable 1e^- intermediates [$\text{H}^+ + \text{e}^- \rightarrow \text{H}\cdot$ ($E^0 = 2.1$ V); $\text{H}_2\text{O} \rightarrow \text{e}^- + \cdot\text{OH} + \text{H}^+$ ($E^0 = 2.8$ V)] are

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precluded because of the high reaction barriers and, concomitantly, rates that are too slow to be of interest.

Complex materials and pathways are required that stabilize intermediates or use multiple electron transfer. H₂ is highly activated by adsorption in Pt. Proton coupled electron transfer (PCET) processes provide a way to build up multiple redox equivalents at single chemical sites or clusters or at surfaces. In PCET, both electrons and protons are gained or lost avoiding charge buildup (e.g., $M-OH_2 - 2e^- - 2H^+ \rightarrow M=O$), providing access to multiple electron transfer pathways that avoid 1e⁻ intermediates.

With solid electrodes, challenges to electrocatalysis arise from the need for systematic manipulation of surface structure and composition to enable low barrier reaction pathways. Such changes are difficult to monitor experimentally, and gaining detailed mechanistic insight into molecular level processes at interfaces is a challenge. The reactivity of molecular catalysts in solution can be systematically varied by synthetic changes and mechanisms probed by the application of a variety of spectroscopic techniques. Although solution reactivity can often be transferred to electrode interfaces by surface binding, loss of catalytic activity by degradation of the interface or catalyst is often a limiting factor. Significant logistical issues arise in the design of practical devices ranging from electrode design and maximization of surface area, to limitations imposed by membranes and membrane diffusion, to electrochemical cell design for large-scale applications.

Electrocatalysis is the theme of this special issue of ACS Catalysis. Listing titles and lead authors by topical areas provides a revealing introduction to contemporary research in this critical area:

Fuel Cell Anodes: Electrocatalysis for Polymer Electrolyte Fuel Cells: Recent Achievements and Future Challenges (Schmidt); Degradation Mechanisms of Pt/C Fuel Cell Catalysts under Simulated Start–Stop Conditions (Meier, Mayrhofer); Ensemble Site Requirements for Oxidative Adsorption of Methanol and Ethanol on Pt Membrane Electrode Assemblies (Smotkin); Tetrahedral Pt Nanocrystal Catalysts Decorated with Ru Adatoms and Their Enhanced Activity in Methanol Electrooxidation (Sun); Pd-Modified Tungsten Carbide for Methanol Electro-oxidation: From Surface Science Studies to Electrochemical Evaluation (Chen); Mechanism of the Electrocatalytic Oxidation of Formic Acid on Metals (Cuesta).

Fuel Cell Cathodes: Role of Metal Coordination Structures in Enhancement of Electrocatalytic Activity of Ternary Nanoalloys for Oxygen Reduction Reaction (Chen, Zhong); Catalytic Activity of Platinum Monolayer on Iridium and Rhenium Alloy Nanoparticles for the Oxygen Reduction Reaction (Adzic); Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction (Stamenkovic); Surface Composition and Lattice Ordering Controlled Activity and Durability of CuPt Electrocatalysts for Oxygen Reduction Reaction (Yan); Electrocatalytic Activity and Stability of Titania-Supported Platinum/Palladium Electrocatalysts for Polymer Electrolyte Membrane Fuel Cell (Popov).

Chemically Modified Surfaces: Surface Structures and Electrochemical Activities of PtRu Overlayers on Ir Nanoparticles (Sung); Activation of Tungsten Carbide Catalysts by Use of an Oxygen Plasma Pretreatment (Koel, Chen); Electrochemical Characterization of Shape-Controlled Pt Nanoparticles in Different Supporting Electrolytes (Feliu).

Energy Storage, Graphene: Origin of Reduced Graphene Oxide Enhancements in Electrochemical Energy Storage (Kamat); Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, And Its Potential Applications (Wang). Lithium–Air Batteries: Electrocatalysts for Nonaqueous Lithium–Air Batteries: Status, Challenges, and Perspective (Zhang, Wang, Liu).

Electrosynthesis: Nonaqueous Electrocatalytic Oxidation of the Alkylaromatic Ethylbenzene by a Surface Bound Ru^V(O) Catalyst (Meyer); Highly Selective Electro-Oxidation of Glycerol to Dihydroxyacetone on Platinum in the Presence of Bismuth (Koper); Pronounced Surface Sensitivity of Hydroxylamine Oxidation on Fold Single-Crystal Electrodes in Acidic and Neutral Aqueous Solutions (Scherson).

Solar Fuels: Hydrogenation of CO₂ over Ru/YSZ Electro-promoted Catalysts (Vayenas).

Hydrogen: [Ni(PMe₂NPh₂)₂](BF₄)₂ as an Electrocatalyst for H₂ Production (DuBois and Bullock); Is Base-Inhibited Vapor Phase Polymerized PEDOT an Electrocatalyst for the Hydrogen Evolution Reaction? Exploring Substrate Effects, Including Pt Contaminated Au (Bard).

There is a great deal of interesting science in this collection of papers that point the way to the science-based solutions that we need to address one of the great challenges of our time. Enjoy!

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