

The Rising and Receding Fortunes of Electrochemists

This is the golden age of electrochemistry. Never before has this discipline found itself at the nexus of so many developing technologies: batteries, capacitors, fuel cells; solar-to-electrical energy conversion at liquid junctions; nanocrystalline solar cells; and organic solar cells. New electrochemical energy-harvesting technologies are also being explored for thermal energy harvesting,¹ and these are just the electrochemistry-related technologies pertaining to energy. Capacitive water deionization and electrochemical sensors and actuators are being widely explored, and the use of electrochemical methods in electronic manufacturing, coatings, and the synthesis of materials (including aluminum) remains as important as ever.

Energy is an international priority and an abundance of research funding has been made available for applied electrochemistry. Prominent programs just the United States include The Energy Innovation Hubs, grants from the ARPA-E, many of the Energy Frontier Research Centers (EFRCs), and others. This funding is directed at all of the energy-related topics listed above. This infusion of resources—particularly from the U.S. Department of Energy—has attracted new practitioners into these areas. Not surprisingly, at *ACS Nano* we have witnessed rapid increases in the submission of manuscripts related to electrochemical energy science. Our goal at *ACS Nano* is to publish the best work across these areas to give insight into the opportunities ahead, as new energy-generation and storage solutions increasingly use nanoscale science and engineering.²

Ironically, *fundamental* electrochemical investigations have not been buoyed by these rising seas. In our view, the need for research that elucidates fundamental aspects of electrochemistry in support of its applications in energy has never been greater. We would welcome greater efforts and a consequent larger number of insightful submissions in this area. We, as a community, are just starting to appreciate that so-called “electrical double-layer capacitors” adsorb ions (often partially desolvated) to store energy, and that there is no room for the formation of a classical Helmholtz layer in microporous carbon electrodes.³ Textbook schematics of the double layer at metal surfaces that show highly oriented water dipoles contradict the latest research findings, suggesting that layers of water at metal surfaces have frustrated structures.^{4,5} Understanding the effects of ion charge, radius, and hydration energy on adsorption interactions of ions on oxide surfaces is much more complex.⁶ These are amongst the pressing fundamental issues that should be addressed by electrochemists.

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Grant support for work in this area has been part of the problem. Historically, programs at the U.S. Office of Naval

Research (ONR), Department of Energy (DOE), and the National Science Foundation (NSF) filled this niche, but these programs disappeared in the 1990s, well in advance of the recent excitement and investment in applications. While some fundamental science is being carried out at the various EFRCs as well as through NSF-funded programs, there do not appear to be any programs, at any U.S. agencies, focused on fundamental electrochemistry science issues. Historically, these programs not only provided financial support but also knitted the community together, fostering interactions between electrochemists working on fundamental science issues. The Basic Energy Sciences Division of DOE and Chemistry Division of NSF would be obvious sources of support in the United States, and we hope that those and other funding agencies around the world have the will to support fundamental electrochemical science.

Key issues that are ripe for investigation include the following: the kinetics of coupled electron transfer and ion insertion/deinsertion at the surfaces of insertion materials; ion transport in charged and uncharged nanometer-scale channels; the structure of electric double layers in various electrolytes (from aqueous to ionic liquids) and at interfaces with different surface chemistries and topographies; the contribution of self-exchange-based charge transfer in photoelectrochemical and energy storage systems (see Figure 1); and the electrochemical behavior of recently discovered materials, such as two-dimensional carbides, silicene,

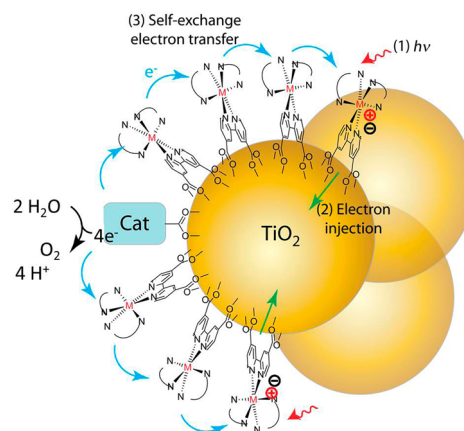


Figure 1. Steps in dye-sensitized photoelectrochemical water oxidation: (1) sunlight absorption by molecular dyes, here tris(bipyridyl) inorganic coordination compounds anchored to nanocrystalline TiO_2 ; (2) excited-state electron injection/transfer from excited dyes into TiO_2 ; (3) self-exchange electron transfer between neighboring M^{n+} and $\text{M}^{(n+1)+}$ dyes and accumulation of multiple charges at electrocatalysts to ultimately drive multiple-electron-transfer reactions, here O_2 evolution through water oxidation. Image courtesy of Shane Ardo.

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or numerous dichalcogenides. The roles of charge transfer and “pseudocapacitance” are increasing in capacitive energy storage, but how do we define the border between “intercalation capacitors”⁷ and conventional battery materials, such as graphite or layered metal oxides? On the subject of batteries, the community is moving beyond lithium ions to Na⁺, K⁺, Mg²⁺,⁸ and even Al³⁺,⁹ requiring fundamental understanding of intercalation and electrochemical reactions involving those ions. These topics are among the fundamental electrochemistry issues that we hope will be addressed and will result in papers that we can share on the pages of *ACS Nano* in the not-too-distant future.



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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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