



Future of interfacial electrochemistry: from structure-function relationships to better understanding of charge transfer reactions and (photo)electrocatalytic reactivity

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Electrochemistry is a field of science that deals with chemical changes produced by electricity as in electrolytic cells or with the production of electricity by chemical action as in galvanic cells. Electrochemistry finds wide applications: in addition to industrial electrolytic processes, electroplating, and the manufacture and use of batteries and fuel cells, the principles of electrochemistry are used in corrosion protection, chemical synthesis, and in chemical analysis including electrochemical sensing. International community has recognized both fundamental and applied aspects of electrochemistry by awarding Nobel Prizes: in 1959 to J. Heyrovsky for polarography, in 1992 to R. A. Marcus for theory of electron transfer, and in 2019 to J. Goodenough, M. S. Whittingham, and A. Yoshino for development of lithium-ion batteries. In all above cases, as well as during the recent period of the advancement of electrochemical science and technology, the primary focus has been on the development and characterization of the solid-liquid interfaces (sometimes formed with semi-liquid or semi-solid electrolytes) that has given rise to interfacial electrochemistry as a rapidly expanding discipline.

The research in the field of electrochemistry is identified by progress in theory and modeling in support of experimental work. Further development of electrochemical devices (e.g., electrochromic displays, electroanalytical sensors, batteries, and fuel cells) or technologies (e.g., electrosynthesis, electroplating, water splitting for hydrogen economy, corrosion protection, production of chlorine, conversion of carbon dioxide, and nitrogen fixation) would require continuing progress in the understanding of charge transfer reactions, and structure—interfacial reactivity relationships, as well as in

the description of the interfaces on the molecular or atomic level [1–12]. The growing availability of both ex situ and in situ surface analytical, particularly the operando methods, would be helpful in this respect [1]. With the advent of nanotechnologies, cross-disciplinary activities in many areas of natural and life sciences are becoming feasible [5–10].

The scope of research in interfacial electrochemistry ranges from electrocatalysis (practice, high-level theory, electrode surface structure, reaction environments, relevance to fuel cell science and technology) to electrochemical charge transfer reactions, electroanalysis, enzymatic or bioelectrochemical catalysis, chemical and biochemical sensing, and photoelectrochemistry [5, 9, 10]. The importance of theoretical approaches for predicting electrocatalytic reactivity by advanced DFT calculations should also be mentioned here. Furthermore, the progress in the area will be dictated by such issues as new research instrumentation, energy storage, rational fabrication of catalytic materials for various electrochemical applications, intentional surface modification and related interfacial reactivity, nanometer-scale technologies, and prospects in electrosynthesis. Research activities in the growing area of redox-flow batteries are currently stimulated by the need to find a rational storage technology for wind and solar electricity. One of the approaches to increase current densities at electrodes is by accelerating the kinetics of electrode processes. This can be achieved simply by choosing appropriate electrode materials but, in many cases, controlled modification and activation of electrode surfaces through introduction of catalytic species [7] will have to be considered.

Electrochemical generation of valuable chemicals and fuels necessitates direct or indirect use of energy and, in this respect, more pronounced application of renewable energy sources, including sunlight, could be envisioned. In particular, the photoelectrochemical approaches, which utilize long-lived charge carriers (photogenerated at the semiconductor-electrolyte interfaces) having the ability of initiating and

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driving chemical reactions, should be mentioned [5]. Both n-type and p-type semiconductor/liquid junctions can be used to convert solar energy into electrical energy, as well as directly into chemical energy by means of photoelectrolysis. In this respect, research activities will be focused on the preparation of stable efficient photoelectrodes exhibiting possibly high activity and selectivity toward a single specific product. There is a need to understand better the influence of the morphology of semiconducting materials and the presence of certain active facets or low coordinated sites on their activities. Introduction of co-catalysts and interfacial modifications, e.g., by fabrication of robust, non-inhibiting over layers having also the capability of controlling the adsorption energy and possible activation steps, will be crucial for such technologies as photoelectrochemical conversion of carbon dioxide (artificial photosynthesis) [12], nitrogen fixation, or splitting of water and hydrogen production. For example, sensitization with quantum dots is a promising option but more research is needed to find new materials able to absorb the light efficiently.

Regarding significant progress in interfacial electrochemistry, there are many challenges ahead with respect to the need of better understanding, characterization, and intentional designing of new potent and durable catalytic materials. For example, the nature of surface chemical bonds (e.g., between catalysts and reactants) remains insufficiently understood despite significant progress in the identification of surface structure and the adsorbate binding sites for variety of systems including CO₂ and its reaction intermediates. Closer collaboration of experimental electrochemists with theoreticians should be helpful in this respect. Also, contribution of interfacial electrochemistry to develop and describe precisely solid-liquid interfaces of importance to bioelectrochemistry (e.g., to study nitrogen fixation) needs further attention. Reaction rates and knowledge of elementary steps involved in certain electrocatalytic processes, such as electrooxidations of organic fuels, are as yet not fully acceptable for the low-temperature fuel cell technologies. The degradation of electrode materials (e.g., catalytic interfaces) is far from being satisfactory for many applications. Nanoscale procedures emerging from the electrochemical science and technology require further consideration [6].

In conclusion, combination of the intellectual strength of electrochemists, recent advances in high technology, growing expectations related to the electrochemical energy conversion and storage, as well as many hot environmental issues (e.g., low-temperature carbon dioxide conversion to fuels and utility chemicals, and nitrogen fixation leading to production of ammonia), together with necessity of fast, reliable, and inexpensive analytical or bioanalytical sensing makes the future for interfacial electrochemistry bright and exciting.

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