

Electrochemical Surface Science: Basics and Applications

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The great success of the *Surfaces* Special Issue entitled “Electrochemical Surface Science (EC-SS): Basics and Applications” reflects the great vitality and relevance of the addressed topic. EC-SS stems from the merging of two different disciplines, i.e., surface science (SS) and electrochemistry (EC), which dates back to ca. four decades ago. The two separate disciplines mainly contributed either a methodological approach (SS, aiming at understanding the microscopic processes occurring at surfaces/interfaces at an atomic level) or a selection of the objects to study (EC, aiming at describing the phenomena at electrified interfaces). The combination of the two is nowadays making possible the challenge of unraveling the complex mechanisms of the electron transfer processes occurring at electrodes, i.e., truly interface-driven phenomena which encompass both solid/liquid, solid/solid, and solid/gas interfaces. This hybrid approach has had an enormous impact on fields such as electrocatalysis [1–3], solar energy harvesting [4–6], corrosion, electrochemical energy storage and conversion devices [7], and sensors [8].

Among them, electrocatalysis is omnipresent and plays a key role. Actually, processes at electrodes are often kinetically limited to efficiently run multi-charge transfer reactions. An electrocatalyst is usually needed, i.e., a substance that can reduce the overall activation barrier height of the redox chemical reaction via complex surface-chemistry steps (adsorption/desorption of reactants and products, low kinetic barriers for charge transport) and determine the product selectivity distribution. The figures of merit of an electrocatalyst are nowadays determined following the standard parameters of catalysis, i.e., turnover frequency and number. Determining such parameters and correlating them with the electrocatalyst structure is a task highly facilitated by the adoption of the hybridized EC-SS method.

A historical perspective is useful to better understand the evolution of electrocatalysis. At the beginning of the 20th century (1905), Julius Tafel [9], in Switzerland, reported on the hydrogen evolution reaction (HER) on various electrode materials, thus establishing a quantitative method for HER electrocatalysts benchmarked through the “Tafel equation” [10]. The HER two-electron process, which started to be academically studied in the 1950s, is still under development in many laboratories in the world [11]: the main goal is to provide a sustainable route for the preparation of molecular hydrogen through the electrochemical splitting of water (water splitting; WS). Actually, WS is expected to promote the envisioned hydrogen economy [12], based on molecular hydrogen as an energy vector for the development of a sustainable energy infrastructure established on the efficient interconversion of chemical energy into electricity and vice versa.

One of the current key concepts in electrocatalysis is the replacement of noble-metal-based electrocatalysts with those based on elements that are abundant on Earth [13,14]. The role played by the synergetic EC-SS approach in such a paradigmatic revolution is similar to that it already played in the 1980s, when platinum-based electrocatalysts were optimized [15,16]. In addition, nowadays, two more relevant key concepts have appeared, i.e., in situ and operando techniques. In situ or operando characterization tools aim to monitor the electrochemical reaction while the electron transfer process is occurring [17,18]. The difference between the two terms is subtle. The in situ term relates to experiments where the experimental conditions (e.g., pressure, atmosphere, potential, current, electrolyte, etc.) are controlled during acquisition, but no temporal discrimination is explicitly taken

into account. On the other hand, operando tools are related to the study of the system in real life applications. When applied to electrocatalysis, this means obtaining more detailed electrochemical information while monitoring the working electrodes with other techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), Raman spectroscopy, ultraviolet visible (UV-vis) absorption spectroscopy, X-ray absorption near-edge structure (XANES), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), etc.

In this Special Issue, a total of 27 scientific papers (one of which is a review) report some of the latest advances in the field of EC-SS. It was a particular target of the Guest Editors to demonstrate the importance and the large scope of EC-SS through examples from a variety of systems and applications. Four papers are related to innovative methods for characterization. As expected, electrocatalysis papers make up the lion's share, but other interesting topics such as sensors, switchable interfaces, potential driven self-assembly on surfaces, and flexible electrodes are also addressed. The Guest Editors hope that the readers will appreciate the different contributions closest to their own field of research.

Conflicts of Interest: The authors declare no conflict of interest.

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