Editorial: Fundamentals and Theoretical Electrochemistry

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Angela Molina is a Professor of Physical Chemistry at the University of Murcia (Spain) and the Head of the research group Theoretical and Applied Electrochemistry, where she has led more than 24 research projects and supervised 14 PhD Theses. Her scientific contributions cover the theoretical treatment of very different electrochemical problems including simple and complex charge transfer mechanisms at macroelectrodes and microelectrodes, molecular electrocatalysis as well as ion transfers across liquid|liquid interfaces. The result of her scientific activity has given rise, among other contributions, to more than 230 papers, one book and six book chapters.

The section Fundamental and Theoretical Electrochemistry of this volume is devoted to review recent contributions in the field and it includes twelve different topics elaborated by reputed experts. In my opinion, the research approaching and developing the principles of any scientific field is of great interest, especially in the current state of affairs where, due to the extraordinary advance of instrumental and computational techniques, most of the electrochemist’s research is related to the interpretation of experimental results via ad hoc tools. Far less frequently, though not less important, are the advances in the theoretical resolution of real (and why not, ideal) problems that have much contributed to the progress of science and will certainly do so in the future.

In this issue, interesting mechanistic considerations of the proton coupled electron transfer are discussed through the theoretical comparison between concerted and stepwise pathways which are outstanding both in surface and molecular electrochemistry (see pp. 104–109). This topic is closely related to molecular electrocatalysis, activation of small molecules or energy conversion among others.

The enhancement of the advantages of ac voltammetry in a broad range of electrode processes by introducing the software package MECsim that provides an advanced though user-friendly simulation tool for comparing experiments and theory with the uncompensated resistance and capacitance being included as a function of the applied potential. By using zero amplitude or frequency for the sine function, MECsim becomes a dc simulation package.

The most important challenges about the theoretical and computational studies of electrochemical systems at the nanoscale are the nano-electrodeposition models which have allow us understand the selective growth of facets are considered here (see pp. 1–6). This theory is based on the interaction between charged species by using the Density functional theory and/or heuristic potentials to emulate nano-electrochemical complex environments.

The use of electrochemical methods has demonstrated to be very helpful to analyze the redox enzyme catalytic reactions has demonstrated to be very helpful (see pp. 110–120). Interesting progress has been made in the kinetic and thermodynamic dependence of intramolecular electron transfer along the redox chains that connects the active site to the electrode. A comparison...
between enzymatic bond and molecular catalysis by using electrochemical tools is very valuable.

The electrochemical behavior of surface confined molecules is an emerging topic in the literature and it is very usual that the voltammetry of these systems deviates from the ideal models, a fact that complicates the comprehension of their functionality. Among the different causes of the non-ideal character of these systems, the presence of intermolecular interactions and its quantitative analysis by using Cyclic Voltammetry is analyzed in detail, in the case of the most common thiol monolayer systems (in pp. 22–26).

The gold-sulfur bond is involved in the chemical design of a great number of modified electrodes or platforms for more a more applications. The true nature of this bond is analyzed (in pp. 7–15). By using both electrochemical, spectroelectrochemical and atomic microscopies in order to rationalize its behavior and develop potential improvements in the reactivity of these systems.

Mathematical modeling to predict and optimize the performance of enzymatic electrodes and fuel cells as promising alternative to traditional power sources provides also important contributions. In order to analyze the physical and chemical insight of the implicated processes their modelization should consider: species transport, enzymatic reactions and heterogeneous electron transfer reactions between the electrode and the mediator or the active centre of the enzyme. For this purpose, different methods of resolution of non-linear reaction-diffusion equations have been discussed (see pp. 121–132).

Currently there is a lack of quantitative information on the electronic properties of the catalyst materials for the oxygen evolution reaction (OER). The substrate on which the catalyst is supported can affect both the redox chemistry within the oxide film and the OER activity. Theoretical computational methods based on DFT are applied to investigate the energetics of OER, although further work is required to look into the kinetics of the surface multistep reaction (see pp. 40–45). In situ spectroscopic measurements are of fundamental assistance to unravel the molecular catalytic mechanism.

A number of theoretical and experimental studies of ion transfer across an interface between two immiscible electrolyte solutions (ITIES) have been published. In the case of finite kinetics ion transfer there have been little agreement between experimental data obtained with different electrochemical techniques at macroscopic and nanoscopic ITIES. Experimental studies of the apparent standard rate constant k0 for the TEA+ remains open the controversial issue of whether the higher k0 values obtained by steady state voltammetry at nanoscopic interfaces could be related with the fluctuation enhancement of the interfacial charge transfer rates. (see pp. 133–139).

The main benefit of miniaturized interfaces between two immiscible electrolyte solutions (ITIES) as microholes, micro-capillaries or micro-pipettes is the decrease of uncompensated resistance and the capacitive current. Theoretical aspects of the ion-transfer electrochemistry have been developed that do not differ from the electrochemistry of microelectrodes and microelectrode arrays when the flux lines are symmetrical at both sides of the ITIES. This is not the case when the diffusion profiles are different in the aqueous and organic solutions as at microcapillaries or micro-pipettes (see pp. 66–72). However, truly comprehensive models to enable a complete characterization under dynamic electrochemical conditions have yet to appear.

Though the resolution of Scanning electrochemical microscopy (SECM) in the micrometric scale, recent pioneering studies have reached the nanometric one. The advances in nanoscale SECM measurement in different areas are: imaging of metal nanoparticles, nanogap voltammetry, characterization of different nanoparticles and nanoelectrodes. Electron transfer kinetics were compared with different numerical simulations. Fundamental aspects of SECM measurement as feedback mode, heterogeneous reactions, etc. and nanoscale SECM studies have been revised (see pp. 46–52).

The control of metal availability is essential for the plants, animals and human health. For this purpose it is necessary to consider the kinetic interconversions and transport processes that influence the most electroanalytical data. This fact implies to solve the reaction-diffusion equations of the several metal species. An extensive theoretical work has been developed to describe the metal speciation by using electroanalytical techniques with special emphasis on the concept of lability degree, the results being very useful to give quantitative lability criteria (see pp. 80–87).

Attending to the increasingly broad scope of Electrochemistry, it is hardly possible to embrace all the topics of interest such that unfortunately some important areas could not be covered in this Section for different reasons. Among them, I would like to at least mention the development of the theoretical framework in some cutting-edge fields such as the interpretation of discrete and low time scale events as arise in nanoimpact experiments [1,2] and in electrophysiology [3], the mathematical modelling of heterogeneous charge transfers at different electrodes, microelectrodes and nanoelectrodes [4,5,6,7], the molecular aspects of interfacial mechanisms and kinetics [8,9], and the modelling of semiconductor systems [10] among others.
References