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Electrochemistry as surface science – or Romeo without Juliet

In a recent book on electrochemistry – first edition 1994 – the definition of electrochemistry is as follows:

“Electrochemistry is, first and foremost, a branch of surface science, and is specially concerned with the electrified interface. ...”

Such a statement is certainly not unique nowadays, and many colleagues incline to accept it. Although the pivotal role of interfaces, or more correctly interphases, is indisputable, we should query this standpoint.

In my opinion electrochemistry is a particular field within chemistry that has several links to physical, analytical, organic, polymer and industrial chemistry. In addition, one should not forget the interdisciplinary fields, such as bioelectrochemistry, or the interrelationship with physics. Historically, electrochemistry belongs to physical chemistry. It originated from the lucky encounter of studies of electricity and magnetism with the chemistry that had just emerged from alchemy.

Electrochemistry had a special significance for the rise of physical chemistry. In fact, the achievements and efforts of van't Hoff, Ostwald and Arrhenius played an especially important role in causing physical chemistry to become recognized as a separate and important branch of chemistry.

The intensive research on electrolyte solutions caused, however, an unbalanced situation. Until the late sixties of the 20th century, ionics has dominated textbooks and conferences. The recognition of electrode kinetics as opposed to Nernstian equilibrium electrochemistry can be dated from the 60 s. (Electrochemistry, apart from power sources and technology, is taught and cultivated as a branch of analytical chemistry in the United States, according to P.H. Rieger this is due to the capture of physical chemistry by chemical physicists in the 40 s, while in Europe the subject belongs to physical chemistry.) The increased interest in fuel cells led to the development of electrocatalysis and, logically, the perception of the inherent link between heterogeneous catalysis and electrochemistry. Soon the electrochemists

adopted and started to use the results of the catalytic research, and surface electrochemistry was born. This was a really important event and had a positive impact on our field. It caused some colleagues to start to consider electrochemistry as a surface science. The pendulum swung in this direction. Furthermore, the new techniques especially scanning probe microscopy, yielding images of surfaces down to the atomic scale, obviously fascinated all of us. Electrochemistry is, however, not just a surface science. It can easily be proved that in most cases – and it is especially true for polymeric and solid mixed conductors – the current is controlled by the mass and charge transport processes occurring in the bulk electrolytes or in the polymer layers. The charge transfer reactions are coupled to the motion of the electrons and ions; in other words, the interfacial impedances contain also the rate constants and diffusion coefficients characteristic of the bulk processes. It is also well known that even the distribution of charged and uncharged species in the interphase, i.e. the structure of the electrical double layer, is connected with the composition of the adjoining phases.

The performance of any device, e.g. solid state batteries, solid oxide fuel cells, sensors, or electrochromic displays, strongly depends on the properties of the bulk phase. The development and improvement of these devices are impossible without a detailed knowledge of the mechanism of charge transport and the interrelationship between composition and structure. Therefore, an important part of electrochemical research is the investigation of bulk liquid, polymer or solid phases.

In summary, I acknowledge the importance of the surface, but the reduction of electrochemistry to a branch of surface science cannot be accepted in view of the wide spectrum and also the tradition of this discipline.

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