

Editorial

Electrocatalysis: Fundamentals and Applications

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Electrocatalysis is a special field in Electrochemistry that has gained a special growth after the late eighties due to the application of new hybrid techniques. However, most of the applications have run for academic purposes but not for technical uses in the industry. Nowadays, the application of new concepts of electrocatalysis for industrial electrochemical processes has appeared as a necessity and not only attracting attention for chemists but for engineers. Therefore, industrial electrocatalytic processes have only been presented in the literature from the chemical engineering point of view with few further electrochemical explanations and mainly during the late seventies. The design and preparation of an electrocatalyst (electrodes for technological uses) are based on new concepts such as a controlled surface roughness, atomic topographic profiles, defined catalytic centre sites, atomic rearrangements, and phase transitions in the course of the electrochemical reactions.

Maybe the best interpretation of electrocatalysis is due to A. J. Appleby as an electrochemical reaction with an adsorbed species, either as reactant and/or product, which can change the kinetics of the reaction and in some cases also the mechanism. Although the old conception of electrocatalysis is mainly related to an experimental field of electrochemistry when using platinum-type metals, the advances in theory and modeling are main keys for a successful interpretation of the data.

The perspective and limitations of electrocatalysis in the laboratory together with their theoretical implications are also presented to give the readers a clearer view of

the problems inside electrocatalytic reactions. This special issue also gathers the experiences of different authors who have worked on the principles of electrocatalysis with relevancy to experimental situations of particular importance in electrochemical engineering. This is the case of the work by T. Fahidy in the use of the Bayer's rule for an electrochemical reactor in order to avoid the possibility of reactor breakdown, reactor's safety, and environmental considerations well beyond purely scientific quantities.

One of the most important features of electrocatalysis arises from the different electrode kinetics using different crystallographic orientations for the electrode surface. A cathodic treatment develops (111) stepped planes similarly to the electrofacetting performed after applying the square wave program shown with X-ray diffraction patterns. These arrangements are well explained in the paper by C. Zinola, using combined techniques and particularly studying the methanol electrooxidation reaction. In spite of being most of the electrocatalytic reactions studied in the scientific community only for rather simple species, some of them involve low-weight amino acids, showing changes in the adsorbed configurations and chiral responses when the nature of the electrode surface is changed, as shown by K. Watanabe. Chiral behavior was clearly observed as an oxidation current difference between the enantiomers of alanine, aspartic acid, and glutamic acid.

The fast and contemporary advances in electrocatalysis have been already treated in other books but only considering the progress in the application of surface science and

ultrahigh vacuum techniques to electrochemistry with no extrapolation to the possible industrial applications of these findings. Some combined techniques, such as differential electrochemical mass spectrometry, show the possibility of the continuous analysis of an electrode reaction with the detection of volatile or gaseous products in the course of the electrochemical reaction as shown by M. J. Lázaro for carbon dioxide electroreduction. Differential electrochemical mass spectrometry studies showed that the carbon support degradation, the distribution of products, and the catalytic activity toward the carbon dioxide electroreduction depend significantly on the surface chemistry of the carbon support.

There are various applications of electrocatalysis for technological electrochemical reactions, organic electrosynthesis, galvanoplasty, electrode sensors, fuel cells, batteries preparations, and so forth. Some of them are presented here in order to give an insight into the possibilities of this science. Thus, the avoiding of interferences in the case of hydrogen peroxide electroreduction has been gained using alloys such as palladium-gold electrodes as reported by R. Mussarlieva with application for glucose biosensors. The surface topography of the electrode modified with Pd + Au mixed in proportions 90:10, exhibiting optimal combination of sensitivity and linear dynamic range towards hydrogen peroxide electrochemical reduction.

However, it seems that the main application is the case of fuel cells and one of the scopes is the possibility of long-lasting experiments without contamination or poisoning of the electrode surfaces. A. S. Aricó studied the continuous use of IrO₂/Pt electrocatalysts in fuel cells with good results that are also presented in this special issue. The IrO₂/Pt composition of 14/86 showed the highest performance for water electrolysis and the lowest one as fuel cell. Polymer electrolyte fuel cells are one of the most used devices for low-to-medium power density sizes. However, platinum electrocatalysts are often changed to platinum/ruthenium alloys because of the application of the electrocatalytic Langmuir-Hinshelwood surface mechanism. In this issue the use of dendrimers during the synthesis of platinum/ruthenium electrocatalysts for polymer electrolyte fuel cells shows interesting results that are strongly dependent on the physical characteristics of the alloy as presented by E. Pastor. After the activation of the catalysts by heating at 350°C, the real importance of the use of these encapsulating molecules and the effect of the generation of the dendrimer become visible. Not only the use of alloys of combined electrodeposited species offers electrocatalytic differences for fuel cell application, but also the preparation of Au core-Pd shell/C electrodes as shown by X. Liu for a direct borohydride-hydrogen peroxide fuel cell. The results show that the Au-Pd/C catalyst with core-shell structure exhibits much higher catalytic activity for the direct oxidation of NaBH₄ than pure Au/C catalyst, i.e. a direct borohydride-hydrogen peroxide fuel cell, in which the Au-Pd/C with core-shell structure is used as the anode catalyst and the Au/C as the cathode catalyst.

New advances relevant to electrocatalysis such as spectroscopic or hybrid techniques with new theoretical considerations act as a final point from them it is possible to evolve to a new projection of the electrocatalytic reaction

itself. One of the purposes of this special issue is to present the field of electrocatalysis as an interfacial approach to a dynamic and permanently changing electronic-to-ionic conductor interphase with real technical applications.

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