

## Editorial

# Advances in Electrocatalysis

**Milan M. Jaksic,<sup>1,2</sup> Wolfgang Schmickler,<sup>3</sup> and Gianluigi Botton<sup>4</sup>**

<sup>1</sup>Institute of Chemical Engineering and High Temperature Chemical Processes-Patras, FORTH, 26500 Patras, Greece

<sup>2</sup>Institute of Food Technology, Faculty of Agriculture, University of Belgrade, 11080 Belgrade, Serbia

<sup>3</sup>Institute of Theoretical Chemistry, Ulm University, 89081 Ulm, Germany

<sup>4</sup>Department of Material Science and Engineering and Canadian Centre for Electron Microscopy, McMaster University, Hamilton ON, Canada L8S4M1

Correspondence should be addressed to Milan M. Jaksic, milan@iceht.forth.gr

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*“All the ideas that have enormous consequences are always simple ideas.”*  
(LEV TOLSTOI).

Electrocatalysis and search for promising electrocatalysts effectively started its development after two distinct core reveals in the science: (i) Sir William Grove inventive discovery and theoretical definition of (H<sub>2</sub>/O<sub>2</sub>) fuel cells and their fundamental structure in 1842 and (ii) Tafel plots in the year 1905, when various metals were distributed and ranged on the  $\eta = a - b \log j$  coordination chart, with clear distinction amongst good and bad, or, on more or less *polarizable*, mostly transition elements or their composite electrode materials. In fact, until now the main criterion to characterize electrocatalysts has been primarily based on the Tafel plot assessed polarization and exchange current density, certainly now advanced for the atomic or nanolevel characterization of the actual catalytic surface and theoretical search for their interrelating correlations. There on the first place comes the density functional theory (DFT) and calculations (DFCs), where primarily *d*-band density of states is correlated with electrocatalytic activity.

The most intensive growth of the field of electrocatalysis effectively started in the earliest 1960s and continuously further grows with exponential trend in the number of the highest level published papers and studies. Thus, many authors have been in search to find and reveal the first electrochemist who introduced the term electrocatalysts or electrocatalysis in the electrochemical science, for the priority in creating the field. By this way, we usually find some

almost unknown names, who never enriched electrocatalysis with any substantial theoretical contributions, and it is clear that much earlier electrochemical science named such achievements as—*depolarization*, the term, which almost disappeared after introducing the name electrocatalysis, otherwise the latter being in good relation with the more general field of heterogeneous catalysis, though these have so far never been officially integrated in the science. In other words, these two fields are based on the same fundamental kinetic parameters, both recognize the energy or enthalpy of activation, but the main separation line comes from polarization itself and broad meaning of the electrochemical activation energy. Heterogeneous catalysis is the science for almost a century preceding electrocatalysis, participates with a higher-order number of creative scientists, mostly leads within chemical branches, and we never succeeded to gather together on a meeting to consider two fields: heterogeneous catalysis and electrocatalysis, their common points and specific differences. The point is that polarization is the basic parameter, key variable, and main criterion in electrocatalysis, but not the common point of any significance for catalysis at all, and the state-of-the art still besides the hydrogen electrode reactions and some less significant in metal deposition, electrochemical science, while missing many additional decisive parameters and complementary criteria in electrode kinetics, so far failed to resolve any

decisive and significant mechanism, the first of all but not the most important in aqueous media for the oxygen electrode reactions. In fact, there exists one common point—the electrochemical promotion of catalysts (EPOCs), when by imposed external polarization and negligible Faradaic current flow, one alters work function of heterogeneous catalyst, and in some issues this way dramatically increases the actual proceeding reaction rate and/or the excited catalytic activity. Meanwhile, except some individual issues, these two fields never found any motive to strengthen their creative forces and capacities, and proceed together.

The main imperative guiding aim, challenge, and purpose of electrocatalysis are associated with aqueous media, and founded on hydrogen and oxygen electrode reactions, to substantiate the main target—*hydrogen energy*. Hydrogen as an ideal (sustainable, renewable, inexhaustible, and environmentally clean) fuel might establish the reversible interrelation between the matter and energy in the nature: to return exactly, in the same shape and amounts, what is previously taken from, water to water, and thence make all states and nations in the world equal and independent in energy sources and needs. Since hydrogen does not exist in any significant free state in the Earth, while its water sources are unlimited, to produce hydrogen by electrolysis and subsequently use as a fuel in L&MT PEMFCs, implies remarkable polarization losses in both directions, while in an ideal issue, one tends to approach reversibly balanced input and output. Photovoltaic electrocatalytic solar generation of hydrogen, as being substantially based on the inexhaustible free energy source, certainly could prevailingly and even completely compensate both the polarization inputs for its nominal production by electrolysis and overvoltage in fuel cells. By this way, the overall energy balance even might be effectively brought within the apparent reversible framework between hydrogen evolution and fueling in PEMFC. Unfortunately, although advanced photovoltaic solar electrocatalysis is doubtless still the best promising inexhaustible conversion energy source, it is yet faraway from its economical substantiation. All other aspects in PEMFC energy conversion and generation belong to electrocatalysis. Meanwhile, regardless tremendous fascinating progress in PEMFC electrocatalysts, except for some specific applications, such as in the space program, when the energy losses and profits are of secondary significance, in electrocatalysis for energy conversion we face all the time the same substantial problems and in many aspects still stay on the same positions, where initially was sir William Grove himself.

Mostly, electrochemists use to state that only Pt and its modifications satisfy requirements for electrocatalysts in PEMFCs energy conversion. Amongst so many transition metals this is a rather sad conclusion, and even more so, since even Pt itself prevailingly fails to satisfy the basic electrocatalytic requirements in approaching or establishing the operating reversible potential values. In other words, all energy diagrams so far scanned from LT PEMFCs show the sharp potential drop from almost reversible oxygen electrode value down to a plateau at about 0.6 V versus RHE, or the energy waste for more than a half of theoretically available amount. Cyclic voltammograms, meanwhile, in

addition indicate that the established stable potential range in the energy conversion coincides and corresponds to the reversible adsorption-desorption peaks location of the primary oxide (Pt-OH) so that the polarization determining species (PDS) or the main obstacle is the surface oxide (Pt=O). There has so far practically been done nothing in such a respect to double the converted energy yields of hydrogen feeding fuel cells and/or effectively reduce the number of unit cells for more than a half and still keep the same theoretically available capacity. Some alloying transition metals (Co, Ni, and Fe) succeed to reduce the interatomic Pt-Pt distance, this way weakening Pt=O adsorptive bonds and thereby increasing a little the overall electrocatalytic activity. The externally induced Pt-OH spillover effect and its interference with Pt=O promises to shift the plateau in the conversion energy diagram to the more positive potential range for the ORR, and these both have traced some paths towards the reversible oxygen electrode, so far never attained (accessed) experimentally, just because of the polarization imposed by the surface oxide (Pt=O). Otherwise, instead of two actual contemporary fuel cells running roughly at 0.6 V in energy source, one might theoretically operate with the one unit of about doubled capacity (about 1.2 V), and it has been the main target in electrocatalysis for more than a century. The expectancies from such similar and new approaches have been the main purpose and task to initiate the present “*Advances in Physical Chemistry*” (APC) special issue and try to sum up or reveal eventual new trends and new advances in contemporary and forthcoming age in electrocatalytic science. Unfortunately, scientific papers are usually and mostly written on an affirmative and seldom critical manner to reveal and highlight main obstacles and unresolved problems, while the latter when clearly specified, usually impose some stimulant trends and inspirations for new forthcoming generations to substantiate them.

The discouraging fact is that even if electrochemical science succeeds to resolve all just discussed kinetic and electrocatalytic problems and enable us to use the entire theoretically available voltage of the cell composed from hydrogen and oxygen electrodes, Pt nevertheless might effectively impose serious economical problems when employed as the electrocatalyst in PEMFC for massive car traction. In other words, if all vehicles in the actual world would turn on hydrogen fuel and PEMFC driving force, Gordon Conference for such purposes already estimates its annual necessity of hundreds tons. In other words, something that amounts from 20 to even 30 percent of the actual annual production (roughly about 20,000 tons) worldwide. In such circumstances Pt price might be remarkably increased, while Pt still could be employed, in particular with providing more than 85 percent of its recovery and decreasing its loading (the lowest might be about  $60 \mu\text{g cm}^{-2}$  of geometric surface). The alternative way would be PEMFC with alkaline membrane and cheaper and more available electrocatalysts (Ni, Co, and Ag), but with relatively higher polarization.

Two main breakthroughs in the preceding century fundamentally advanced and enriched electrochemical science, engineering, and technology: cationic selective membranes (DuPont’s Nafion and/or Asahi Glass Flemion), sustainable

in most severe production conditions (chlorine and chlorate cells), and simplified titanium metal electrowinning, as a cheap and unique constructive material in chemical industry, and ideal carrier for electrocatalysts in most significant and massive industrial electrochemical processes. Initially, one inventive man and his named enterprise (Oronzio de Nora Company, Milan, Italy) developed and granted to the existing world all the leading optimized industrial model cells for unlimited scale-up in electrolysis (chloralkali, classical and membrane type cells, chlorate production, water splitting, hydrochloric acid electrolysis, etc.), and even more so, were the first to launch RuO<sub>2</sub>/TiO<sub>2</sub> mixed oxide electrocatalyst on Ti carrying electrodes, today the most massive and most important electrocatalytic production worldwide (more than 30 Mio tons capacity annually). Along with equally efficient electrocatalysts for the HER, membrane cells operate now almost at the reversible hydrogen and chlorine electrode potentials. Meanwhile, De Nora Company successfully introduced electrocatalysts for the ORR, to replace the HER, and succeeded to save for about 0.8 volt for producers who prefer energy savings instead of the industrial hydrogen evolution in hydrochloric acid and chloralkali electrolysis. Such general statements reliably testify for the remarkable progress, tremendous outstanding achievements and unpredictable prospects of electrocatalysis in industrial electrochemical processes, particularly in organic electrosynthesis. Thus, it might be interesting to stress that such significant and massive industrial electrocatalytic processes do not represent electrocatalysts developed or invented by the leading research centers or recognized universities and leading electrochemists in the world of science, but engineers in factories who intensely live with and experience an intimate relation with everyday occurrences in practice.

*Main Papers Hints.* A unified electrocatalytic (W. Schmickler et al.) model for electrochemical electron transfer reactions, primarily focused on the electrochemical adsorption of a proton from the solution—the Volmer reaction—on a variety of systems, such as bare single crystals and foreign metal on a variety of (111)-substrates, nanostructured surfaces that explicitly account for the electronic structure of the electrode, and provides a framework describing the whole course of bond-breaking electron transfer, enabled to explain catalytic effects caused by the presence of surface *d*-bands, and in application to real systems, the parameters of this model—interaction strengths, densities of states, and energies of reorganization were obtained from density functional theory (DFT) enabling to discuss in details the interaction of the surface metal *d*-band with the valence orbital of the reactant and its effect on the catalytic activity, as well as other aspects that influence the surface-electrode reactivity, such as strain and chemical factors, the hydrogen electrocatalysis thence being substantially founded on the theory and not on a correlations, the entire goal being to combine DFT and new author theory to elucidate the electronic structure, predict and prove the catalytic activity. Consequent and farreaching consequences of the DFT applications are complementarily presented by S. Mentus et al.

Since fundamental information concerning reaction mechanisms, active sites, and catalytic kinetics gleaned from in situ spectroscopy and provided detailed resolution of the molecular transformations of bond making and bond breaking acts that occur at both gas/metal and solvent/metal interfaces, this became the link and great step ahead to allow a more direct comparison, interrelations, and guidance of heterogeneous catalysis and electrocatalysis and crosscut both areas (A. Wieckowski and M. Neurock). In other words, the knowledge of the complex electrified interfaces, the nature of active centers and their environment in electrocatalysis bears a number of common similarities to the aqueous/metal interfaces for catalytic reactions. Advances in spectroscopy allowed opening the common field for more detailed resolution of the molecular transformations that occur in electrocatalytic systems, along with a more detailed introspection of the nature of the active centers and their environment, compared, contrasted, and interrelated them.

Core/shell Pt monolayer (Pt<sub>ML</sub>) electrocatalysts for the ORR originally developed (R. Adzic et al.) and introduced in electrocatalysis, and further advanced by the modification of surface and subsurface of the core materials, involving the changes on both electronic (ligand) and geometric (strain) properties, primarily use the strain effect (compression on Pd and tensile on Au cores) to induce the shift of *d*-band center as the primary factor to increase the synergy in catalytic activity, while providing each individual Pt atom to be involved in the reaction and keep minimal Pt loading in electrocatalysis. Such an exact monolayer core-shell type of electrocatalysts has dramatically reduced Pt catalyst load relative to the common Pt/C issues and in some inventions increased catalytic activity for more than an order of magnitude.

Complex multielectron transferring mechanism of the ORR as an electrocatalytic innersphere electron transfer process exhibiting strong dependence on the nature of the electrode surface imperatively requires the stability in acidic media and unavoidably imposes the Pt-based limits, in contrast to the involvement of surface-independent outersphere electron transfer component in the overall electrocatalytic process characteristic for alkaline solutions, so that such a surface nonspecificity gives rise to the possibility of employing a wide range of nonnoble metal surfaces as electrocatalytic materials for ORR, while then the whole electrode reaction predominantly leads only to a 2e peroxide intermediate as the final product (N. Ramaswamy and S. Mukerjee). The promoting of the electrocatalytic innersphere electron transfer mechanism by facilitation of direct adsorption of molecular oxygen on the active site has been emphasized with the usage of pyrolyzed biomimetic metal porphyrins as electrocatalysts, while the primary kinetic advantage of performing ORR in alkaline media was found to be the improved stabilization of the peroxide intermediate on the active sites.

Since altermultivalent hypo-d-oxides impose spontaneous dissociative adsorption of water molecules and then pronounced membrane transferring properties, instantaneously resulting with corresponding bronze type (Pt/H<sub>x</sub>WO<sub>3</sub>) for fast H-adatoms spillover under cathodic, and/or its hydrated state (Pt/W(OH)<sub>6</sub>), responsible for Pt-OH effusion,

under anodic polarization, this way establishes instantaneous reversible alterpolar bronze features (or, the specific equilibrium,  $\text{Pt}/\text{H}_{0.35}\text{WO}_3 \rightleftharpoons \text{Pt}/\text{W}(\text{OH})_6$ ), and substantially advanced electrocatalytic properties of these composite interactive electrocatalysts ( $\text{Pt}/\text{Nb}_2\text{O}_5, \text{TiO}_2/\text{C}$ ;  $\text{Pt}/\text{WO}_3, \text{TiO}_2/\text{C}$ ;  $\text{Pt}/\text{Ta}_2\text{O}_5, \text{TiO}_2/\text{C}$ ) for all four hydrogen and oxygen electrode reactions (HER, HOR, ORR, and OER), therefrom consequently resulted mutually interchangeable catalysts for the ideal reversible cell between PEMFC and WE (G. D. Papakonstantinou et al.). Spillover phenomena of interchangeable H-adatoms and the primary oxide ( $\text{Pt}-\text{OH}$ ) have been thoroughly enlightened by various sophisticated contemporary methods and proven as the additional dynamic effect in both electrocatalysis and double-layer charging.

Nanostructured electrodes for bioelectrocatalytic dioxygen reduction catalysed by two copper oxidoreductases: laccase and bilirubin oxidase have recently been developed and introduced as new trend in enzymatic biocatalysis, formerly employed on carbon nanotubes or nanoparticulate carbon carriers, and recently advanced in new nanosized architecture, as conductive metal oxide supports (M. Opallo and R. Bilewicz). Such electrocatalytic nanomaterials are usually adsorbed on the carrying electrode surface or embedded in multicomponent film, and these adsorptive interbonded nanoobjects act as electron shuttles between the enzyme and the electrode substrate providing favourable conditions for mediatorless bioelectrocatalysis. In the latter case, a different mechanism of electron transfer is operative: based on electronic conductivity and not on the redox processes of the mediator, and consequently, nanoparticulate film biocathodes feature mediatorless bioelectrocatalytic effect and current densities competitive with those achieved using osmium polymers (up to  $4 \text{ mA cm}^{-2}$ ).

Nanostructured PdCo alloy electrochemically deposited microelectrodes upon Au substrates, partially dealloyed in the next step to introduce nanopores and produce a rather promising electrocatalyst of highly developed nanointegrated surface, and thereby advanced activity for the ORR, superior relative to Pt/C nanosized issues, has been originally created primarily for the on-chip membraneless microfuel cells, flexible and integratable with other micro-devices in direct methanol fuel cells, suitable because of its nanostructure and therefrom resulting properties of the unique high-catalytic activity and the tolerance to methanol (S. Tominaka and T. Osaka).

Protonic perovskite oxides were introduced as proton conducting ceramic SOFC electrolytes in place of oxide ion conductors so that operating temperature could be reduced from very high to moderate or low levels. At these less stringent conditions, the SOFCs are capable of cogeneration of energy and valuable industrially important chemical products. In particular, ethylene is selectively manufactured from ethane in a fuel cell reactor using on  $\text{FeCr}_2\text{O}_4$  anode electrocatalyst,  $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BCZY) perovskite oxide as the proton conducting ceramic electrolyte, and nanostructured  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$  (LSF) as cathode catalyst, with efficient production of DC energy. The power density increases from 70 to  $240 \text{ mW cm}^{-2}$ , and the ethylene yields from about

14.1% to 39.7% when the operating temperature of the fuel cell reactor increases from  $650^\circ\text{C}$  to  $750^\circ\text{C}$  (Jingli Luo et al.).

Using a multiscale modeling approach, the ripening of monoatomically high Au islands on Au(100) has been studied (T. Jacob et al.). Starting at the microscopic scale, DFT was used to investigate a limited number of self-diffusion processes on perfect and imperfect Au(100) surfaces. This provided the necessary information to generate a reactive molecular dynamics forcefields that was finally used to create an extended process database for subsequent kinetic Monte Carlo studies. This provides important information on effects such as nucleation, aggregation, fluctuation, and the equilibrium shape structures of these islands on Au(100). Further, this hierarchical approach should also be applicable to address other questions related to the characterization of electrocatalyst surfaces.

Other papers in the present issue deal less with electrocatalytic aspects of general significance, but perfectly resolve some individual and specific aims and tasks, and enrich the overall field.

*Milan M. Jaksic  
Wolfgang Schmickler  
Gianluigi Botton*



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