

## ELECTROCHEMISTRY AND NEW MATERIALS

*The prognoses of the advance and possible achievements in the field of refining materials for electrochemical devices, like any other predictions of new scientific discoveries are an extremely complicated and ungrateful task. As one classic said, "... it is always hard to predict, especially if this concerns future..."*

The end of the XXth century was marked by a sharp increase in the number of materials applied in electrochemical technology and scientific research. In certain directions, this breakthrough was prepared gradually, while in other cases its advance seemed to be sudden. This should be considered in the general context of chemistry development for which the purposeful search for materials with desired properties is the main direction. Moreover, the boundary field between chemistry, physics, and material science is characterized by a trend toward explosive extension, and the material science in turn stimulates the contacts between different exact sciences although only approaches the latter.

The both mentioned trends clearly illustrate some recent developments in the field of new materials: high-temperature oxide superconductors (1987), fullerenes (1990), mesoporous silicon dioxide, dendrimers (1992), manganites of rare-earth metals with colossal negative magnetoresistance, hybrid (organic + inorganic) materials (1993), "frontier" materials (transition phases) (1994), synergistic materials (1995). Furthermore, the appearance of various materials with nonlinear responses to external actions, which were named "smart materials", deserves to be mentioned.

Electrochemistry took an active part in every research "boom" that arose immediately after any remarkable properties of a new material groups had been discovered and made worthy contributions to the succeeding systematic studies. This always involved and continues to involve revolutionary changes in the electrochemical methodology, first of all, considerable extension of the research field. As the bright examples, the transition from traditional aqueous solutions to aprotic media and solid electrolytes including polymeric

should be mentioned. Furthermore, the ruthenium-titanium oxide anodes (DSA) which have profoundly changed the most large-scale electrochemical industry, viz., chlorine electrolysis, can be placed between the most remarkable materials of the XXth century [1].

In the second half of the past century, the experience in material science was gained precisely in the studies dealing with materials most promising for practically important electrochemical systems. Below (Table 1), we show certain examples of the discoveries in this field of electrochemical material science which in the time course turned out to be fundamental. The table shows the years of publications in the scientific literature, which may date later than the actual discovery or the corresponding patent.

The material science discoveries listed in this table made a profound impact on the development of both

*Table 1. Some examples of radical discoveries in electrochemical material science*

Date	Discovery
1960s	Using biological substances in electrochemical devices
1963	Pt-Ru electrodes for low-temperature methanol fuel cells
1966	RbAg <sub>4</sub> 5 solid electrolyte
1967	$\beta$ -NaAl <sub>11</sub> O <sub>17</sub> solid electrolyte
1968	RuO <sub>2</sub> -TiO <sub>2</sub> electrodes for chlorine electrolysis
1960s	Surface modified electrodes; Synergetic Alloys for HER
1971	TiO <sub>2</sub> electrodes for water electrolysis
1971/72	Ti <sub>1-x</sub> Ni <sub>x</sub> and LaNi <sub>5</sub> for metal hydride batteries
1972	Electrochemical insertion of Li into various solids
1973	Nafion membrane
1975	New ionic liquids (pyridinium
1976	Nasicon (Na <sub>1-x</sub> Zr <sub>2</sub> P <sub>3</sub> -zSi <sub>x</sub> O <sub>12</sub> )
1977	Doping of polyacetylene
1980s	Conducting polymers

fundamental and applied electrochemistry as a whole and simultaneously strengthened its ties with such science fields as solid state physics and chemistry, semiconductor physics, chemistry and mechanics of polymers, etc. The development of electrocatalysts for electrolyzers and fuel cells strengthened the links between electrochemistry and heterogeneous catalysis and surface science.

By comparing the dates listed in table with the dates of practical application of the corresponding materials in electrochemical devices and industrial technologies, we can see that time delays can often be very great. Thus, no less than 30 years have passed since the first demonstration of the activity of Pt–Ru catalysts [2,3] to their practical use. Moreover, the attempts to explain high activity of ruthenium-based catalysts on the quantum-chemical level were undertaken only recently [4].

Unfortunately, to date there are no books and study books which would exhaustively cover different aspects of electrochemical material science. One of the first monographs on the electrochemical material science [5] only deals with certain kinds of electrode materials used in applied electrochemistry and, moreover, in most part, is out of date. Comprehensive collections of reviews on various materials used in electrochemistry are available (e.g., [6,7]). Books devoted to certain kinds of materials for electrochemical devices are periodically published (e.g., [8]). Surveys devoted to advances in developing new materials for electrochemical devices appear in periodic publications, or special issues summarizing such developments are published. The number of journals devoted to material science constantly increases.

The first important step in the road to generalization of the developments of electrochemical material science should be classification of the materials for electrochemical systems.

## ELECTRODE MATERIALS

We begin with presentation of electrode materials and their simplest classification with respect to composition. Naturally, in this classification, the first place should be given to metals, metal alloys, and composite materials on their basis. Metals are used not only in the compact form but as thin films, in the dispersed or colloidal state (including metals deposited on various supports), and also in the form of compact powders. This brings about a whole spectrum of problems not only technological but also fundamental ones to be solved in future. The most general problems are those which consider how the metal-support interaction, defectiveness of metal particles, and their size (the so-called size-effect [9]) affect the electrochemical properties of materials. The elucidation of contributions made by intergrain boundaries and nonmetal phases formed in them can be assigned to

more specific aspects of these problems. The studies along these directions gained further impetus for the development since the 80s with elaboration of new probe techniques for surface characterization and synthetic methods for well characterized nanostructured materials [10].

Among multicomponent metal materials, synergistic alloys attract special attention, being both promising for practical applications and in connection of the development of general concepts on the synergism nature. At the same time, the number of objects of future studies should involve amorphous and nonequilibrium compositions including those obtained by ion implantation – the peculiarities of their electrochemical behavior still remain much unclear [11]. Finally, intermetallic compounds (IMC) with anomalously high sorption ability with respect to hydrogen and deuterium should be separated into a special group. Two series of such materials with  $AB_5$  and  $A'B_2$  compositions (where A is the rare-earth metal; B is Ni frequently substituted by other transition metals; A' is Ti, Zr; B' is Ni, V, Cr) have already found active practical use as the electrodes in nickel-metalhydride batteries [12,13]. However, the optimization of such materials with the aim of enhancing their degradation stability, capacity, and catalytic activity remains the most important practical problem the solution of which is closely associated with fundamental studies of the hydrogen dissolution mechanism and accompanying processes in the solid phase and on the surface. IMC can display unique electrochemical properties determined by the peculiarities of their electronic structure [14–16].

The second large group of electrode materials consists of semiconducting phases and compositions, including semiconductors of the II–VI and III–V types, refractory compounds (carbides, nitrides, borides, silicides), nonstoichiometric oxides and their analogs, and silicon-based materials [17,18]. Carbon-based electrodes, both highly dispersed and compact, exhibit great diversity of properties [19]; moreover, the number of nontrivial carbon materials increased substantially in the last years due to the appearance of new nanosize systems, viz., single- and multi-walled nanotubes [20] and synthetic materials based on doped diamonds [21,22]. Finally, mention should be made of a relatively new class of semiconducting electrode materials, namely, conducting polymers which can be divided into three large groups, viz., redox polymers, electron-conducting polymers, and ionomers [23]. Studying these materials gave rise to new theoretical concepts on the charge transport in terms of transfer of solitons, polarons, and bipolarons. Such phenomena as charge percolation, capture of electrons, redox switching, etc. were studied. The behavior of electrodes based on conducting polymers is governed by their molecular mass, orientation of chains, ionic doping, incorporation of catalytically active micro- and

nanoparticles with the formation of composites, and other factors. As applied to bulk-rechargeable materials based on transition metal complexes (prussian blue and its analogs), the term "inorganic polymers" is sometimes used, which is associated with numerous similarities in the processes of charge transport in these films and in organic conducting polymers. Crystalline rechargeable electrode materials based of salt-like organic substances are also known, among which tetrathiafulvalene derivatives are studied most thoroughly.

Microheterogeneous composites and ceramics including multiphase oxide materials, multicomponent (both crystalline and amorphous) alloys, metal-oxide compositions, etc. can be classified in the third class of electrode materials. These are the materials with strongly pronounced anisotropy of properties and the peculiar behavior of interphase boundaries. Their practically important properties are of the complex nature, and to reveal the latter on the microscopic level is still an extremely hard problem.

In the fourth class, the intercalation compounds the specific properties of which were studied in detail in the course of development of lithium cells should be placed [24-26]. Actually, they exhibit many similarities with hydrogen-sorbing intermetallic compounds, nonstoichiometric oxides and other substances the bulk composition of which can change reversibly during the electrochemical charging.

Finally, the fifth class comprises surface-modified electrodes [27]. The modification is achieved by underpotential deposition of metal layers [28,29], deposition of self-assembling two-dimensional organic and inorganic layers [30] and supramolecular groups [31], and also by chemical binding of different functional groups and molecules.

Even a brief survey makes us to conclude that the above classification should be improved. Moreover, this is not the only possible classification: the electrode materials may be classified from the standpoint of their practical application. In addition to formulating general requirements to materials such as conductivity (photoconductivity), stability (mechanical and chemical, the open-circuit corrosion resistance, resistance to anodic and cathodic polarization), availability and cost, adverse impact on the environment and human health, one must take into account the key characteristics concerned with the application sphere. Such a classification involves the following groups: materials for electrocatalysis, electrolysis, and electrosynthesis (including catalysts for chiral syntheses); for energy accumulation and conversion (chemical power sources, fuel cells, supercapacitors [32]); for electroanalysis, sensors, and electrochromic devices [33], for electronic and memory devices; and, finally, for fundamental electrochemical studies. The last-group materials should, first of all, have well-characterized structures, like, e. g., single crystal planes which proved to be most

fruitful for fundamental studies of electrochemical interfaces and electrocatalysis. In most publications on electrochemical material science, generalization is accomplished precisely with respect to practical application of one or other types of electrode materials.

## CONDENSED IONIC SYSTEMS

Summing up the development of electrochemistry in the past century, mention should be made of the impressive progress in the field of developing and studying condensed ionic systems. Among the latter, first of all, aprotic solutions of lithium salts which furnished the development of lithium batteries are most prominent [24,34-36]. Some systems can provide high conductivity in the temperature range from -40 to 80°C. Solvents (e.g., certain aliphatic sulfones) stable in an extremely wide potential range, with the "potential window" up to 6 V are put forward, as well as electrolytes for such solvents. Some amine solvents allow one to electrochemically generate solvated electrons in concentrations sufficient for carrying out syntheses with their participation.

The development of chemistry and electrochemistry of high-temperature superconductors [37] resulted in the development of mixed solvents which retain stability in the quasiliquid state up to very low temperatures (approaching the liquid nitrogen temperature).

Ultimately, the interest grows to the electrochemical behavior of supercritical liquids, not only supercritical CO<sub>2</sub> but also other ones [38]. One attractive feature of these systems is the very wide "stability window" (more than 9 V!); in a number of cases, its limits are beyond the thermodynamic stability range due to the high overvoltage of the processes which involve molecules of supercritical liquids. This opens up a wide field for totally new electrosyntheses, preparation of unique functional materials, and development of superpowerful current sources.

After the discovery of low-melting-point organic salts based on imidazolium and pyridinium derivatives [39], the salt melts are divided into high-temperature melts with melting points  $T_{mp} > 473$  K and low-temperature melts for which  $273 < T_{mp} < 473$  K [40]. The latter received the name nontraditional molten electrolytes, although they are sufficiently well studied and have already found practical applications. The examples are electroplating of metals (e.g., aluminum and its alloys) and the development of new supercapacitors. The typical low-temperature melts are AlCl<sub>3</sub>-EMIC (1-ethyl-3-methylimidazolium-chloride), AlCl<sub>3</sub>-BPC (1-butylpyridinium-chloride), corresponding binary melts containing ZnCl<sub>2</sub>, SnCl<sub>2</sub>, GaCl<sub>3</sub>, etc. In certain cases, anions (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and BF<sub>4</sub><sup>-</sup> can be substituted for chloride ion. Recently, a new ionic liquid EMIC 2.3 HF stable in moist air was described, which can have a

pronounced effect on the progress in the field of low-temperature melts technology. New salts based on 1-alkyl-2-methyl pyrrolinium with good conductivity and thermal stability were reported [41].

It is known that the studies of solid electrolytes have formed the basis for the development a number of important aspects of solid state physics and chemistry [42-44]. Owing to the discovery of solid electrolytes with superhigh conductivity at room temperature approaching the conductivity of aqueous electrolyte solutions, a new interdisciplinary field, viz., solid state electrochemistry was born. Solid electrolytes may be divided into four large groups.

First, these are crystalline solid electrolytes with a ionic flow along the lattice channels. The most typical and interesting representatives of this group are AgI, RbAg<sub>4</sub>I<sub>5</sub>, Rb<sub>4</sub>Cu<sub>16</sub>I<sub>7</sub>C<sub>113</sub>, hydrates of heteropolyacids with the Keggin structure. The charge transport in these solid electrolytes is accomplished by the transfer of Ag<sup>+</sup>, Cu<sub>2</sub><sup>+</sup>, Tl<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, F<sup>-</sup> ions.

The second group is comprises glass-like solid substances with unipolar conductivity with respect to Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ag<sup>+</sup> ions. The typical representatives are oxides, sulfides, molybdates, among which the 0.7Li<sub>2</sub>S 0.3P<sub>2</sub>S<sub>2</sub> electrolyte is the brightest example.

The third group is represented by solid polymeric electrolytes. These are polymers with covalently bound groups and mobile counter-ions, among which the -(CF<sub>2</sub>)<sub>m</sub>-CF-O-(CF<sub>2</sub>)<sub>k</sub>-SO<sub>3</sub>H polyacid is the best-known and widely applied. Lithium and sodium salts of polysubstituted sulfonates and polymer-salt complexes with polymer-coordinated cations (organic polyoxides, polyamines, polysulfides, polyacetates, etc.) deserve mention. The conductivity of the latter is largely determined by segmental motion of polymeric chains which solvate cations.

The final fourth group comprises solid electrolytes based on ZrO<sub>2</sub> doped by rare-earth oxides. The most famous of them is ZrO<sub>2</sub>Y<sub>2</sub>O<sub>3</sub>, although with respect to conductivity it ranks below ZrO<sub>2</sub>Sc<sub>2</sub>O<sub>3</sub> and, in the high-temperature range, certain other systems. In these systems, current is carried by O<sub>2</sub><sup>-</sup> ions, which allows designing effective fuel cells and a number of other devices.

## MEMBRANES

Now we turn to yet another main component of electrochemical devices, viz., membranes which perform various functions: electrolytes, atom-permeable or ion-selective barriers, matrix sorbents [45], and, in certain cases, can play the role of electrode materials. Membranes are of the decisive importance for designing electrolyzers, current sources, fuel cells, supercapacitors [32,46], the devices for electrodialysis, sewage treatment and recycling [47], sensors and electrochromic devices, etc. Perfluorated ion-exchange

membranes form a famous family of Nafion membranes which include the Nafion, Flemion, Dow, and Asahi Chemical materials. The general formula of this family is as follows:

These membranes exhibit a conductivity of an order of magnitude of tens  $\Omega^{-1}\text{cm}^{-1}$  and can operate for up to 6000 h without losing their characteristics. The studies on improving the characteristics of Nafion materials and refining the methods of their synthesis, for example, by using heteropolyacids and thiophene are in progress [48,49]. The studies on optimization of partially fluorated and perfluorated polymeric radiation-grafted membranes aimed at the increase in the stability of these materials and improvement of other characteristics, as well as the lowering of their cost are being developed. Composite membranes in which the functions of conduction and mechanical strength are either divided between the components or a certain new function is conferred by an introduced component are gaining in acceptance. Particularly, in the last years, the field of polymeric electrodes for sensoric applications was substantially extended, due to availability of new selective ionophores especially in connection with the development of supramolecular chemistry [50]. A most popular membrane for ion-selective electrodes consists of a plasticized matrix (usually, polyvinylchloride), lipophilic ion-exchange fragments, and a lipophilic covalently-sewed ionophor.

## ELECTROCHEMICAL SYNTHESSES OF NEW MATERIALS

The above examples show how actively electrochemistry absorbs the achievements of the modern material science for solving its own problems. At the same time, the contribution of electrochemistry itself to the development of this branch should be stressed. Mention should be made of electrochemical syntheses of materials and compounds of certain elements in unusual oxidation degrees, electrosynthesis of strong reducers, unique organic electrosyntheses, construction of solid films by using electrocrystallization processes (electrosynthesis of polymers, multicomponent and stoichiometric oxides, new semiconducting materials, polymetallic precursors, semiconducting single-crystals, intercalation and injections materials, etc.). The decisive role of electrochemistry in the development of a wonderful class of materials, viz. electron-conducting polymers (their controlled synthesis, studies of their properties, realization of the well-characterized charge-discharge state) should be stressed. The interest to these materials is high due to their potential applications in electrochemical energetics devices, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, sensorics, development of electrochromic displays, in microsystem technologies, electronic devices, microwave screening, and corrosion protection.

In view of the further developments and applications, the following directions of electrochemical nanotechnology are most promising [51–53]: synthesis of ultrathin layers on rectifying and other transition metals, layer-by-layer deposition of polymetallic compositions, local deposition and etching, lithographic technologies, deposition into natural matrices (template synthesis), preparation of clusters, synthesis of nanotubes, nanowires, and their analogs, electrochemical molecular design of surfaces, etc. Among the important interdisciplinary directions of this kind which are developed with the evident participation of electrochemistry, mention should be made of biomolecular electronics based on employing biological molecules and their models in microelectronic devices.

## CONCLUSION

What are the new electrode materials that can substantially change the wide-scale electrochemical technological process? Is it possible that electrochemists encouraged by the DSA discovery will try to radically change one of the most power consuming electrochemical industries, viz., the aluminum production. At present, this process employs carbon electrodes, and the process of aluminum production consists in its reduction from a cryolite–alumina melt as a result of carbon oxidation. In addition to a number of problems associated with the necessity to periodically change the anodes, the environmental problems, viz. exhausts of toxic products of the anodic oxidation in the cryolite–alumina melt, should be solved. It is quite a long time that electrochemists try to equip the aluminum production with dimensionally stable anodes which would maintain the oxygen evolution reaction. Except for the high stability at temperatures above 900°C, the anodes should exhibit the maximally low overvoltage with respect to oxygen evolution reaction [54]. One can easily understand how complicated this problem is. However, the potentials of electrochemistry in combination with other sciences are most powerful.

The prognoses of the advance and possible achievements in the field of refining materials for electrochemical devices, like any other predictions of new scientific discoveries are an extremely complicated and ungrateful task. As one classic said, "... it is always hard to predict, especially if this concerns future..."

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