Macedonian Journal of Chemistry and Chemical Engineering. Vol. **30,** No. 1, pp. 67–74 (2011)
MJCCA9 – 572
ISSN ISSN 1857–5552
Received: December 22, 2010
UDC: 544.6:502.17
Accepted: March 2, 2011

Education

ENVIRONMENTAL ELECTROCHEMISTRY – IMPORTANCE AND FIELDS OF APPLICATION*

Perica Paunović

Faculty of Technology and Metallurgy, University Ss. Cyril and Methodius, Republic of Macedonia, Skopje
pericap@tmf.ukim.edu.mk

The main goal of this paper is to present environmental electrochemistry as a very important field of environmental engineering which deals with protection and remediation of the Earth's resources. The existing Earth's environmental status as affected by a number of anthropogenic deteriorations is presented. Environmental electrochemistry has great potential to contribute to *i*) pollution detection, *ii*) remediation of polluted air, water and soils, *iii*) recycling of metals (saving of material resources) and alternative sources of energy (hydrogen economy).

Key words: environmental electrochemistry; electroremediation; pollution detection; alternative energy sources

ЕКОЛОШКА ЕЛЕКТРОХЕМИЈА – ВАЖНОСТ И ОБЛАСТИ НА ПРИМЕНА

Главна цел на трудот е да се прикаже еколошката електрохемија како многу важна област од подрачјето на инженерството на животната средина, која се занимава со заштита и ремедијација на ресурсите на Земјата. Прикажана е моменталната еколошка состојба на Земјата која е значително влошена како резултат на човековите активности. Еколошката електрохемија претставува инженерска дисциплина со голем потенцијал за нејзина примена во *i*) детектирање на загадувањата, *ii*) пречистување на загадениот воздух, водата и почвите, *iii*) рециклирање на металите (заштеда на материјалните ресурси) и *iv*) алтернативните извори на енергија (водородна економија).

Клучни зборови: еколошка електрохемија; електроремедијација; детектирање на згадувањето; алтернативни извори на енергија

1. PRESENT ENVIRONMENTAL STATE OF THE EARTH

To discuss about environmental electrochemistry and its significance on our lives, one should firstly provide a picture of today's environmental situation. In order to perceive and understand this situation, one should go back to the past to see historical movement of the environmental state. The Earth's biosphere and other ecosystems, as well as the cycle of the matter, have been self-sustainable and stationary during every geological or historical period of time. Since their appearance up to modern

* Dedicated to Professor Svetomir Hadži Jordanov on the occasion of his 70th birthday.

era, the human beings, fitted into the Earth's ecosystem consuming its material, food and indirectly energy resources. Human exploitation of metal has been known since long time ago, and even some historical periods of the human civilization are named after the utilized metals such asiron, copper or bronze era. Within this the longest time of the human civilization, around 4500 years, the human exploitation of the natural resources has been sustainable and there has been equilibrium of the matter in the Earth's ecosystem. The Earth compensates the consumed matter by easy decomposition of the matter disposed by humans as a waste material. Vernadsky [1], one of the most famous ecologists in the last century, denoted this period as "*homo sapiens*" era. Since the first industrial revolution up to the middle of the 20th century, as a result of scientific achievements, fast increase of the human population and tendency for having more comfortable life, considerable rise of material and energy resources consumption were initiated. This was accompanied by increased quantities of waste materials and pollution of the environment. In this stage of the Earth ecosystem development, the dominant driving force was not the nature, but the science with the human intellectual activities as a general planetary phenomenon. According to Vernadsky, this period is denoted as "*homo sapiens faber*" era, i.e. era of conscious working man. Further Earth's demographic explosion and consequently increased need for materials and energy, as well as the human aspiration for comforts such as light, warmth, long-distance travelling, variety of material goods, high-tech pleasures etc., caused non-controllable exploitation of material and energy resources and serious disturbance of the Earth equilibrium expressed by irreversible environmental pollution. This short period of the Earth history, since mid of the last century up to now, is denoted as "*homo desapiens faber*" (working man without mind) era by Goltsov [2].

The present picture of the Earth's environment is not so optimistic. The most crucial devastation of the Earth as result of the human activity is the "*greenhouse effect*". The temperature of the Earth is controlled by the balance between absorption and reflection of the solar radiation (infra-red region) [3,4]. The atmosphere constituents responsible for radiation absorption are mainly CO_2, water vapor and ozone. The net effect of the greater content of CO_2 in the atmosphere as a result of the human activities (industry, traffic etc.) is that more energy is retained near the surface of the Earth and the average temperature is therefore higher. Thus, the "greenhouse effect" is accompanied by the *global warming* and the climate change [5, 6]. In 1985, NASA satellite orbiting high above the Earth, detected a hole formed in the protective ozone layer over Antarctica [5]. The *ozone hole* was confirmed by several scientific teams taking measurements of the ice and of the sun's damaging ultraviolet rays. One of the consequences of the damaged ozone layer for human beings is cause of the skin cancer and its fast spreading. In the mid 20th century a new environmental phenomenon appeared – *photochemical smog*. A vital intermediate in the formation of smog is peracetyl nitrate coming from automotive NO_2 and unsaturated hydrocarbons. After series of reactions with photochemically produced NO, a suspension – smog is formed expressed as impairing visibility. Since 1980s, unusual phenomena have been observed such as pestilence of fishes in the lakes, destroyed forests, undermining the stability of the building materials etc. This kind of environmental plague is denoted as *acid rain*. Sulfur dioxide which turns into H_2SO_4 in the rain is a by-product of burning of coal for electricity or in metallurgy. The explosive industrial development and material and energy consumption caused enormous production of *household* and *industrial waste*, containing hazardous and non-degradable components. Disposal of this waste means occupation of the land. The Earth can not decompose it and consequently Earth's equilibrium is disturbed. On the other hand, disposal of hazardous toxic waste is potential danger for the soil and if not properly done may result in *groundwater contamination*. Further, this implies *contamination of food*. Also, contamination of food can be caused by using pesticides and fertilizers.

The other side of the environmental picture is *exhaustion of the material and energy resources*. It was estimated that the mineral reserves of some metal such as Sn, Pb, Zn, W, Cu, Mn, Mo and Ni, will be exhausted during this century, if they are exploited without recycling [7]. The situation with fossil fuels reserves is similar. The exponential growth of the population and industry implied exponential growth of the fossil fuels consumption and consequently, their exhaustion. But, the global pollution as result of the fossil fuels exploitation and their exhaustion are not unique problems. The motive of the most of modern wars is energy, i.e. fossil fuels. These wars are accompanied by chemical, biological or radioactive weapons that cause additional pollution and massive destruction of people and environment in certain parts of the Earth.

So, the last few decades, the mankind is facing to solve the serious environmental and energy problems. The modern science and legislation are oriented towards promotion of cleaner technologies, frugal exploitation of the materials and energy, consuming and using "clean products", safety manipulation with hazardous material etc. As a result of these efforts, a new scientific and engineering area was opened – *environmental engineering*. This is an interdisciplinary area, where electrochemistry found its place and has great potential to contribute in creation of an improved environmental picture on the Earth.

2. ENVIRONMENTAL ELECTROCHEMISTRY

The part of electrochemistry that deals with environmental issues is named *environmental electrochemistry*. Within this work, several fields of application of electrochemistry in solving environmental nuisances will be presented.

Electrochemical processes depend on concentration (pressure) and temperature, the same as the corresponding chemical ones. However, the system where they take place – aqueous medium (electrolyte where two electrodes are immersed) enables the processes to occur at low temperatures and all products (desirables and undesirables) do not leave the system. This is suitable for:

− ***detection of the pollution*** in solid, liquid, gas and bio media (***electrochemical sensors***).

− **remediation** of wastewaters, gases and soils,

− ***metal recycling***, i.e. selective electrodeposition of metals from metal scraps,

− ***alternative sources of energy***, i.e. electrochemical production of hydrogen using renewable energy sources (wind, waves, geothermal etc.) as well as direct conversion of the energy of electrochemical reactions to electricity in fuel cells.

The electrochemical processes offer various distinctive advantages [8] over the corresponding chemical technologies [6]:

− *Environmental compatibility*. The only reagents are the electrons, i.e. direct current and there is no need for addition other chemicals.

− *Versatility*. Various organic, inorganic or biochemical pollutant can be treated, no matter of their aggregate state or charge. The products of the electrolysis often can be useful. There is variety of reactors (electrochemical cells), as well as shapes and materials of the embedded electrodes. Also, the same reactor can be used for different processes. The volume of the treated matter can vary from microliters to millions of liters.

− *Energy efficiency*. Electrochemical processes occur at considerably lower temperature and pressure related to the corresponding non-electrochemical counterparts (e.g., incineration, supercritical oxidation). Electrochemical cells and electrodes can be designed and the parameters can be controlled to minimize power losses.

− *Safety*. Electrochemical processes occur in the mild conditions usually supported by small quantity of added chemicals with innocuous nature.

− *Selectivity*. Electrolysis occurs at strictly defined potential at which specific species reduce or oxidize.

− *Amenability to automation*. Electrolysis parameters and cell design are suited for process automation and control.

− *Cost effectiveness*. The simple equipment, process operation and control as well as possibility for energy efficiency make these processes cost effective.

In the following text, the above fields of environmental electrochemistry application will be described.

3. POLLUTION DETECTION

Development of chemical sensors for environmental monitoring is currently one of the most active areas of the analytical chemistry. Chemical sensors consist of a transduction element covered with chemical or biological recognition layer. Electrochemical sensors are an important subclass of chemical sensors in which an electrode is used as the transduction element. Generally, electrochemical sensors are mini-electrochemical membrane cells mostly using solid electrolyte. According to the used electrochemical method, electrochemical sensor can be categorized as *i*) potentiometric, *ii*) amperometric, *iii*) voltametric and *iv*) conductometric.

Electrochemical detectors are often part of the combined analytical techniques such as ion chromatography or capillary electrophoresis. Electrochemical detection of environment pollutant has advantages over the other techniques. So, trace quantity of phenylurea herbicides in water can be detected by using electrochemical sensors in the HPLC (high-performance liquid chromatography) technique. Compared with UV absorbance and fluorescence methods, this technique offers advantage of higher selectivity, higher sensitivity and 10 fold improvement in detection limit. Due to their portable nature, electrochemical sensors are suitable for ambiance measurements and monitoring. The most important advantage is cost effectiveness.

4. ELECTROREMEDIATION

Electroremediation means cleaning gases, wastewaters and soils by electrolysis. These media can be polluted by heavy metals from electrowining, electrorefining, galvanizing plants or photolaboratories or organic pollutants from organic chemical industry. The principal of electrolysis in all media is the same. For gas treatment, firstly they have to be solved in the aqueous solution by absorption. Electrolysis can be direct or indirect as shown in Figure 1. During *direct electrolysis* (Figure 1a) ions of the pollutants (P) exchange electrons with the electrode and transform itself to non-polluted products (NP). In the case of the *indirect electrolysis*, the electrode exchanges electron with reagent – mediator (M) and the obtained product reacts with the pollutant forming final non-polluted product (NP). The mediator can originate by the electrolyte or by the electrode or to be added to the system from outside. If the mediator remains chemically non-changed in the electrolyte, after removing of the final products *reversible indirect electrolysis* has occurred (Figure 1b). But if the mediator forms compounds with the pollutant and leaves the electrolyte, *irreversible indirect electrolysis* has occurred (Figure 1c).

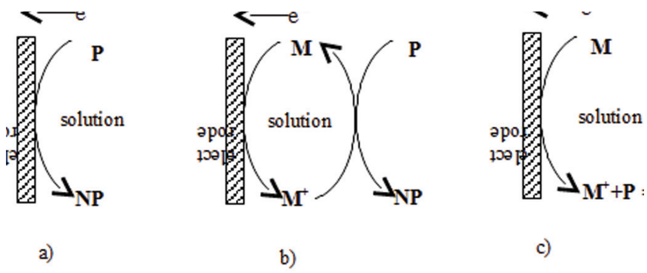

Fig. 1. Electrode reaction during electroremediation: a) direct, b) indirect reversible and c) indirect irreversible electrolysis. P = Pollutant; NP = Non-polluted product; M = mediator

The pollutants during direct electrolysis can be neutralized by *anodic oxidation or cathodic reduction*. By anodic oxidation, mainly organic pollutants can be removed, such as phenols, aromatic amines, halogenated and nitro derivates, waste biomass, carboxylic acid ions, formaldehyde, alcohols, cyclohexane, tributylphosphate etc. Inorganic pollutants which can be treated by this way are cyanide and thiocyanate. Cathodic reduction is a suitable way to clean out chlorinated organic compounds, polychlorinated biphenyls, chlorobenzoic acids, chlorophenols and inorganic pollutants such as oxynitrogen ions, oxychloride species and heavy metals ions.

Indirect electrolysis uses redox couples as mediators – reagents that react with electrodes and further with the pollutants. The most used redox couples are Ag^{+}/Ag^{2+} (for removing ethylene glycol, isopropanol, acetone, organic acids, benzene and tributyl phosphate/kerosene), Fe^{2+}/Fe^{3+} (for treating cellulosic materials, fats, meat packing wastes, ethylene glycol as surrogate waste, sewage sludge etc.), Co^{2+}/Co^{3+} (for destroying chlorinated, e.g. 1,3-dichloro-2-propanol and non-chlorinated organics, e.g. ethylene glycol and organic radioactive waste). In the case of gases treatment, beside the mentioned metal redox couples, the following ones can be used: Br_2/Br^-, $Cr_2O_7^{2-}/Cr_3^{+}$, VO_2^{+}/VO^{2+}, MnO_4^{-}/MnO_2 etc.

There are variety of electrolysis cells intended for treatment of both wastewaters and gases. Depending on the pollutants, the used electrodes can be rotate-cylindrical, static tri-dimensional, porous, screen-electrodes etc., prepared by variety of materials such as Pt, Ti, Ni, steel, metal alloys, glassy carbon, graphite, dimensional stable electrodes (DSA, Ti/TiO_2+RuO_2, Ti/TiO_2) etc. Anodic and cathodic area can be separated by membranes such as bipolar, ion or proton exchange membranes or solid state electrolytes.

Soil electroremediation performs in situ, i.e. electrodes pound into the ground within the contaminated area. The electrolyte is the solution of heavy metals (pollutants) into the soil moisture. In the case of dry soils, the area between electrodes has to be moistened. Positive metal ions go to the cathode where they are reduced, while ions (SO_4^{2-}, Cl^-, PO_4^{3-}, NO^{3-}, F^-, CN^- etc.) go to anode. Ion transport in the soil carries out by diffusion, electroosmosis, electrophoresis and ion migration. The main advantage over the other remediation procedures is that there is no need for channelling or destroying polluted soil area. Metals deposited on the cathode can be recovered in the useful form, so the electroremediation offers metal recycling.

5. METAL RECYCLING

Recycling of materials is the main principle of the environmental engineering or more accurately, of the narrower sub-discipline-waste management. The alarming situation with mineral resources was mentioned in the Section 1. Secondary metal production (metal recycling) from discarded products or production scrap has become a practice for the last few decades in order to save metal resources. Besides saving resources, recycling also offers considerable energy saving. For instance, energy benefits for secondary metal production are: 94 % for secondary Al, 75 % for secondary Cu, 70 % for secondary Pb, 40 % for secondary steel and 10 % for secondary Zn [9].

The principle of recycling is very simple. Each material should be treated in a way similar to that by which Nature treats water. The water is used, rejected into rivers, lakes and oceans, whence it re-evaporates forming clouds which rain down again as fresh water. Metals are not volatile, so we can recover them, not by distillation process, but by some other separation method. Electrolysis in aqueous electrolytes (electrochemical method) is the most suitable method for separation of different metals from metal scraps. The principle of metal separation is the following: different metals begin to dissolve on the anode and consequently to deposit on the cathode according to the value of the standard electrode potential in the electrochemical series.

For example, during recycling of the car body scraps, first operation is colour removing by burning. Further, the scraps should be shortened and treated by dissolving (the case of electrolysis in electrowining conditions) or formed as anodes (the case of electrolysis in electro refining conditions) [10, 11]. By further selective electrolysis almost all metal components of the scraps can be recovered.

6. ALTERNATIVE SOURCES OF ENERGY

The most of the world scientific community considers hydrogen as the fuel of the future, after fossil fuel era. Electrochemical production of hydrogen using renewable sources of energy (solar, wind, water, gravity etc.) and its transformation to electricity are the most promising substitution for fossil fuels which will be exhausted soon. When and how hydrogen energy technologies will be commercialized and will become a main energy system is beyond of the scope of this paper.

The energy system in which hydrogen plays the main role is known as "hydrogen economy". The concept hydrogen economy is a closed loop of hydrogen production, transportation to energy centers or to electricity conversion sites and conversion in electricity by fuel cells (see Figure 2).

The term "hydrogen economy" was coined by J. O'M. Bockris in the early seventies of the last century [12]. The main goal of hydrogen economy development is establishment of global energy system in which hydrogen will be produced from available renewable energy sources and converted to electricity by fuel cells and further to be applied instead of fossil fuels in transportation, residential, industrial and other sectors. In the last few decades, the growth of the hydrogen economy system affected high development of many scientific fields and mobilized great part of the world scientific community. Hydrogen economy is an interdisciplinary field in which the leading role has the electrochemistry (investigation of hydrogen/oxygen evolution reaction in different media, hydrogen storage), and then material science (production of advanced electrode materials for hydrogen evolution/oxidation or oxygen evolution/reduction), polymer science (development of polymer membranes as solid electrolytes for hydrogen electrolysers/fuel cells), mechanical engineering (design of appropriate hydrogen electrolysers/fuel cells) etc. [13]. Recently, the global most attractive scientific area is nanomaterials and nanotechnologies. Many of these research activities are focused on hydrogen economy (development of nanotechnologies for producing nano-scaled electrode materials for hydrogen evolution/oxidation, using carbon nanotubes as support material, etc.) [14–17].

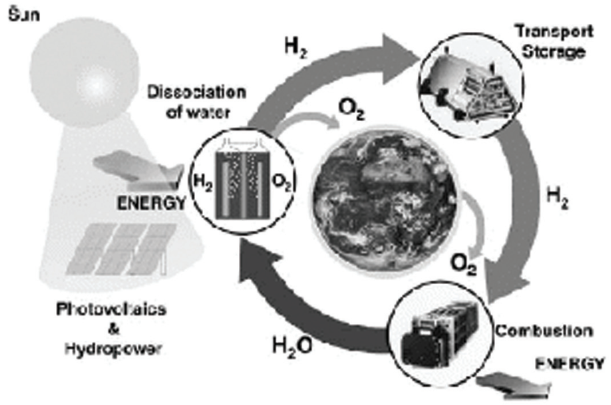

Fig. 2. The loop of the "hydrogen economy"

Hydrogen is not only a fuel, but also an energy carrier of the future that could provide painless transition from fossil fuels to "hydrogen era". As a fuel, hydrogen has many advantages compared to fossil fuels, as:

− clean fuel with high caloric value (100 % H_2),

− closed loop fuel vs. product: H_2O is source for production and also product of combustion,

− production from/to electricity with high efficiency (50÷60 %),

− conversion to energy by different ways (combustion, electrochemical conversion, hydriding),

− Storage and transport possible in all aggregate states (gas, liquid and metal/chemical hydrides),

− Environmental friendly (see Figure 3).

In Figure 3, the cycling of matter in hydrogen production/conversion is shown. The source of hydrogen production is water, while water is a product of hydrogen conversion to electricity or combustion. The oxygen from the atmosphere disbursed in fuel cells is released from the hydrogen electrolyser and goes back to the atmosphere. This means that hydrogen has a renewable nature as a fuel. On the other hand, this renewable nature makes hydrogen environmental friendly fuel.

Energetic (environmental) revolution?

Let's go back to the history to retrospect technological revolutions (Figure 4). Any technological revolution causes remarkable change of lifestyle followed by new materials, products and services providing new life comfort quality. On the other hand, every technological revolution is connected to a certain source of energy, i.e. certain kind of fossil fuel. Beginning of the industrial revolution (steam machine appearance), on the other side, meant beginning of mass consumption of coal as a convenient energy source. Further, electricity revolution is based on usage of coal which appears as a main energy source, too. Appearance of oil causes automotive revolution. This revolution causes oil to be the main energy source. Correlation between information revolution and natural gas is not cause-consequently based, but it is only temporal. And finally we are coming to the point that was discussed in the introductory note, i.e. exhaustion of fossil fuels and harmful consequences of their long-term exploitation. Thus, the mankind is faced with an energy crisis and all efforts are focused on invention of a new sustainable energy sources. Intensive research and pilot projects last few decades foreshadow new energy revolution.

Therefore, hydrogen economy including economic electrochemical production of hydrogen using renewable sources of energy (solar, wind, hydro-potential, gravity etc.), transportation to hydrogen stations, to consumers or to fuel cell stations for further conversion of electricity, invention of new cheaper but efficient electrode material for hydrogen evolution/oxidation, new hydrogen electrolysers/fuel cells etc., is in the focus of the energy revolution.

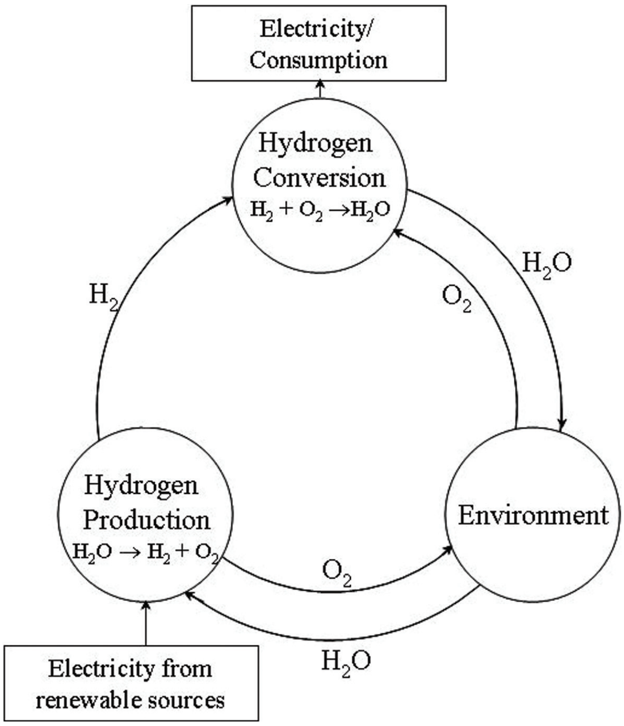

Fig. 3. Circulation of the matter in the "hydrogen economy" loop

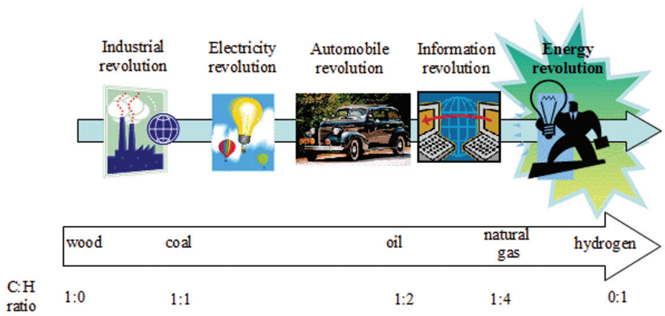

Fig. 4. History of technological revolutions and fossil fuels

REFERENCES

[1] V. I. Vernadsky, Biosphere and Noosphere, *American Scientist*, **33** (1945), 1–12.

[2] V. A. Goltsov, Vernadsky's Creative Heritage and the Present, *International Scientific Conference, Proceedings,* Donetsk, Ukraine, (2001).

[3] J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry 2B*, Kluwer Academic Publishers, 2004,1989–2043.

[4] J.A. Salmond, A. G. Clarke and A. S. Tomlin, The Atmosphere, in R. M. Harrison (Ed.), *The Royal Society of Chemistry* 2006, 8–76.

[5] J. O'M. Bockris and T. N. Veziroglu with Debbi Smith, *Solar Hydrogen Energy – The Power to Save the Earth,* McDonald Optima, 1991, 43–49.

[6] S. E. Manahan, Environmental Chemistry, CRC Press LLC, 2000.

[7] D. Janke and L. Savov, Circulation of materials, *Erstes Freiberger Europa Seminar: Resources for Tomorrow – Material Recycling,* TU Bergakademie, December, 1997, 1–12.

[8] K. Rajeshwar and J. Ibanez, *Environmental electrochemistry*, Academic Press, Inc., 1997.

[9] R. van Berkel, Eco-efficiency in primary metals production: Context, perspectives and methods, *Resources, Conservation and Recycling*, **51** (2007), 551–540.

[10] J. O'M. Bockris, N. Bonciocat and F. Gutmann, *An Introduction to Electrochemical Science*, Wykeham Publications, London, 1974.

[11] С. Хаџи Јорданов, П. Пауновиќ, *Електролиза – теорија и технологија*, Технолошко-металуршки факултет, Скопје, 2008.

[12] J. O'M Bockris, A Hydrogen economy, *Science*, **176** (1972), 1323.

[13] P. Paunović in J. P. Reithmaier et al. (eds.)*, Nanostructured Materials for Advanced Technological Applications,* Springer Science + Business Media B.V., 2009, 391–398.

[14] S. G. Neophytides, S. H. Zaferiatos and M. M. Jakšić, Novel Trends in Electrocatalysis: Extended Hypo-Hyper-d-Interionic Bonding Theory and Selective Interactive Grafting of Composite Bifunctional Electrocatalysts for Simultaneous Anodic Hydrogen and CO Oxidation, *Chem. Ind*., **57** (2003), 368–392.

[15] E. Slavcheva, I. Radev, G. Topalov, E. Budevski, Sputtered electrocatalysts for PEM electrochemical energy converters, *Electrochimica Acta*, **53** (2007), 362–368.

[16] P. Paunović, O. Popovski and I. Radev, Investigation of cell assemblies prepared out of electrocatalysts aimed for hydrogen evolution, *Bull. Chem Technol. Macedonia*, **24** (2005), 133–141.

[17] Perica Paunović, Ivan Radev, Aleksandar T. Dimitrov, Orce Popovski, Elefteria Lefterova, Evelina Slavcheva, and Svetomir Hadži Jordanov, New nano-structured and interactive supported composite electrocatalysts for hydrogen evolution with partially replaced platinum loading, *International Journal of Hydrogen Energy*, **34** (2009), 2866–2873.