

## TOWARD SUSTAINABLE HYDROGEN ECONOMY: ELECTRODE MATERIALS – NON-PLATINUM ELECTROCATALYTIC SYSTEMS

P. Paunović

“Sts Cyril and Methodius” University,  
Faculty of Technology and Metallurgy,  
P.O. Box 580, MK-1001 Skopje,  
Republic of Macedonia  
E-mail: pericap@tmf.ukim.edu.mk

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### ABSTRACT

*The role and importance of hydrogen economy is given within the energetic and environmental problems facing mankind. Electrocatalytic activity of metals is quoted as well as physical and chemical pathways to improve performances of electrode materials. Some characteristics of advanced nano-structured hypo-hyper d-electrocatalysts deposited on multiwalled carbon nanotubes (MWCNTs) are shown. Non-platinum electrocatalysts approach the activity of conventional Pt/Vulcan XC-72 catalyst, while catalyst containing only 20 % Pt in metallic phase exceeds it so far.*

*Keywords: energy crisis, hydrogen economy, hypo-hyper d-electrocatalysts, nano-structured materials, multiwalled carbon nanotubes MWCNTs.*

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### INTRODUCTION

#### IS MANKIND FACING THE POST-FUELER ERA?

Fossil fuels were and still are the most convenient and available energy sources. But the unclosed loop of their exploitation, i.e. extraction, transportation, processing and use, makes them environmentally unfriendly and unsustainable source of energy. The products of fossil fuels combustion, CO<sub>2</sub> and CO, do not revert to the source, but instead go into the atmosphere, accompanied with other gases and cause serious pollution. Unsaturated hydrocarbons cause smog, respiration diseases and cancer. CO and NO<sub>x</sub> combine with hemoglobin in the blood causing fainting or even death. This pollution is worldwide known as “green-house effect” and its impact on environment and humanity is well known [1]. On the other side, the non-renewable nature and enormous consumption rate of fossil fuels contribute to their soon total exhaust. So, our civilization will be facing serious energy crisis in near future. This situation is consequence of the Earth’s demographic explosion that implies rise of energy need and its exploita-

tion. The rise of human needs and comfort as light, warmth, long-distance travelling, many kinds of material goods, high-tech pleasures, etc., contributes to higher energy consumption. The final price of present life-quality including many material and technological goods and pleasures is global environmental disturbance with long-term consequences as well as total exhausting of the most convenient source of energy fossil fuels.

As it can be seen from Fig. 1, the trend of rising curves of both world population and energy consumption over period of 5000 years is almost the same which means energy consumption is directly caused by number of human population [2, 3]. First billion of the human population was reached at the beginning of 19<sup>th</sup> Century after even 4600 years. Normally, the needs and consumption of energy in this period are minimal. For next billion only 100 year were enough. In next 100 years (19<sup>th</sup> century) humanity reached second billion, while next century was characterized with demographic explosion and reaching even 6 billion human beings on the Earth. Normally, this period was followed with enormous technological development that needed large quantity of energy.

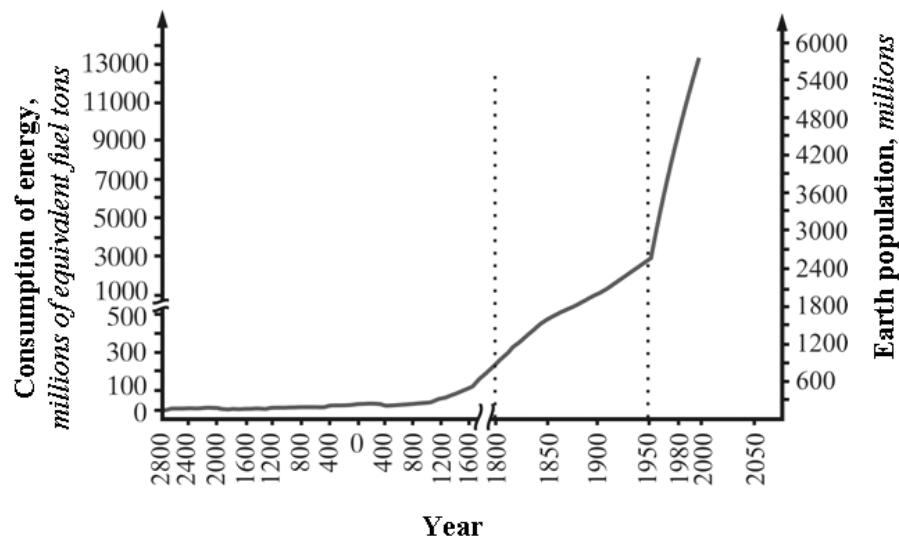


Fig. 1. The rise of the Earth's population and energy consumption.

The famous environmentalist V. Vernadsky [4], being worried about increased amount of both  $\text{CO}_2$  in the atmosphere and geological waste on the Earth, denoted the period from the first industrial revolution to the fifties of the last century as “homo sapiens faber era” (Fig. 1), within human beings behave not like homo sapiens but homo sapiens faber - working man who does not care much about environment. But, the next period of the humanity up to present was characterized with further rise of natural resources consumption as well as pollution and waste production. In the previous context, V. Goltzov [5] denoted this period as “homo desapiens faber era” (working man without mind).

As a result of such a situation, the modern science is facing a challenge to find out alternative source of energy which can satisfy the global energy needs, but also to be environmentally friendly. The question that imposes is: **what fuel will be the main energy source in the future?** The answer can be found by analysis of the fossil fuels history, with respect to the hydrogen to carbon ratio (HCR). Rise of hydrogen contribution in fuels is obvious: starting with wood that is low in carbon content, coal with HCR near 50:50, oil or gasoline with 67:33 and finally natural gas with HCR of 75:25. So, further extrapolation reveals that pure **hydrogen is a logical alternative**. In this context, in the last few decades, the hydrogen economy as system of hydrogen production/conversion to energy has shown as very perspective.

## 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 (Fig. 2).

The term “hydrogen economy” was coined by J. O'M. Bockris in the early seventies of the last century [6]. This idea was supported worldwide by leaders of scientific community such as D. Gregory [7], T. N. Veziroglu [8], C. Marchetti [9] and others. The main goal of hydrogen economy development is establish-

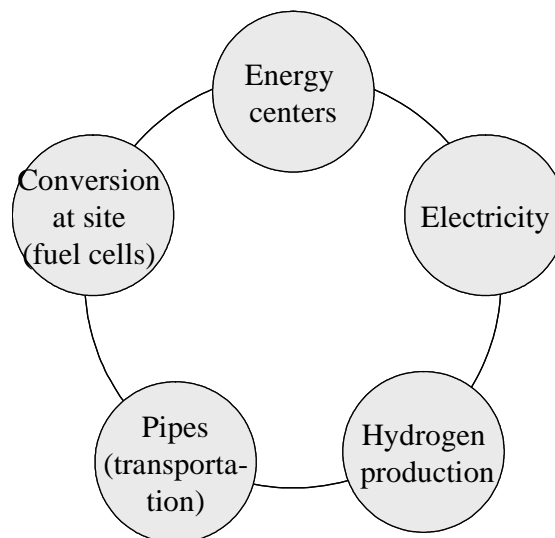


Fig. 2. The loop of the “hydrogen economy”.

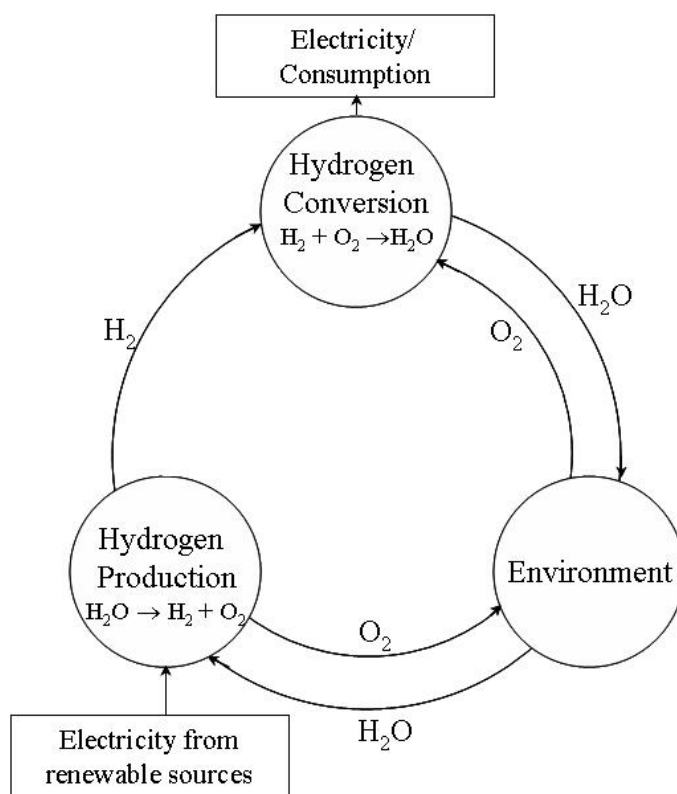


Fig. 3. Circulation of the matter in the “hydrogen economy” loop.

ment of global energy system in which hydrogen will be produced from available renewable energy sources and converted to electricity by fuel cells and further 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 a part of electrochemistry research or narrower electrocatalysis [10, 11] (investigation of hydrogen evolution reaction/oxidation in different media), material science (producing advanced electrode materials for hydrogen evolution/oxidation reaction), polymer science [12, 13] (development of polymer membranes as solid electrolytes for hydrogen electrolysers/fuel cells), mechanical engineering [14] (design of appropriate hydrogen electrolysers/fuel cells) etc. Recently, the global most attractive scientific area is nanomaterials and nanotechnologies. Many of these research activities are concerned on hydrogen economy (development of nanotechnologies for producing nano-scaled electrode materials for hydrogen evolution/oxidation, using carbon nanotubes as support material, etc.) [15-18].

Hydrogen is not only fuel, but 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 into 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 Fig. 3).

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

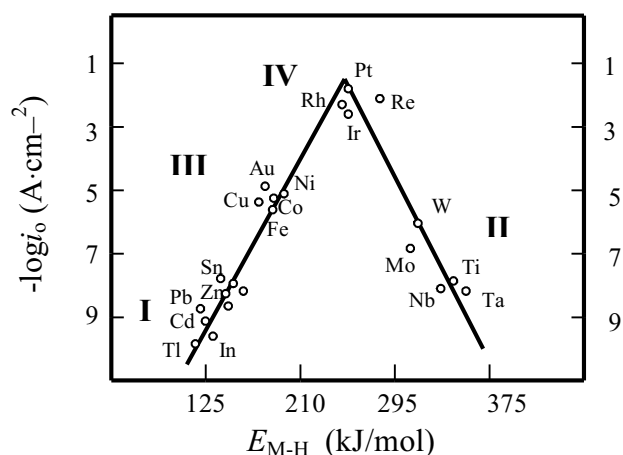


Fig. 4. Changing of the electrocatalytic activity in the plot of logarithm exchange current density ( $\log i_0$ ) for hydrogen evolution vs. strength of formed metal-hydrogen bond.

### ELECTROCATALYTIC ACTIVITY OF ELECTRODE MATERIALS

One of the most important part of “hydrogen economy” loop are electrochemical hydrogen generation and conversion to energy. So, electrode material on which hydrogen evolution/oxidation occurs is very important, because it can reduce the cost of hydrogen production or increase the efficiency of conversion to electricity. The higher the catalytic activity of the electrode material the lower the overpotential, the lower

energy consumption and finally the more cost-effective hydrogen production/conversion.

Numerous investigations on hydrogen evolution reaction (HER) mechanism [19-21] (type of reaction, the rate-determining step and especially reaction rate), have pointed out that electrode material is not only an inactive substrate but plays active and significant role in the reaction. Differences in the reaction rate values ( $i_0$ ) over wide range of magnitude (even  $10^{10}$  times for Pt versus Hg) imply that the electrode material behaves as a catalyst for hydrogen evolution/oxidation. This heterogeneous catalytic process includes adsorption phenomena and formation of intermediars between reacting species and substrate atoms/ions. Thus, the adsorptive characteristics of electrode materials are of great importance for their electrocatalytic behavior. According to P. Sabatier’s principle [22], electrode material shows optimal electrocatalytic activity when the strength of the adsorption electrode to H-atom has an intermediate value. The higher strength implies high activation energy for further electrochemical transformation and desorption, and is not favorable for the purpose. The weaker bond leads to premature desorption of the intermediar from the electrode surface, so no electrochemical transformation occurs.

This Sabatier’s intuitive assumption has been confirmed by further numerous studies. The results have

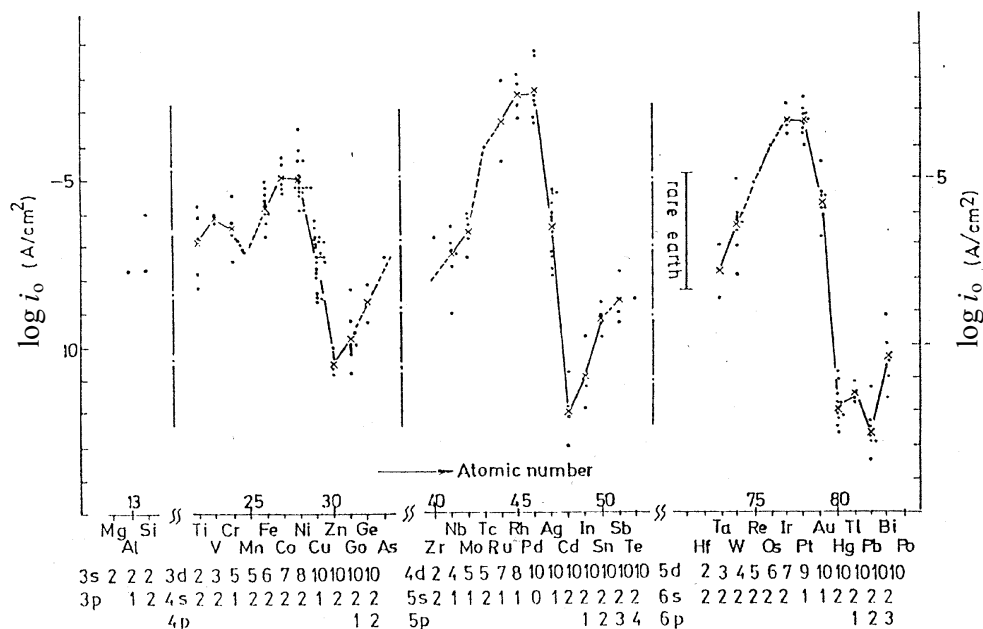


Fig. 5. Dependence of exchange current density ( $\log i_0$ ) for hydrogen evolution along the transition series of the Periodic Table.

been summarized into Volcano shaped plot of the exchange current density ( $\log i_0$ ) versus the bonding adsorption strength ( $DE_{M-H}$ ) of transition metals, given by S. Trasatti [23] (Fig. 4).

Four groups of metals could be distinguished in Fig. 4, whereat I and II being Sabatier's extremes in very strong (II) and very weak (I) hydrogen adsorption, showing respectively low electrocatalytic activity ( $\log i_0$ ). The group IV (platinum group of metals) shows optimal values of  $DH_{M-H}$  for the higher electrocatalytic activity.

The electrocatalytic activity for HER, as a function of the atomic number of elements of each transition series, is shown in Fig. 5. This plot is result of H. Kita's comprehensive analysis of a number of results by different authors for all transition metals [11, 19]. Generally, the catalytic activity increases with atomic number, achieves maximum with the VIII group of metals and sharply decreases to a minimum values at IIB group of metals. The platinum group of metals (Ni, Pd and Pt) has the highest electrocatalytic activity. Kita [19] pointed out that electrocatalytic activity depends neither on the type or composition of the electrolyte, nor on the electrode surface treatment, nor on the state of aggregation (solid or liquid). The crucial factor determining electrocatalytic activity is the bulk property of the metal or more exactly, electronic configuration. The optimal electronic configuration for this request has the platinum group of metals with average  $d^8$ -configuration. This configuration has at least two vacant unpaired  $d$ -electronic sites of the same catalyst atom for further hydrogen atoms recombination in  $H_2$  molecule.

As shown above, the best individual catalysts for HER are Pt, Pd and Ni. But is this the maximum that could be achieved in electrocatalysis for HER? The performances of pure bulk metals are not enough for cost-effective hydrogen evolution/oxidation. Is it possible to enhance the electrocatalytic properties of individual metals? How to achieve that?

#### ENHANCING ELECTROCATALYTIC ACTIVITY OF PURE METALS

The answer of the question above is confirmative. There are two basic approaches in improving the electrocatalytic activity of pure bulk metals. The first

one is based on increase of the real surface area of electrode material (physical approach) where the rise of the catalytic activity is result of the so called "size-effect". The second one alludes increase of intrinsic activity through alloying of metals (chemical approach) and corresponding effect is called "intrinsic effect".

#### Physical approach

In this context, the question that arises is how to increase electrode activity, i.e. hydrogen electrolyser/fuel cell efficiency having the same quantity of some metal, e.g. platinum. The unique path to solve this problem was increasing real surface area of the electrode vs. its geometric surface (roughness factor,  $S_R/S_G$ ), or vs. its mass (specific surface area,  $m^2 g^{-1}$ ). So, involving porous medium as electrode provides considerable increase ( $10^3$ - $10^4$  times) of limiting current density  $i_L$  and consequently power density. Improving of these parameters makes the fuel cells practically useful. This idea is not so recent. It dates from the "cradle days" of classical electrochemistry. Even before first theoretical consideration and suggestion for practical application of A. Westphal in 1880 [24], Plante has used porous electrodes in lead batteries in 1849 [25]. But, more than 1 century porous electrodes were not seriously practically applied, so the classical electrochemistry achieved its technical progress on use of planar (bulk) electrodes.

For a long time, the porous medium was considered as unpromising due to fundamental nature of pores – numerous pores per  $cm^2$  are long and resistive, that promotes significant IR drop. Instead of this fact, the real resistance is not so high and considerable current densities can be achieved. The logical explanation of this paradoxal statement was given by C. Wagner [26]. Within each pore there is a meniscal meeting place for solid, liquid and gas phase (three phase boundary). The size of this meniscus varies from molecular diameter of water to diameter of capillary tube. Thus, the length which contributes to resistance is not of whole pore, but multiple shorter (maximum pore diameter), so the whole resistance is considerably lower than the expected one.

In a porous electrodes diffusion layer thickness is  $10^{-7}$ - $10^{-4}$  cm instead  $10^{-2}$  cm of planar electrode. Thus, the local limiting current density in three-phase boundary region will be  $10^3$  to  $10^4$  times higher than that on planar electrode.

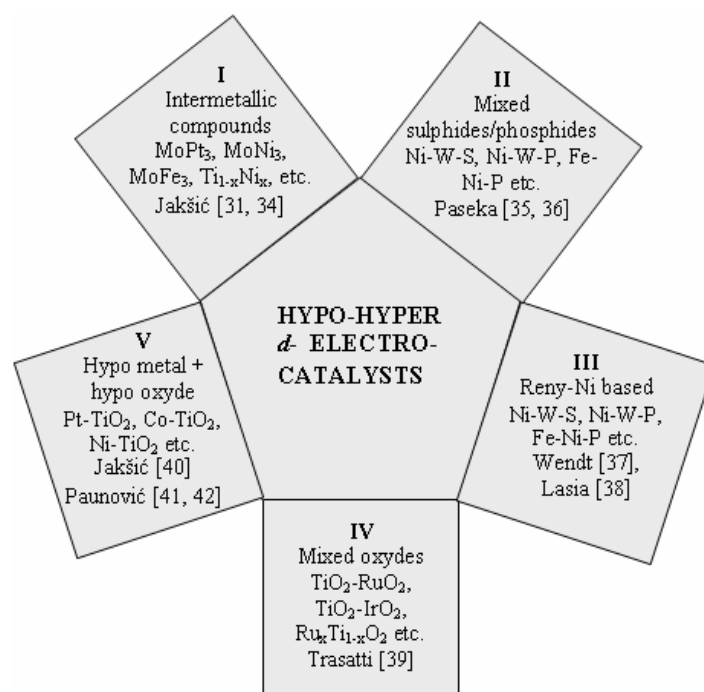


Fig. 6. The main groups of hypo-hyper *d*-electrocatalysts.

Involving porous electrodes for successful and economical work of fuel cells represents a beginning of new era in electrochemistry - **modern electrochemistry**.

Increase of the real surface area of the porous electrode can be achieved by reducing the grain size of the electrocatalytic material. So, maximal surface area can be reached by using nano-structured electrocatalysts. So, nanotechnologies are priceless tools of modern electrocatalysis. There are many methods for producing nano-scaled catalytic materials [27]. They are distinguished in two main groups: bottom-up and top-down. Bottom-up approach alludes obtaining nanostructures during production of the materials, as sol-gel method, boron-hydride reduction, electrodeposition, vapor-phase deposition, magnetron sputtering, vacuum-arc deposition, etc. Top-down techniques alludes further mechanical reduction of particle size of already produced micro-scaled material, e.g., milling, machining, mechanical alloying, etc.

In classical aqueous fuel cells/hydrogen electrolyzers, the porous electrodes are meeting place of three phases: solid (electrode), liquid (electrolyte) and gas (product/reactant). To obtain an effective electrode by porous catalytic material, one has to provide: *i*) mechanical stability, *ii*) hydrophobicity of pores and *iii*) high electric conductivity. The first two can be provided by in-

volving Teflon (PTFE, polytetrafluoroethene), while the last one by using material with both high conductive and high developed surface area, usually carbon blacks (Vulcan XC-72, Acetylene Black, etc.). These electrodes are known as gas-diffusion electrodes (GDEs). GDEs have several functions: *i*) as a catalyst support, *ii*) ensure high-developed three phase boundary where the electron exchange reaction takes place and *iii*) separates the liquid reactants from the gaseous products (hydrogen and oxygen) as well as provide fast transportation of liquid reactants/gaseous products to/from the three phase boundary. They have been successfully used in water electrolysis/fuel cells, and in metal-air batteries for different applications, as powering electric trucks or cars and other technical and military needs [28]. Instead of its advantages and revolutionary role in electrochemistry, GDEs have some disadvantages that limit their application and can not satisfy the needs of modern technology.

Unfortunately, pores used to be source of a lot of troubles, especially when three phase electrodes are concerned. So, in case of poor gas drainage, the evolved gas accumulates in pores and blocks their surface area. Pores could also diminish the electrical conductivity of both metal structure or electrolyte (saturated with gas bubbles) or evolving gas could eventually destroy the porous metal structure, etc. Also, diffusion limitations

can not allow high current densities at lower overpotentials.

In order to overcome the disadvantages of the 3 phase electrodes, in modern electrolyzers, 2-phase porous electrodes with proton exchange membranes (PEM) were introduced. These membranes have bifunctional role: as a separator of cathodic and anodic area and as a solid electrolyte, which can selectively transport cations across the cell junction. Using polymer membrane, there is no concern connected with liquid electrolytes as e.g. corrosion, watertight compartment and safety issues. Also, the membrane is chemically resistant and long-term stable. Recently, the most used membranes are those based on polifluorosulfonic acid/PTFE copolymer, commercially named Nafion®PFSA [12]. The temperature operating region of Nafion®PFSA is below 100°C. In order to amplify the operating temperature range even up to 350°C, polybenzimidazole (PBI) membranes can be used [13].

### Chemical approach

The need for active, stable and cheaper electrocatalysts motivated intensive research, resulting in development of multicomponent catalysts. First attempts in this area, logically, were to alloy the most individual electrocatalysts as Pt-Pd, Ir-Re, etc. [20]. But the resulting synergetic effect did not satisfy the expectations. Later on, the attempt of M. Jakšić et al. [30] to alloy good individual catalyst (Ni) with metal behaving as a poor individual catalyst (Mo), resulted with synergetic effect, i.e. activity of the produced non-platinum catalyst was comparable with that of platinum. It was predicted and proved that combination of *d*-metals with dissimilar electronic character exhibits pronounced synergetic effect [31]. As a result, combination of hyper *d*-electronic transition metals (good individual electrocatalysts) with hypo *d*-electronic transition metals (poor individual catalysts) becomes subject of scientific and technical interest. A “new era” of modern electrocatalysis was opened.

The phenomena of synergetic effect achieved by alloying metals from the right and the left side of transition series can be explained by Jakšić’s interpretation of the Brewer resonance bond-valence theory of intermetallic compounds [31-33]. This theory offers better understanding and thermodynamic prediction of stabil-

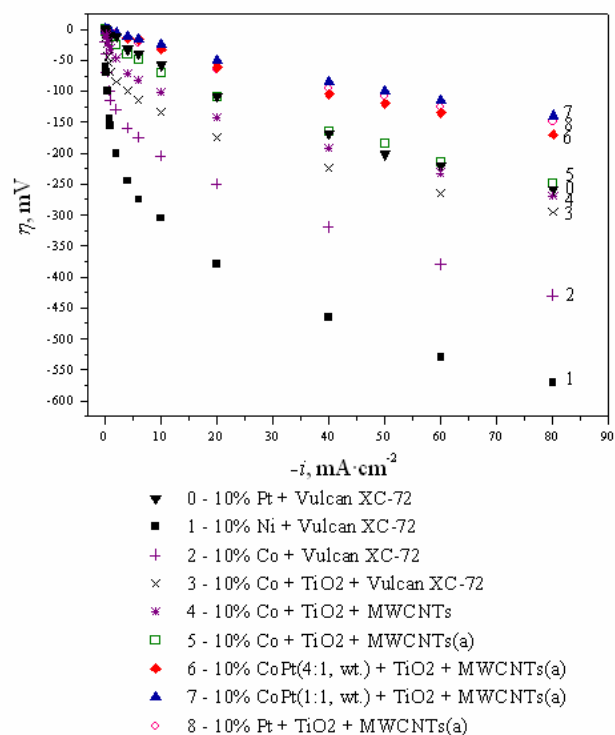


Fig. 7. Polarization curves of the non-platinum hypo-hyper *d*-electrocatalysts.

ity and properties of intermetallic compounds as most promising electrocatalytic materials for HER.

The both, crystalline structure and thermodynamic properties depend on electronic configuration. The *d* orbitals from diffuse and extending in the space at the beginning of the transition series become more localized and stabilized going to the right side. They cannot overlap with delocalized *s* and *p* electrons, so the main *d* bonding comes from *d*-*d* bonding. Also, the bonding energy of *d* electrons increases very markedly from 3*d* to 5*d* transition series. This is in opposite to the general trend amongst all compounds with *s* and *p* electrons. For example, the most stable intermetallic compound would be Pt-Hf, Pd-Zr and Ni-Ti, along each transition series, where Pt-Hf compounds are the most stable.

Intermetallic compounds named Laves phases with high level of symmetry (spherical) of crystal with average *d*<sup>8</sup> average electronic configuration have the most improved *d* electron orbital overlap and show extrastable physical properties, thus and electrocatalytic activity. This average electronic configuration provides two vacant unpaired *d* electrons suitable for further recombination of H<sub>2</sub>. Usually mixing atoms of different size in

Table 1. Overpotential for hydrogen evolution reaction of the studied electrocatalysts at reference current density of 60 mA cm<sup>-2</sup>.

Sample N <sup>o</sup>	Catalysts composition	$\eta_{60}$ , mV
0	10% Pt + Vulcan XC-72	220
1	10% Ni + Vulcan XC-72	530
2	10% Co + Vulcan XC-72	380
3	10% Co + 18% TiO <sub>2</sub> + Vulcan XC-72	265
4	10% Co + 18% TiO <sub>2</sub> + MWCNTs	235
5	10% Co + 18% TiO <sub>2</sub> + MWCNTs(a)	215
6	10% CoPt (4:1 wt.) + 18% TiO <sub>2</sub> + MWCNTs(a)	135
7	10% CoPt (1:1 wt.) + 18% TiO <sub>2</sub> + MWCNTs(a)	115
8	10% Pt + 18% TiO <sub>2</sub> + MWCNTs(a)	125

the crystal structure with equivalent lattice sites reduces the thermodynamic stability of intermetallic phase. But, in the case of the Laves phases, the high difference of atomic size yields to maximizing of their stability. The forming of substitutional intermetallic phases causes increase of the electronic density of state at the Fermi level, which enhances the electrocatalytic properties. This results in increased catalytic activity compared with that of individual metal with the same average electronic configuration.

Hypo and hyper *d*-components may be not only in elemental state, but also in higher oxidation state. Depending on valence state of the hypo and hyper *d*-components, we can distinguish these electrocatalysts into five main groups, as shown in Fig. 6.

#### ADVANCED ELECTRODE MATERIALS

The importance of the innovation of non-platinum electrode materials for water electrolyzers/fuel cells within the hydrogen economy was already described above. The still leading electrode material is platinum deposited on carbon support material - Vulcan XC-72. But, the commercial application of Pt is limited due to its high cost and low abundance. About 50 % of the modern fuel cell cost is attributed to membrane electrode

assembly (MEA) in which Pt cost is more than 70 % [43]. On the other hand, according to some analysis [43], the present resources of Pt are enough to cover only 20 % of the automotive industry needs. What about the remaining 80 %? What about the future electricity needs that are considerably higher than in the automotive industry? Considering the above facts, the main goal of the modern electrocatalysis and material science employed in hydrogen economy, is to reduce or even to replace platinum in the MEA, keeping the same level of efficiency.

The main activity of the present author and his group is production, characterization and modification of non-platinum hypo-hyper *d*-electrocatalysts for hydrogen evolution/oxidation. Nano-scaled electrocatalysts were prepared by sol-gel method [44]. Metallic phase (10 %) was deposited on carbon blacks -Vulcan XC-72. As metal phase Ni and Co were used. Why Co and Ni? Ni is non-noble metal of platinum group, while Co is near Ni in the periodic table, having similar properties. It was expected both catalysts to show close catalytic activity for hydrogen evolution. But, Ni-based catalysts (sample 1) showed as very inferior activity related to that of Co-based one (sample 2, see Fig. 7 and Table 1). Difference in overpotentials for hydrogen evolution at reference current density of 60 mA cm<sup>-2</sup> was 150 mV.



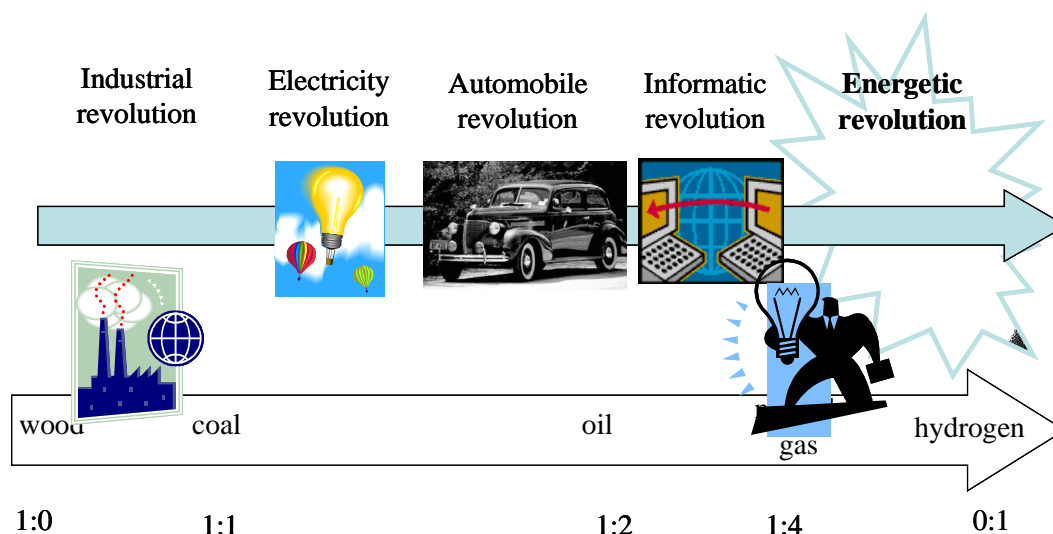


Fig. 8. History of technological revolutions and fossil fuels.

This is result of very higher size of Ni particles (15-20 nm) compared with those of Co (near 2 nm). Thus, the real surface area of active catalytic centers dispersed over the catalyst's surface is considerably higher in case of Co-based electrocatalyst. In the further text improvement of the Co-based electrocatalyst will be discussed.

First modification step of the starting Co-based electrocatalyst was addition of hypo *d*-phase TiO<sub>2</sub> (anatase). Hypo *d*-component has a bifunctional role, as a catalyst support (with carbon phase) and contributes to the catalyst's overall synergetic effect by so called Strong Metal-Support Interaction (SMSI). The unique role of anatase form of titania in improvement of catalytic activity in both heterogeneous chemical catalysis and electrocatalysis has been noticed by other authors [45, 46]. Addition of anatase in the catalyst's support contributes to decrease of overpotential for hydrogen evolution for even 115 mV. This considerable rise of catalytic activity of modified Co-based (sample 3) electrocatalyst is result of strong hypo-hyper *d*-interaction between Co and TiO<sub>2</sub> [42, 47], and consequently increase of intrinsic catalytic activity.

In the next modification step, instead of conventional carbon substrate Vulcan XC-72, multiwalled carbon nanotubes were (MWCNTs) involved. Their inner structure, geometry, surface area and conductive characteristics are favourable for use as a carbon substrate of the nano-scaled electrocatalysts. Extra-conductive properties enable easier electron exchange with hydrogen protons, which intensifies formation of adsorbed hydrogen

atoms and further hydrogen molecules. Their high developed surface area enables better dispersion of active catalytic centres across the catalyst's surface. On the other hand, MWCNT's high **inter- and trans-particle nano porosity** as well as its geometry (empty cylinders) do facilitate the escape of hydrogen molecules from catalyst's surface [17, 42]. Decrease of hydrogen overpotential in this modified catalyst (sample 4) compared with the previous modified one (sample 3) is 30 mV.

Further, purification/activation of MWCNTs was made [48]. During this operation, two main processes occur: (i) removing of other carbonaceous phases such as amorphous carbon and (ii) shortening, thinning and opening of the MWCNTs, followed by amorphous carbon generation. Opening and shortening of the MWCNTs, and the increased number of defective sites as results of the amorphous carbon generation, results in increase of their real surface area and reactivity - characteristics are suitable for carbon substrates used for electrocatalysts. These changes in support material contribute to higher catalytic activity for hydrogen evolution of the Co-based hypo-hyper *d*-electrocatalyst. In this case (sample 5), hydrogen overpotential decreases for 20 mV related to the previous Co-catalyst deposited on as prepared MWCNTs (sample 4). This activity is very close to that of the traditional Pt electrocatalyst (Pt/Vulcan XC-72, sample 0). So, the maximal activity of non-platinum Co-based catalyst approaches Pt-based one, and slightly exceed it. But, the performance of these electrocatalysts in proton exchange membrane (PEM)

electrolyte at lower cathodic overpotentials was not so impressive, while at higher overpotentials their activity approaches the performance of a traditional Pt catalyst [17].

Therefore, in the next phase of investigations, catalysts with mixed metallic phase were prepared, containing 10 % CoPt (Co:Pt = 4:1, wt., sample 6 and Co:Pt=1:1, wt., sample 7) and Pt-based catalyst (sample 8) with analogous composition produced in the same conditions as the previous ones. All of these catalysts showed impressive catalytic activity considerably exceeding the activity of conventional platinum (sample 0). The best catalytic activity shows the catalysts with mixed metallic phase Co:Pt = 1:1, wt., (sample 7), while the catalysts with mixed metallic phase Co:Pt = 4:1, wt. (sample 6) is less active but still very close to the activity of pure Pt-based catalyst (sample 8). At the first glance, it is a paradox the catalyst with double higher amount of Pt (sample 4) to be less active. But, there is logical explanation for this order of catalytic activity. Let's consider that catalytic activity depends on hypo-hyper *d*-interaction as well as surface area (particle size) of the metallic catalytic centers dispersed over the catalyst' surface. The intrinsic hypo-hyper *d*-interaction is the same in all catalysts. They all have better porosity and dispersion of the metallic phase as result of MWCNTs usage as catalyst support as well. Thus, the improved activity of the catalyst with less amount of platinum obviously is related to the considerably lower size of Pt crystallites in the mixed systems. As it was shown from the XRD analysis [49], the size of Pt crystallites in the sample 8 is near 12 nm, while in the mixed systems (samples 6 and 7), Co promotes considerably lower (up to 3-4 times) size of Pt particles. The lower amount of Pt is compensated by the highly developed surface of Pt-phase in the mixed systems.

It is obvious that hypo-hyper *d*-electrocatalysts (hypo-oxides + hyper-metals) are very promising in reducing platinum in the electrocatalysts aimed for hydrogen evolution. In this context MWCNTs have considerable contribution as an extraordinary carbon support.

## CONCLUSIONS

Let's go back in the history to retrospect technological revolutions (Fig. 8). Any technological revolu-

tion causes remarkable change of lifestyle followed by new materials, products and services providing new life comfort quality. On the other side, every technological revolution is connected to certain source of energy, i.e. certain kind of fossil fuel. Beginning of the industrial revolution (steam machine appearance), on the other side, means beginning of mass consumption of coal as a convenient energy source. Further, electricity revolution is based on usage of coal which appears as the main energy source, too. Appearance of oil causes automotive revolution, while this revolution causes oil to be the main energy source. Correlation between information revolution and natural gas is not cause-consequence based, but only temporal. And finally we are coming at 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 humanity is faced to energy crisis and all efforts are focused on invention of 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 electrolyzers/fuel cells, etc., is in the focus of the energy revolution.

This paper is a small, modest contribution, i.e. a drop into the sea named energy revolution.

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