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Electrocatalysis and the Production of Nanoparticles

Metin Açıkyıldız, Ahmet Gürses,
Mehtap Ejder Korucu and Kübra Güneş

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1. Introduction

Electrochemistry has much in common with surface science, but the application of the principles of catalytic activity to the reactions taking place in an electrochemical environment is not straightforward. Electrochemical reactions of practical interest imply at least one step where an electron is transferred between species coming from the solution side or the electrode surface. As a result, electrochemical reactions occurring at the interfaces are governed by the interaction of the reactant both with the solvent and with the electrode [1].

It is undeniable that electrocatalysis is a very important subject. This is not only for the obvious situations, for example, increasing the amount of energy obtained from a fuel cell, but also for every kind of electrochemical reaction which is going to be developed industrially, because the cost of producing a certain amount of a substance is simply proportional to the total amount of electricity which is needed, and this depends upon the overpotentials at the electrode–solution interfaces [2].

Electrocatalysis is one of the most actual fields of contemporary electrochemistry. Although Bowden and Rideal are the true originators of studies of rates on a series of different materials, Horiuti and Polanyi have wrote the first paper which began the theory of electrocatalysis [2]. In the 1920s, Bowden and Rideal made a series of measurements of hydrogen evolution overpotential as a function of current density for a number of metals and then the electrocatalysis term was coined in 1936 by Kobozev, but in the next 30 years little attention was paid to this phenomenon [3].

Electrocatalysis is the field of catalysis that deals with the catalysis of redox reactions. Redox reactions not only play a key role in a multitude of devices, in particular electrochemical power sources such as fuel cells, batteries, and electrolysis cell, but also in many naturally occurring processes, especially those related to energy conversion in living systems. There is growing

awareness that the way that mankind will secure future availability of sustainable energy will depend heavily on electrochemistry, as it allows the storage and consumption of electrons in chemical bonds at ambient conditions. It is the task of electrocatalysis to make this process as efficient, reversible, robust, and cost-effective as possible [4].

Electrocatalysis and heterogeneous catalysis are closely related in that they involve well-controlled sequences of elementary bond-breaking and making processes and share many common mechanistic principles in the transformation of molecules over supported metal and metal oxide catalysts [5].

Electrocatalysis is not limited to heterogeneous catalysts: molecular catalysts, either in solution or immobilized on a conductive but otherwise inert support, may also catalyze redox reactions. Therefore, the field of electrocatalysis bridges many areas of catalysis [4].

In electrocatalysis, the high performance of electrodes is the result of some combinations of surface reactivity, electronic and ionic conductivity and electron hole pair separation and facile mass transport of molecules, which is furnished by the architectural design of both electrodes in the cell, i.e., the arrangement of material in space. In electrochemical reactions, the electron is a reactant that scales with the electrified surface area. This fact poses the issue of the optimum pore size of electrode materials compatible with the highest electrocatalytic activity. In this respect, it should be noted that micropores (less than 5 nm) are not useful because electro-chemical reactions require ionic conducting media for charge balance, and the mass transport rate of ionic species into micropores becomes several orders of magnitude lower than in the bulk of the solution. Therefore, in electrocatalysis surface accessibility is maximized by using materials with meso or macropores structures. Accordingly, since some decades ago, this issue has become of considerable interest from the standpoint of electrochemical research [6].

Traditionally, for laboratory and small-scale plants, platinum was the first choice as electrode material for both cathodic and anodic processes. Platinum metal in a shape of bars, foils (continuous and latter perforated) or gauze, was used over a long period. Nevertheless, platinum was not accustomed in commercial use, due to its disadvantages (too expensive, extensive corrosion when used for $Cl_{2(g)}$ production, etc.) [3].

Literature survey made from 2005 to 2013 shows that there are a lot of studies focused on development of alternative materials and their usages at the different electrocatalytic applications. These materials can be classified as noble metals, alloys or metallic composites; polymer based metallic composites, carbon-supported metallic composites, carbon-based materials etc.

In a few specific studies, the noble metals were used alone and in these researches, the efficiency of nanostructured Pd film [7], single crystalline platinum [8], porous gold [9], and Pt particles [10] were investigated in terms of electrocatalytic reactions and electroanalysis.

Figure 1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the Au porous textile-like sheet arrays (AuPTSAs) developed by one-step electrodeposition with the assistance of N-methylimidazole, without any template, seed, or surfactant. It was determined that the AuPTSAs which displayed remarkable improvement of the electrocatalytic activity over polycrystalline Au nanoparticles for methanol oxidation.
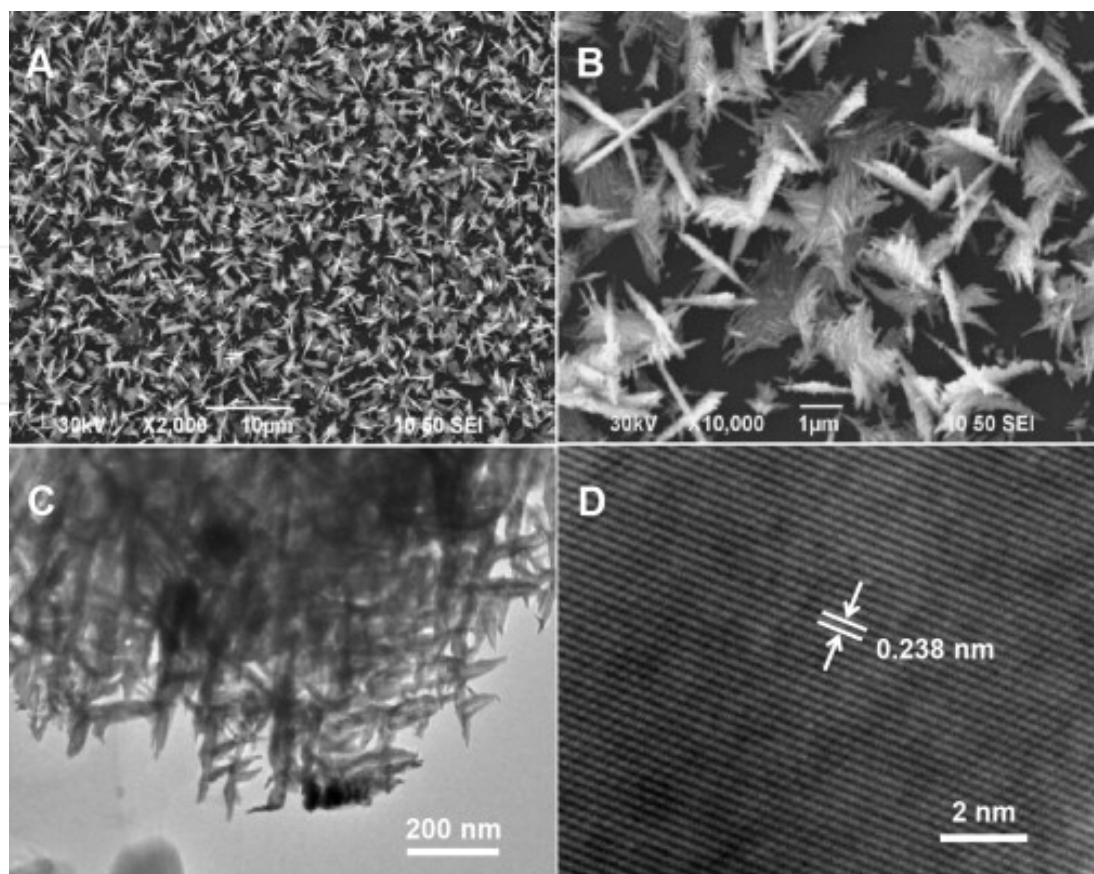
Figure 1. Low (A, C) and high (B, D) magnification of SEM (A, B) and TEM (C, D) images of the typical AuPTSAs using the applied potential of −0.4 V for 600 s in the electrolysis solution containing 10 mM $HAuCl_4$, 1.25 M N-methylimidazole, and 0.5 M H_2SO_4 [9]

In addition, alloys or metallic composites such as Co_3O_4 and Ag/Co_3O_4 [11], Au and Au-Pd core-shell nanoparticles [12], electrodeposited Pd coatings on gold [13], titanium supported Pt [14], nanosized Pt/IrO_2 [15], Ni, Pt, and Ni-Pt nanoparticles [16], Pt supported on nano-tungsten carbide [17], nanostructured Pt/SnO_2-SbO_x-RuO_2 [18], Au-Pt [19, 20], Pt and Pt–Pd core-shell nanoparticles [21], Pt-Sn [22], SnO_2-Au nanoparticles [23], Fe-containing Se/Ru composite [24], titanium supported nanocrystallite Pt and Pt_x-Sn_y [25], $Pt_{25}Cu_{75}$ and $Pt_{20}Cu_{20}Co_{60}$ nanoparticles and Pt-Carbon [26], platinum modified by ruthenium and tin [27], manganese oxide nanorods modified Au, Pt and glassy carbon [28], nano TiO_2 supported Pt [29], bimetallic PdNi nano-particles [30], transition metal modified ruthenium-selenium [31], Pt-Sn nanoparticles [32], titanium oxides supported Pt [33], and $Ru_xCr_ySe_z$ [34] were used as catalysts.

Figure 2 shows the SEM images of the titanium supported nanocrystallite platinum and platinum-tin catalysts prepared by electrodeposition techniques. It was determined that the modification of Ti with Pt and/or PtSn (i.e. Pt/Ti and Pt-Sn/Ti electrodes) had many advantages compared to Pt/Pt and Pt-Sn/Pt electrodes and the combination effect of Pt, Sn and Ti improves the catalytic activity and the stability of the prepared electrode through complete oxidation of the intermediate product of methanol oxidation. It was dedicated that the introduction of a

small amount of Sn deposited with Pt improved the catalytic activity and the stability of prepared electrode and the optimum molar ratio of Pt:Sn was found as 8:1 for binary catalysts.
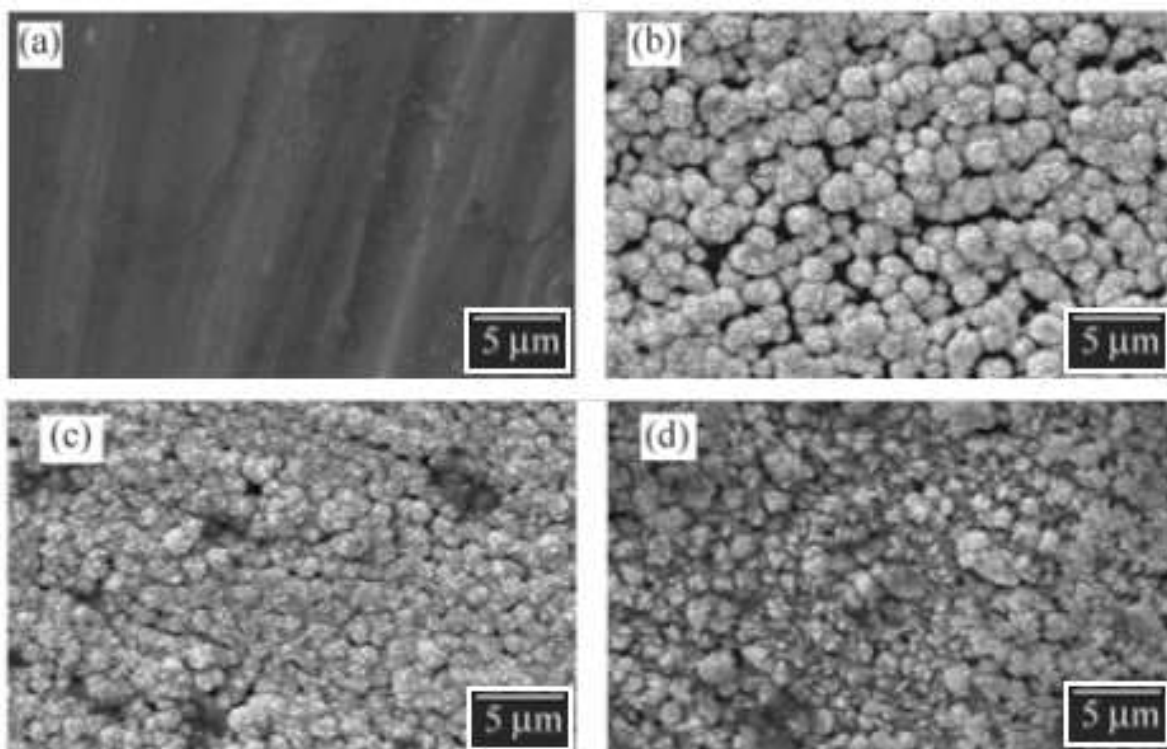

Figure 2. SEM patterns of the (a) Ti, (b) Pt/Ti (galvanostatic deposition), (c) Pt/Ti (potentiostatic deposition) and (d) Pt-Sn/Ti [25].

Poly(3,4-ethylene-dioxythiophene) coated platinum [35], myoglobin immobilized $LiMn_2O_4$-chitosan [36], MnO_2-polypyrrole composites [37] were used as polymer based metallic composite catalysts.

It was recently found in a work [36], the new electrochemical biosensor constructed by immobilization of bovine myoglobin and $LiMn_2O_4$ in a thin film of chitosan on the surface of carbon ionic liquid electrode has a good electrocatalytic activity toward trichloroacetic acid with a lower detection limit. In addition, it was determined that the obtained $LiMn_2O_4$ microspheres as the cathode material for lithium ion batteries had high discharge capacity and good cycling stability. The SEM images of α-MnO_2 precursor and $LiMn_2O_4$ microspheres calcined at 750 ºC were shown in Figure 3.

The carbon supported mainly nano-sized metallic composites given in Table 1 emerge a critical importance both qualitatively and quantitatively. In order to achieve fine dispersion, high utilization and stable nanoscale metallic particles, catalyst-supporting strategies have been explored. Compared to bulk metal catalysts, supported catalysts show higher activity and stability. Carbon particles are frequently used as catalyst supports because of their relative stability in both acidic and basic media, good electric conductivity and high specific surface
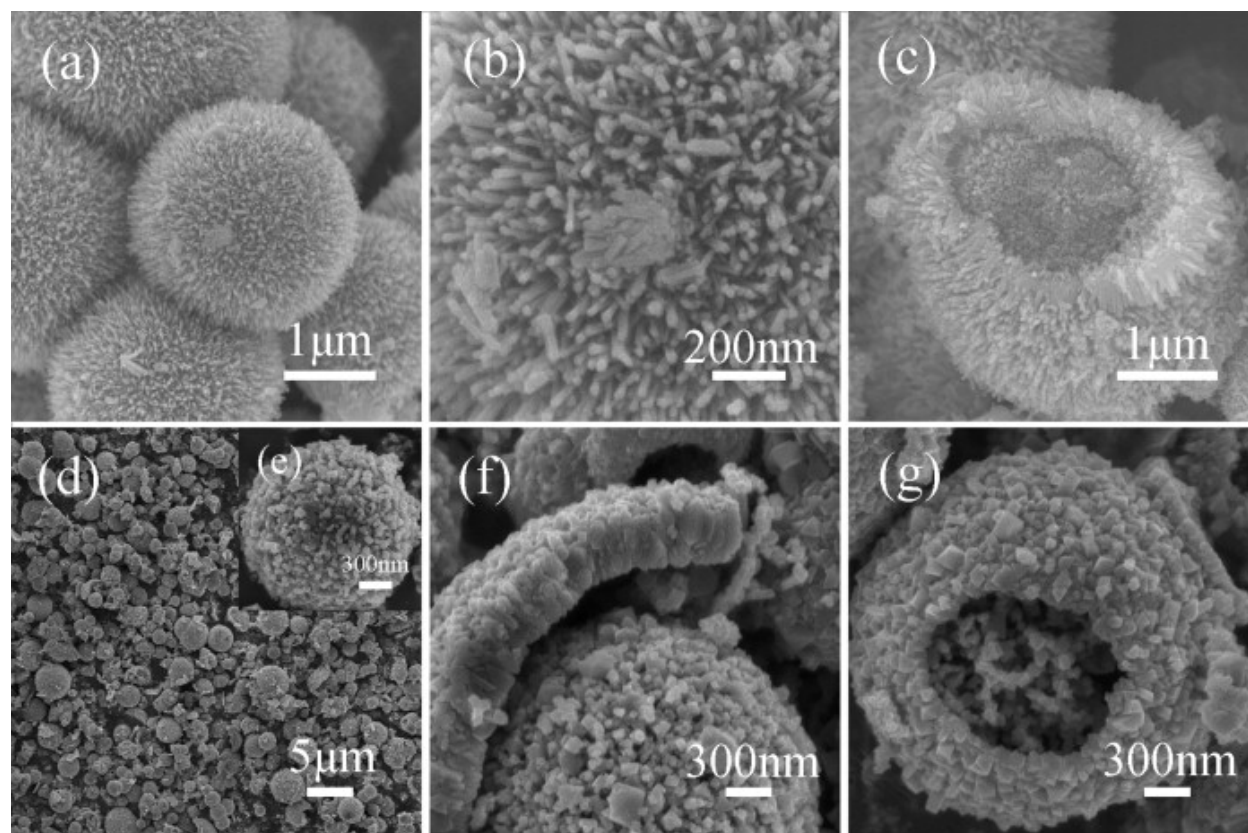
Figure 3. The SEM images of α-MnO$_2$ precursor (a-c), and LiMn$_2$O$_4$ microspheres calcined at 750 ºC (d-g) [36].

area [38]. The carbon black, nanostructured carbon materials and mesoporous carbon are the most used carbon based catalysts supports.

Catalysts	References
Carbon supported monometallic materials	
Pt	[39-54]
Pd	[49,55]
Ru	[51, 56, 57]
Au	[58]
Ir	[59]
Carbon supported binary materials	
Pt-Ru	[47, 50-54, 60-63]
Pt-Sn	[53, 61, 64-67]
Pt-Pd	[53, 68-70]
Pt-Co	[71, 72]
Pt-CuO	[73]
Pt-MoO	[74]
Pt-Rh	[53]

Catalysts	References
Carbon supported binary materials	
Pt-Sb	[75]
Pt-Cr	[61]
Pd-Co	[55, 76, 77]
Pd-Fe	[55]
Pd-V	[78]
Au-Zn	[79]
Au-Pt	[58]
Au-Pd	[58]
Ag-WC	[80]
Ru-Se	[56, 81]
Ir-Sn	[59]
Ni-TiO$_2$	[82]
Carbon supported ternary materials	
Pt-Co-Ru	[83]
Ru-Fe-Se	[56]
Pt-Cr-Ru	[84]
Carbon supported quaternary materials	
Pt-Mn-Cu-X (X: Fe, Co, Ni, and Sn)	[85]
Pt-Mn-Mo-X (X: Fe, Co, Ni, Cu and Sn)	[85]
Single-walled carbon nanotube supported	
Pt	[86, 87]
Pd	[88]
Multi-walled carbon nanotube supported	
Pt	[86, 87, 89]
Pd	[90]
Pt-Pd	[91]
Pt-Ru	[92]
Pt-Au	[93]
Pd-Ni	[94]
Ni-Fe	[95]
Pt-M (M: Fe, Co, and Ni)	[96]
Pt nanoparticles on carbonized polyaniline nanotubes	[97]
Carbon nanotubes and active carbon supported Pt	[98]
Pt supported by multi-walled carbon nanotubes coated with sulfated TiO$_2$	[99]
PtRu alloy catalyst supported on graphene-carbon black	[100]
Reduced graphene/Pd nanocomposite modified with glassy carbon	[101]
Pt supported on reduced graphene oxide-ordered mesoporous carbon	[102]

Catalysts	References
Cd-doped cobalt nanoparticles encapsulated in graphite shell	[103]
Pt and nickel oxide nanoparticles at glassy carbon	[104]
Carbon xerogels supported Pt	[105, 106]
Carbon aerogel supported Pt	[107]
Pt-Ru and Pt-Ru supported on H_2O_2 treated carbon black	[108]
Pt deposited on unsupported and carbon supported Ru nanoparticles	[109]
Oxidized glassy carbon supported Pt/Ru nanoparticles	[110]
Pt monolayers deposited on carbon-supported Ru and Rh nanoparticles	[111]
Pt nanoparticles supported on functionalized graphene	[112]
Polyoxometalate-deposited Pt/C	[113]
Pt–SnO$_2$ nanoparticles supported on graphitized mesoporous carbon	[114]
Fe associated with pyridinic nitrogen	[115]
Active carbon supported Ir-V nanoparticle	[116]
Silicotungstic acid stabilized Pt-Ru nanoparticles supported on carbon nanofibers	[117]
Polypyrrole/carbon supported Pt	[118]
Au and MnOx nanoparticles deposited on glassy carbon	[119]
Pt/carbon hollow nanospheres	[120]

Table 1. Catalysts from carbon supported metallic composites

One of the most important applications related to the electrocatalysis is fuel cells. The performance of methanol fuel cells is limited due to both the CO poisoning of the anode surface and the low catalytic activity of Pt-based anodic catalyst. Adsorbed CO has been identified as a key surface poison and the later pathways have been attracted great interest because their optimization can improve energy conversion efficiency at low potentials. Thus, the Pt(111) surface is expected to facilitate the methanol oxidation through the direct pathway and exhibits a good CO tolerance [39].

The Pt octahedron nanoparticles on supported carbon black were produced by Liu et al [39]. The TEM and HRTEM images of the Pt octahedral and tetrahedral nanoparticles were given in Figure 4. The authors have determined that the defect and step sites introduce on the surface of the Pt octahedron nanoparticles by applying a number of potential cycles. Further cycling lead to the formation of Pt(100) terraces. The enhanced catalytic activity observed after a number of potential cycles was due to the formation of the defect and step sites, and the rapid decay in the long-term performance was ascribed to the formation of Pt(100) terraces. They stated that the surface structure significantly affects the methanol decomposition process.

Porous graphene [121], graphitic carbon nitride [122], nitrogen-containing multi-walled carbon nanotube modified glassy carbon electrodes [123], and nitrogen-doped graphene [124] can be grouped as carbon-based catalysts. The SEM images from two of these catalysts are shown in Figure 5. Figure 5A shows the interconnected 3D porous network of graphene sheets on the electrochemically reduced grapheme oxide modified electrode surface. After chitosan
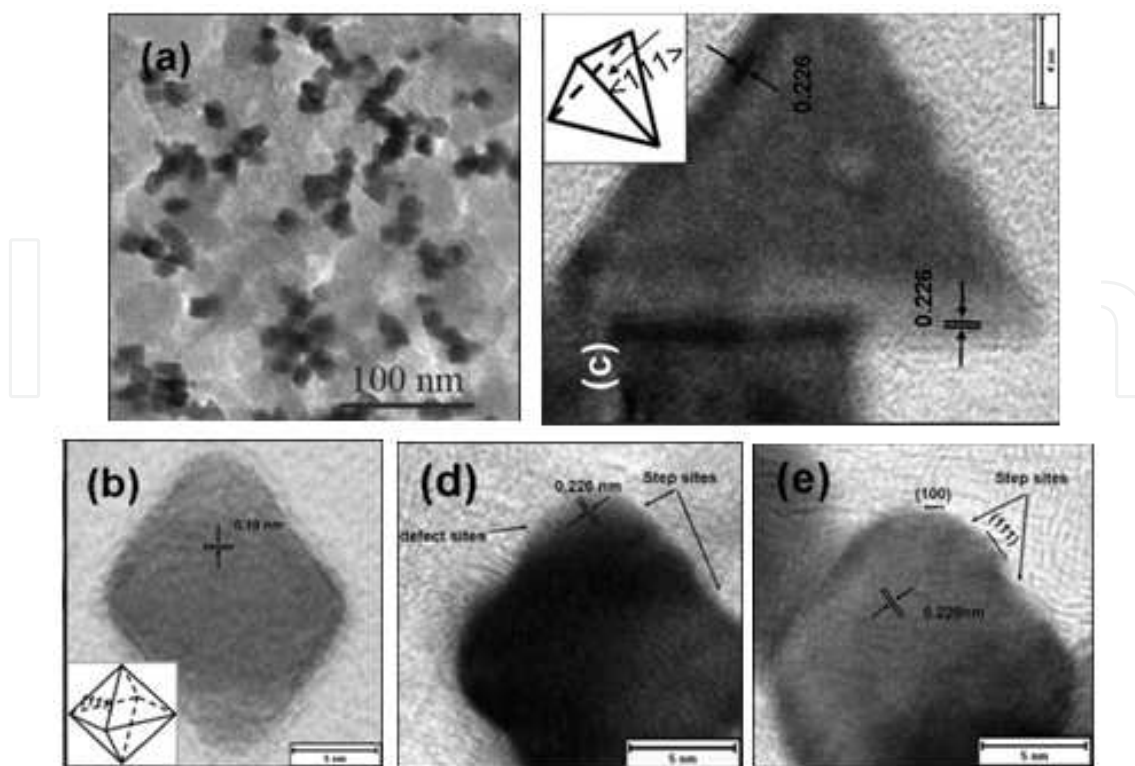
Figure 4. (a) TEM image of the Pt octahedron nanoparticles on supported carbon black. (b) HRTEM image of a single Pt octahedron nanoparticle; inset: the geometrical model of the Pt octahedron nanoparticle. (c) HRTEM image of a single Pt tetrahedral nanoparticle; inset: the geometrical model of the Pt tetrahedral nanoparticle. (d) The typical HRTEM image of a single Pt octahedron nanoparticle after 50 cycles. (e) The typical HRTEM image of a single Pt octahedron nanoparticle after 100 cycles [39].

addition to this electrode, it was argued that the electrode is a good material platform promising for construction of the third-generation enzyme biosensor, biofuel cells and bio electrochemical devices.
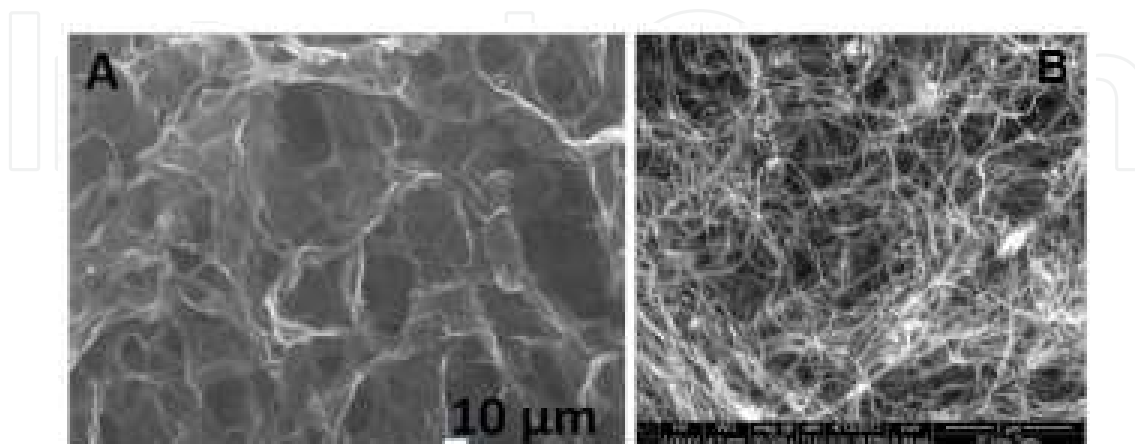

Figure 5. (A) SEM images the surface of the electrochemically reduced graphene oxide modified electrode [121] and (B) nitrogen-doped multi-walled carbon nanotubes deposited on glassy carbon [123]

Figure 5B shows the surface morphology of the nitrogen-doped multi-walled carbon nano-tubes deposited on glassy carbon. It was determined that the nitrogen doped carbon nanotube materials demonstrate a high electrocatalytic activity for O_2 reduction in alkaline solution.
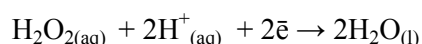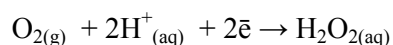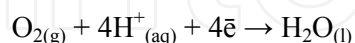
The specific catalysts such as glucose oxidase/graphene/gold nanocomposites [125], The heat-treated cobalt–porphyrin/carbon [126], SiO_2 supported catalyst powders [127], palladium doped glassy carbon, nitrogen implanted glassy carbon and argon implanted glassy carbon [128], hybrid nanocomposites modified glassy carbon electrode [129], hemoglobin immobi-lized on poly (styrene-alternative-maleic acid)/multiwalled carbon nanotubes blends [130], active carbon-supported cupper phthalocyanine [131], Pt nanoparticles supported by zeolite-type mesoporous $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid super-acid [132], carbon-ceramic supported bimetallic Pt-Ni nanoparticles [133], Ni nano-pottery structure [134], Pt nanoparticles modified with ethylidyne [135], poly(3,4-ethylenedioxythiophene)-modified screen-printed electrodes [136], Pt nanoparticles on nitrogen-doped magnetic carbon nanoparticles [137], carbon supported gold, carbon powder and carbon powder grafted with anthraquinone derivatives [138] were not included to the above groups.

Figure 6 indicates the SEM images of Ni nano-pottery structures produced by electrodeposi-tion in a nanoporous alumina template. The researchers used these nanostructures as cathode catalyst for hydrogen evolution reaction (HER) in alkaline water electrolysis. Their catalytic activity was compared to that of the Ni nano-rod and film and the result shows that the HER activity was greatly enhanced when using the Ni nano-pottery structure which mainly resulted from both larger and higher numbers of surface reactive sites.
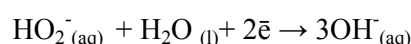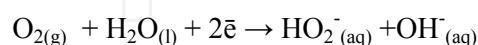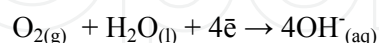
Figure 7 summarizes the electrocatalytic applications in which are used electrode materials described and classified above. From this figure, it can be seen that the catalytic activity tests of electrode materials are generally performed with oxygen reduction and methanol oxidation reactions.

The mechanism of the electrochemical oxygen reduction reaction is quite complicated and involves many intermediates, primarily depending on the natures of the electrode material, catalyst, and electrolyte [139]. It can be presented as follows in acidic or alkali medium.

In acidic media;

$$O_{2(g)} + 4H^+_{(aq)} + 4\bar{e} \rightarrow H_2O_{(l)}$$

$$O_{2(g)} + 2H^+_{(aq)} + 2\bar{e} \rightarrow H_2O_{2(aq)}$$

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2\bar{e} \rightarrow 2H_2O_{(l)}$$

In alkali media;

$$O_{2(g)} + H_2O_{(l)} + 4\bar{e} \rightarrow 4OH^-_{(aq)}$$

$$O_{2(g)} + H_2O_{(l)} + 2\bar{e} \rightarrow HO_2^-_{(aq)} + OH^-_{(aq)}$$

$$HO_2^-_{(aq)} + H_2O_{(l)} + 2\bar{e} \rightarrow 3OH^-_{(aq)}$$
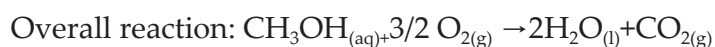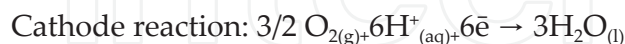
The reduction pathways such as the 1, 2, and 4-electron reduction pathways have unique significance, depending on the applications. In fuel cell processes, the 4-electron direct pathway is highly preferred [139].

With growing crisis in energy conservation and environmental pollution, a particular empha-sis has been placed on sustainable conversion of environment-friendly feedstock to valuable

matters and energy. Fuel cell technology provides a sustainable strategic manner for energy conversion with high-efficiency and cleanliness, but it has to rely on simple small-molecular high energy-containing fuels such as hydrogen, methanol, methanoate, and ethanol [80].

Electrochemical reactions involved in the methanol fuel cell include an anode reaction for oxidizing of fuel and a cathode reaction for reducing of hydrogen ion and oxygen. These reactions are as follows:

Anode reaction: $CH_3OH_{(aq)} + H_2O_{(l)} \rightarrow 6H^+ + 6\bar{e} + CO_{2(g)}$

Cathode reaction: $3/2\ O_{2(g)} + 6H^+_{(aq)} + 6\bar{e} \rightarrow 3H_2O_{(l)}$

Overall reaction: $CH_3OH_{(aq)} + 3/2\ O_{2(g)} \rightarrow 2H_2O_{(l)} + CO_{2(g)}$

As shown in the above reactions, methanol and water react with each other to produce carbon dioxide, six hydrogen ions, and six electrons at the anode. At the cathode, the hydrogen ions, electrons, and oxygen react to produce water. The overall reaction consists of the production of water and carbon dioxide via the reaction between methanol and oxygen. Through these reactions, a large portion of energy corresponding to the heat of combustion of methanol is converted to an electrical energy. In order to facilitate these reactions, both the anode and the cathode of the methanol fuel cell comprise catalysts [140].
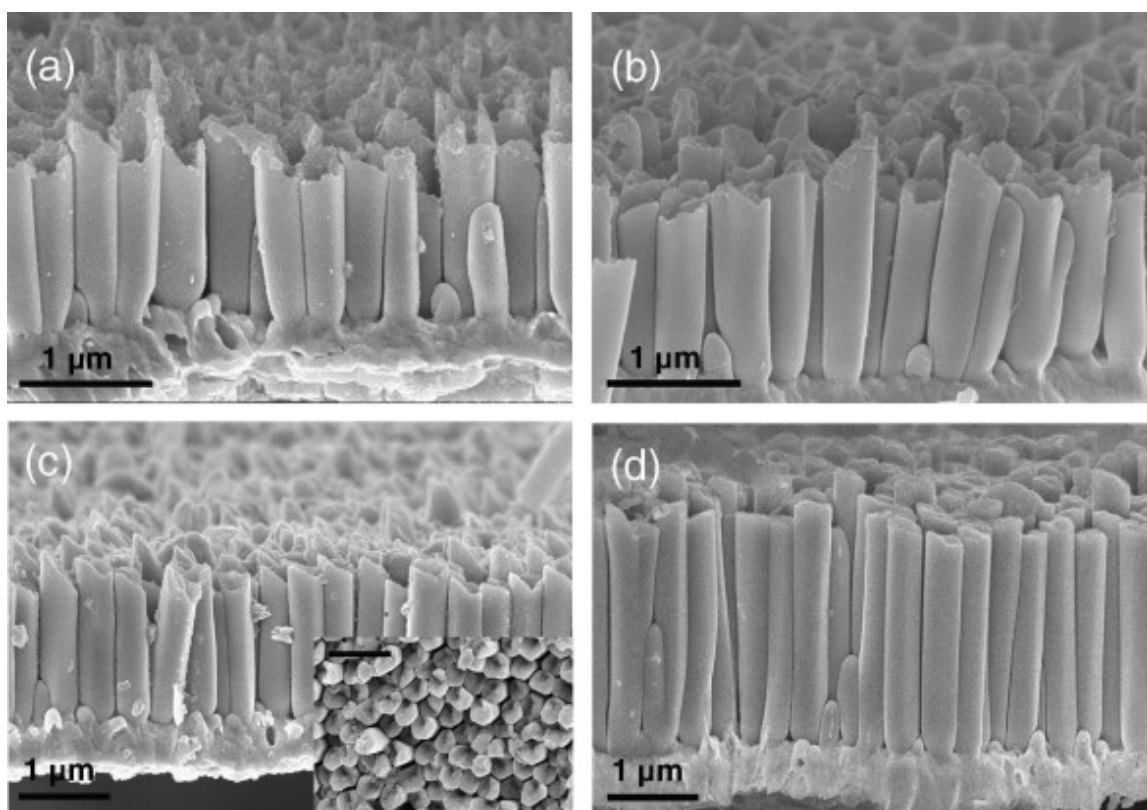

Figure 6. SEM images of Ni nanostructure obtained at different deposition times (a) 150, (b) 300, (c) 350, and (d) 600 s [134].

Most of electrocatalysis appears to be centered on fuel cells in which are carrying out the oxidation of hydrogen, oxygenates, or hydrocarbon molecules to CO_2 and the reduction of oxygen to water and more specifically proton exchange membrane (PEM) [5].

The oxygen reduction reaction (ORR) is an important cathode reaction in fuel cells. However, this reaction is kinetically slow and the cathodic polarization in fuel cells is usually over 0.3 V, accounting for the major part of the voltage loss in a single cell. So far, the best catalyst for the ORR has been Pt, which is expensive and limited in natural resource. Promoting the activity of Pt and searching for alternatives are two basic approaches to solve this problem [14].
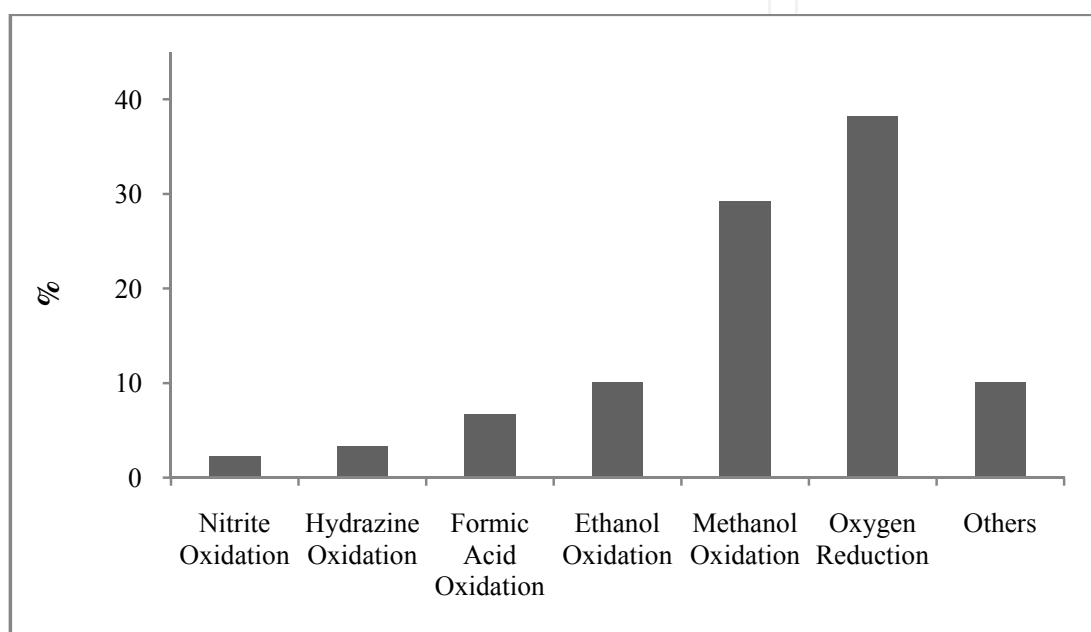

Figure 7. The testing reactions for the catalysts and their percentages of application (2005-2013)

The electrochemical reduction of a proton source to produce hydrogen (H_2) gase is a reaction of both fundamental and economic significance. Electrocatalysis of this reaction can be achieved homogeneously via protonation and electrochemical (or photo-chemical) reduction of a suitable Brønsted base in solution. Advances in this area have afforded molecular electrocatalysts that employ cobalt, molybdenum, nickel, or iron, instead of platinum that is currently the preferred electrocatalyst for proton reduction in water. Given the interest of developing H_2-production electrocatalysts based on cheap and abundant materials, synthetic models of the iron–iron hydrogenase enzymes have been the subject of numerous studies [141].

Methanol, ethanol, and 2-propanol are the main alcohols used directly as fuels in the direct alcohols fuel cells (DAFCs). Methanol is nonrenewable, volatile and a flammable substance; moreover, it has a high toxicity. The use of methanol may result in major issues if applied to portable devices. On the other hand, ethanol is less toxic and has a higher energy density compared to methanol [103].

2. Improvements in electrocatalytic materials and nanoparticles

It should be noted that ready-to-use electrocatalytic materials are complex systems where the resultant performance, i.e., activity, selectivity, and stability, depends on many factors. Even a single-supported nanoparticle in contact with an electrolyte represents a multi parametric system: different facets, surface defects, interactions with the support material, surface and bulk composition, size effects, specific properties of the electrochemical interface, electrolyte composition, and other parameters control its catalytic properties [4].

The rates of electrocatalytic reactions depend upon the surface structure and composition of the electrode as well as on the applied potential. The former includes the chemical composition of the electrode surface, its long-range geometry (with possible surface reconstructions or relaxations) and the in situ surface atomic arrangement on a short range scale whereas the later follows the changes that result in the atomic structure as well as the electronic structure of the metal. Recent developments in electrocatalysis have been driven by progress in ab initio theory of catalysis, development of new experiment methods to study materials and surfaces and the synthesis of new catalytic materials. The discovery of new nanoscale materials with unique surface structures and geometric architectures often provide unexpected surface properties as well as enhanced electrocatalytic performance [142].

The common criteria for a high performance catalyst are: (i) a narrow nanoscale size distribution; (ii) a uniform composition throughout the nanoparticles; (iii) a fully alloyed degree and (iv) high dispersion on carbon support [38]. In principle the catalytic activity can be increased either by a fine dispersion of the nanoparticles (NPs) or by modulating the electronic properties of the catalyst NPs by interaction with support chemical or morphological defects; as an example, a way to enhance the durability of the catalyst support assembly in the case of oxygen reduction is to strengthen the catalyst NPs support interaction by introducing into the substrate defects that can act as trapping sites for anchoring the catalyst NPs [128].

Most current studies on electrocatalysis based on the use of ensembles of nanostructured metal materials to understand the structure-function relationship. An important aspect of nanostructured metal materials is their structure-dependent catalytic activity. It has been shown that the electrocatalytic activity of nanostructured metallic materials is extremely sensitive to their sizes. Due to differences in electrochemical activity at different crystal surfaces, the shape of the nanoparticles also greatly alters their functionality. There had been numerous research efforts reported to control the shape of metal nanoparticles to obtain optimized activity in electrocatalysis [143].

Nanoparticles are widely investigated for their catalytic activity due to their high surface area to bulk atomic ratious and the achievable high surface area at low bulk concentration and associated lower cost. Studies of the reactivity of nanoparticles as catalysts for electrochemical reactions involve the adsorption or growth of nanomaterials onto solid substrates, e.g. carbon materials, oxide materials, metal substrates or molecular templates, which allow formation of an electronic contact required to control electrochemical reactions. The potential is then applied through the substrate material. Although the substrate is chosen with a low activity for the

specific catalyzed reaction, the potential distribution at the interface and the electrochemical results might be influenced through the substrate double layer. To decouple substrate–nanoparticle and substrate–electrolyte interaction from the electrochemical results is therefore not straightforward [12].

Nanoparticles have been used extensively in the fields of physical, chemical and material sciences in the past few years. These materials have a high specific surface area, large pore size and unique features, such as surface plasmon absorption, improved magnetic property, high reactivity, and enhanced catalytic activity. They are also expected to show advantages for use as electrocatalysts due to their large active surface areas, small catalyst loading and abilities to prevent aggregation between particles. Among the nanoparticles, metal nanoparticles are objects of great interest in modern chemistry and material researches, where they find application in such diverse fields as photochemistry, nanoelectronics, optics, catalysis, and electrocatalysis. In fact, often enough these particles do possess physical as well as chemical properties, which are distinct both from the bulk phase and from isolated atoms and molecules. Use of noble metal nanoparticles seems to be inevitable in fuel cells. So far only platinum micro/nanoparticles are chosen as the main anode and cathode material in fuel cells. However, transition metals (Ni, Cr, and...) alloyed with platinum are also found to be efficient catalysts to decrease the CO poisoning effect in the electro oxidation of fuels. Further these catalysts are effective to reduce the cost compared to pure platinum based catalysts [144].

Generally, Pt has long been regarded as the best electrocatalyst for both anode and cathode in fuel cells. However, large-scale commercial application of fuel cells has been hindered largely by the high price of the Pt catalysts due to the limited reserve of Pt in nature, poor kinetics at the anode caused by reaction intermediate adsorption on Pt catalyst and the degradation of cathode performance because of poisoning of Pt catalyst resulting from diffusion of fuel molecules from the anode across membrane and CO poisoning. As a result, various catalysts such as Pt-based alloys, transition-metal macro cycles and Pt-based catalysts have been researched to solve the problems above and the latter presents much more activity and better long-term stability under fuel-cell operation conditions in comparison with others [102].

There is no doubt that many researchers would agree that the oxygen reduction reaction is more important than any other in respect to electrocatalysis. This is because it gives rise to the principal over potential in fuel cells and fuel cells are in a stage of rapid development so that anything related to increasing the efficiency of them is economically important [2]. Overpotential value related to the charge transfer processes at the anode or cathode is the ones that could be lowered by the proper selection of electrode material. This is the issue of the electrocatalysis.

Just to show the tremendous savings which could be obtained by improved electrocatalysis of the oxygen reduction reaction (and any corresponding one with the same types of i_0) it can be started with a familiar equation (Eq 1), derived from Tafel's Law, and said that the change in overpotential at a given current density in the irreversible region with two different i_0's are given (roughly of course) by:

$$\Delta\eta = 2\frac{RT}{F}ln\frac{(i_0)_1}{(i_0)_2} \tag{1}$$

where; $\Delta\eta$ is the overpotential (V), $2RT/F$ is the so-called "Tafel slope" (V), i_0 is the current density (A/m^2). There is only one assumption in this equation and that is that this value for transfer coefficient (α) in the relevant Tafel equation for the reaction is about one-half, which is a widely observed value (though for certain rate determining steps, it may indeed be substantially increased, thus reducing the overpotential) [2].

Of course, everybody knows that "platinum is a good catalyst" and this phrase has often given rise to the impression that one has to look for a substance which will be, in a universal way, "a good catalyst". There are several reasons why platinum has been brought out and focused upon and two of them are that it is an easily available substance which can catalyze substances at highly anodic potentials without being decomposed. In this sense, it has wide applicability. Indeed, one of the difficulties in finding other catalysts, better than platinum, is that, although one might make theoretical calculations which would indicate a given substance to be a better catalyst than platinum it may not withstand the anodic potentials which are often met in, *e.g.*, the reduction of oxygen and undergo decomposition itself, thus making it impractical to use [2].

Platinum was found to be the electrode material on top of which hydrogen evolves with minimum overpotential. From purely academic, the problem how to lower the overpotential (thus lowering the product price) gets on importance with the growth of technical processes of electrolysis. Performed on a large scale, their economy depends greatly on the electricity consumption per unit product, i.e. on the value of cell voltage [3].

3. Applications of electrocatalytic materials

The goal of the applied electrocatalysis is to improve the electrode activity for the wanted reaction, but at the same time to prevent (or slow down) side reactions. Technical reasons request the selected electrode material to be stable (without corrosion and wear), economical reasons favor cheaper materials, while environmental concern is in favor of nonpolluting electrode materials [3].

The transition from one-metal-only electrocatalyst to a two or more metal (or their compounds) catalysts was not at all easy. It took almost 30 years from the first rhodium electrodeposited on titanium electrocatalyst till the first titanium-based anodes in the cathodic protection of rebar in concrete. In this process, rhodium and platinum electrodeposited on titanium (1958), paint/thermal decomposition coatings (1960), first mixed metal oxide coatings (1965), Pt/Ir coated first titanium based electrodes (1968), and first non-precious metal alloys (1974) were produced and titanium-based anodes in electrogalvanizing (1984) and in the cathodic protection applications (1986) were used. Development of electrocatalysts without precious metals started in the middle 1970's and then extended over a long period [3].

The strategy lying behind this important switch from one type of electrocatalysts, made out of rather expensive and limited in quantities precious metals, to the new type of compound catalysts engineered trivial components, but promising unrestricted possibilities was fully correct [3].

Pt and other group VIII metals are known to be very active in the electrocatalytic oxidation of alcohols and the reduction of oxygen in fuel cells, automotive exhaust catalysis, and hydro-genolysis, and hydrogenation catalysis in the conversion of petroleum and renewable resour-ces. This is predominantly the result of the well-established Sabatier's Principle which suggests that the metals in middle of the periodic table demonstrate optimal metal-adsorbate bond strengths necessary to balance surface reaction steps and product desorption steps [5].

Gold first became recognizable as a catalyst when clusters deposited on several metal oxides exhibited oxidation towards carbon oxides at low temperature. Nowadays this effect is thoroughly investigated due to techniques and tools allowing studying the size and shape of the particles and their correlation with catalytic activities. Gold nanoparticles (AuNPs) catalyze a number of reactions either suspended in solution or deposited on the electrode surface [145].

The knowledge obtained from model experiments can be successfully used to design "real-world electrocatalysts". For example, one of the main modern paradigms of the proton exchange membrane fuel cells (PEMFCs) electrocatalyst preparation is to produce high surface area nanoparticulate materials where the catalyst nanoparticles are supported on an electron-ically conducting carbon support. As stability issues strongly dominate in selection of elec-trocatalyst material, Pt-based materials are used at the cathode side of present state-of-the-art PEMFCs [4].

In general, a fuel cell is an electrochemical device which requires electrocatalysts at the anode oxidize the fuel to produce electrons and protons and at the cathode reduce oxygen and consume the protons and electrons produced (as shown in Fig. 8).

The vast majority of polymer electrolyte membrane fuel cell work has been performed using Nafion® as the electrolyte [146]. The proton conducting membrane allows the proton to rapidly transfer from the anode to the cathode whereas the wire which connects the two electrodes allows for electron transfer. The fuel oxidation at the anode and the reduction of oxygen which occurs at the cathode are shown [142].

The differences in the rates of reaction at the anode and cathode dictate the potential at which the cell can operate and the maximum current density. On the anode side, the challenge is to efficiently catalyze the oxidation of hydrogen or oxygenate fuels such as methanol, formic acid or ethanol. Unfortunately, the fuel sources are often contaminated by CO or other species that can poison the electrode surface. On the cathode side, the requirement is to effectively reduce oxygen, usually from air and to prevent the dissolution and loss of catalyst. The most active electrocatalytic materials are typically comprised of expensive transition metals nanoparticles such as Pt that are too costly to provide viable commercial solutions. Core–shell nanoparticles have of a very thin shell of the active Pt catalyst supported onto a second metal. To synthesize these systems, bimetallic nanoparticles are often leached in acid to remove the excess of the electro-dissolving non-noble element leaving the protective layer composed of the Pt or the Pt
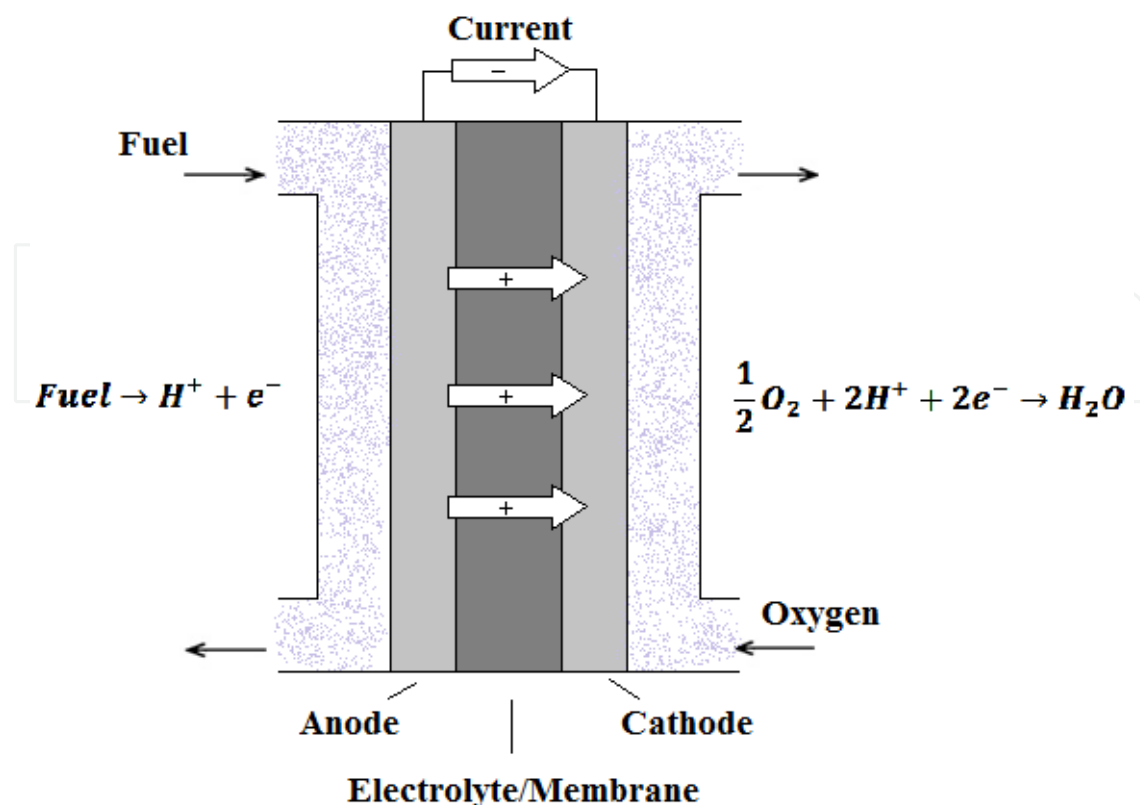
Figure 8. Schematic illustration of a fuel cell

enriched surface phase. In other words, the electro-dissolution creates de-alloyed Pt bimetallic catalysts that are composed of an inexpensive core element with platinum present only in the nanoparticle shell. This leaves the composition of the material in active usage and close to the nominal (started) alloyed/bimetallic specification [142].

4. Conclusion

Electrocatalysts are of ubiquitous importance and can be found in a large array of research fields and applications, including corrosion science, development of electroanalytical sensors, waste water treatment, electro-organic synthesis and energy conversion devices (e.g. batteries, fuel cells and solar cells). In the context of the increasing global energy demand and continuous depletion of fossil fuel-reserves, the exploitation of renewable carbon-neutral energy sources, such as sunlight, is one of the greatest scientific challenges of this century. The production of hydrogen through water splitting, either electrochemically or photochemically, seems to be a promising and sustainable solution to the storage of energy in a chemical and stable form, before converting it back into electricity, for example in a hydrogen-driven fuel cell. Electro-catalysis is the key enabling technology for these processes.

In recent years, research in electrocatalysis has experienced a significant progress mainly through the application of very modern research techniques and the use of improved electrode

materials. The widespread interest in nanostructured materials mainly originates from the fact that their properties (optical, electrical, mechanical and chemical performance) are usually different from those of the bulk materials. In addition, the development of high resolution instrumentation and new developments in analytical chemistry and electrochemical techniques permits the detailed characterization of atomic distribution, before, during, and after a reaction takes place, giving unprecedented information about the status of the catalyst during the reaction, and most importantly the time evolution of the exposed catalytic surfaces at the atomistic level.

In order to reduce the usage of precious metals and, thus, cost, the best possible performance has to be extracted from a given amount of catalyst. This involves mainly catalyst preparation, pretreatment, electrode preparation and, in the case of supported catalysts, also the choice of a suitable support. Tremendous progress has been made in developing preparation methods, carbon supports and down-selection approaches for catalysts in recent years. Several simple and tunable methods have shown a superior ability to synthesize state-of-the-art catalysts. Some new carbon materials have been demonstrated to be feasible as catalyst supports, although their applications still face some challenges in terms of synthesis, metal loading and electrode preparation. Combination of these advanced metal loading methods and excellent carbon supports could bring about a breakthrough in the exploration for a new generation of catalysts in the near future.

In addition, we predict that the efforts for the development of new catalysts with different characteristics will increasingly continue in the future too. Further improvements considering the exploration of these materials will help to commercialization of the fuel cells. We feel that there is a need for further works in the investigation of the effectiveness of these materials in the alternative areas as chemical catalyst, chemical sensor, and biological biosensor.

Author details

Metin Açıkyıldız[1], Ahmet Gürses[2], Mehtap Ejder Korucu[3] and Kübra Güneş[2]

1 Kilis Aralık University, Faculty of Science and Art, Dep. of Chemistry, Kilis, Turkey

2 Atatürk University, K.K. Education Faculty, Dep. of Chemistry Education, Erzurum, Turkey

3 Kafkas University, Faculty of Science and Literature, Dep. of Chemistry, Kars, Turkey

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