

Ethanol electrooxidation on the Co@Pt core-shell nanoparticles modified carbon-ceramic electrode in acidic and alkaline media

Biuck Habibi*, Serveh Ghaderi

Electroanalytical Chemistry Laboratory, Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran.

Article Information

Article History:

Received:

26 May 2016

Received in revised form:

07 July 2016

Accepted:

11 July 2016

Keywords

Co@Pt nanoparticles

Core-shell

Electrooxidation

Ethanol

Acidic media

Alkaline media

Abstract

In this study, the electrocatalytic activity of the Co@Pt core-shell nanoparticles toward the ethanol oxidation reaction has been investigated in detail by cyclic voltammetry and chronoamperometry in an acidic and alkaline media. The physicochemical data obtained in an alkaline solution were compared to those in an acidic solution. The obtained results demonstrate that while Co@Pt core-shell nanoparticles exhibit a good electrocatalytic performance for ethanol oxidation reaction in both media; the Co@Pt core-shell catalyst presents more catalytic activity (1.4 times), exchanges current densities (about 8 times), and high electrochemical active surface area (1.2 times) and stability (about 2 times) in the alkaline medium. The effect of some experimental factors such as electrolytes (H_2SO_4 and NaOH) and ethanol concentrations was studied and optimum conditions were suggested. From these points, we concluded that the ethanol oxidation reaction can be improved with an alkaline electrolyte and the oxidation reaction is highly dependent on the pH of the electrolyte. These results indicate that the system studied in the present work; Co@Pt core-shell nanoparticles on a carbon-ceramic electrode, is the most promising system for use in alkaline fuel cells.

1. Introduction

The global energy crisis, extending environmental problems, and their effects on our planet have been exacerbated in recent decades, and it is generally accepted that the energy required in our changing world should be achieved, as much as possible, through environmentally friendly means.

Electrocatalytic energy conversion plays a vital role in the development of sustainable technologies for decreasing consumption of fossil fuels and mitigating global warming [1, 2]. In this sense, fuel cell technology has been considered as an efficient route to solve the problem of the eventual exhaustion of fossil fuel. Fuel cells directly convert chemical energy to electrical energy with high efficiency and potentially

*Corresponding Author's Tel & Fax: +98-41 34327541
E-mail address: B.Habibi@azaruniv.ac.ir

low emission of pollutants. Therefore, fuel cells are receiving considerably attention from both science and industry [3-5]. The potential application of direct alcohol fuel cells (DAFCs) in portable electronic devices has been attracting increasing interest because of their high efficiency, low emissions and facile systems [6-9]. It is known that platinum (Pt) is widely used as a catalyst due to its catalytic effects on the alcohols oxidation reaction in DAFCs [10, 11]. The problems of Pt-based DAFCs commercialization are its high cost, scarcity of Pt and the release of poison after starting to work. Therefore, some studies have focused on the preparation of special nanostructures to continue and enhance Pt catalytic activity while dramatically decreasing the total mass of Pt necessary in electrocatalysts. A further step in the reduction of Pt in electrocatalysts is the synthesis of nanomaterials with core-shell structures with Pt as the shell of the nanostructure [12-14]. Core-shell nanostructures can be considered as a kind of phase separation of an alloy into a core surrounded by a shell composed of a metal [15, 16]. These nanostructures have two important features: First, a core-shell structure can leverage on the use of a low-cost metal core and a noble metal overlayer to substantially reduce the cost of the electrocatalysts. Second, pure Pt deposited on the surface of a non-Pt substrate displays significantly altered surface electrocatalytic activity [17-19].

In recent years, there has been considerable interest in the electrochemical oxidation of small organic molecules on core@shell-based electrocatalysts because of its potential utility in electrooxidation [20-24]. It has been shown that core@shell-based electrocatalysts have high activity and high stability in comparison with other electrocatalysts. On the other hand, from the point of the performance of the electrocatalysts in different aqueous electrolyte, acidic and alkaline, several papers have focused on comparative study of fuel oxidation in different electrolytes [25-27]. At the functional level, one of the primary differences between acidic and alkaline fuel cells is that the simple alcohols oxidation kinetic in alkaline fuel cells is superior to acidic fuel cells. Also, electrocatalysts in an alkaline media exhibited

higher catalytic activity in the alcohols oxidation reaction than those in an acidic media. Complete oxidation of fuel is difficult to achieve in acidic solutions, and so attention has been directed to higher pH [28, 29].

In our previous work [22], we successfully demonstrated the possibility of the fabrication of core-shell nanoparticles (Co@Pt) (sizes; 10-35 nm) with Co as the core and Pt as the shell. The obtained electrocatalyst, Co@Pt core-shell nanoparticles with a modified carbon-ceramic electrode (Co@Pt/CCE), was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS), X-ray diffraction (XRD) and cyclic voltammetry (CV). In that work, we proposed that the obtained results would open doors for further exploration of this electrocatalyst in the electrooxidation of other alcohols. So, based on the electrocatalytic behavior of Co@Pt nanoparticles toward ethylene glycol and glycerol oxidation [22], the electrocatalytic activity and stability of chemically prepared Co@Pt core-shell nanoparticles catalyst toward ethanol oxidation in acidic and alkaline solutions were investigated for the first time in the present study. It was found that the catalytic activity of Co@Pt core-shell nanoparticles for ethanol electrooxidation is a function of the type of electrolyte. Principally, this is the continuation of our previous work on the role of core-shell nanoparticles in fuel cell applications [22].

2. Experimental

2.1. Reagents and chemicals

Hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), cobalt (II) nitrate [$\text{Co}(\text{NO}_3)_2$], sodium borohydride (NaBH_4), ethanol, methanol, hydrochloric acid, sodium hydroxide, sulfuric acid and high purity graphite powder were obtained from Merck. Methyltrimethoxy silane (MTMOS) was from Fluka. All these substances were pure and required no further purification. All solutions were freshly prepared with double distilled water.

2. 2. Instrumentation

All electrochemical measurements were carried out in a conventional three-electrode electrochemical system at room temperature using an AUTOLAB PGSTAT-100 (potentiostat/ galvanostat) equipped with a USB electrochemical interface and controlled by GEPS software. A carbon-ceramic electrode (CCE) supported by a catalyst layer (Co@Pt nanoparticles) was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and the counter electrode, respectively.

2. 3. Synthesis of the Co @Pt nanoparticles

The Co@Pt nanostructures were prepared according to our previous work [22]. Briefly, the Co@Pt particles were synthesized using $\text{Co}(\text{NO}_3)_2$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as metallic precursors, and NaBH_4 as the reducing agent. Firstly, to obtain the Co cores, a solution of Co^{2+} ions was added dropwise into the solution containing the NaBH_4 at room temperature and magnetically stirred. The obtained product was separated and washed by centrifugation at 3000 rpm. Secondly, to obtain the core-shell nanoparticles (Co@Pt), the Co cores were suspended in a fresh solution of NaBH_4 and a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was slowly added under magnetically stirring, and then the mixture was stirred for 30 min. During this period, the color of the mixture gradually darkened from light green to dark black, indicating that Co@Pt nanoparticles had been formed.

2. 4. Preparation of the electrocatalyst

The sol-gel derived carbon-ceramic electrode (CCE) was used as the substrate for loading the electrocatalyst [30]. A carbon-ceramic electrode was constructed as in our previous works [31-33]. Firstly, a portion of 0.9 mL MTMOS was mixed with 0.6 mL methanol and 0.6 mL of 0.5 M HCl as the catalyst. The mixture was magnetically stirred until a homogeneous solution resulted. Next, 0.3 g graphite powder was added and the mixture was shaken for several minutes. Subsequently, the homogenized

mixture was tightly packed into a Teflon tube (with a 3.9 mm inner diameter and 10 mm length) and dried for at least 24 h at room temperature. A copper wire was inserted through the other end of the tube to set up electric contact. The CCE surface was polished with 1500 emery paper and rinsed with distilled water. Then, 20 mg of catalyst was ultrasonically suspended in a 5 mL solution containing 50 μL Nafion (5% wt) in double distilled water for 30 min to obtain a uniform ink. Finally, 5 μL of well-dispersed catalyst ink was transferred onto the top of a freshly polished CCE surface and allowed to dry under ambient condition.

3. Results and discussion

3. 1. Electrochemical characterization of Co@Pt nanoparticles

Fig. 1 shows the cyclic voltammograms (CVs) of Co@Pt/CCE in a 0.5 M H_2SO_4 and 0.5 M NaOH solution at the scan rate of 50 mV s^{-1} . The potential scan window is -0.4 to 1.3 V and -1.1 to 0.8 V (vs. SCE) for acidic (Fig. 1A) and alkaline (Fig. 1B) media, respectively. The CVs of Co@Pt/CCE in the acidic and alkaline media showed some differences: (I) the hydrogen adsorption/desorption peaks in the acid media were more well-defined than in the alkaline media. (II) The double-layer region in the alkaline electrolyte was not as wide and well-defined as the corresponding region in the acidic electrolyte due to OH^- adsorption in this region (around -0.6 V). The CV for the Co@Pt/CCE in the alkaline media confirmed that the formation of OH^-_{ad} initiated at Pt-H under the potential deposition (H_{upd}) region [34]. In the acidic media the potential region of the hydrogen adsorption/desorption that occurred with bisulfate desorption/adsorption was separated from the reversible/irreversible oxide formation by the double-layer region (around 0.0 V). In the alkaline media, however, the hydrogen desorption was immediately followed first with the reversible adsorption of OH^- and then by the irreversible oxide formation. (III) It is evident that the potential for OH^-_{ad} and the formation of Pt-oxide and its reduction

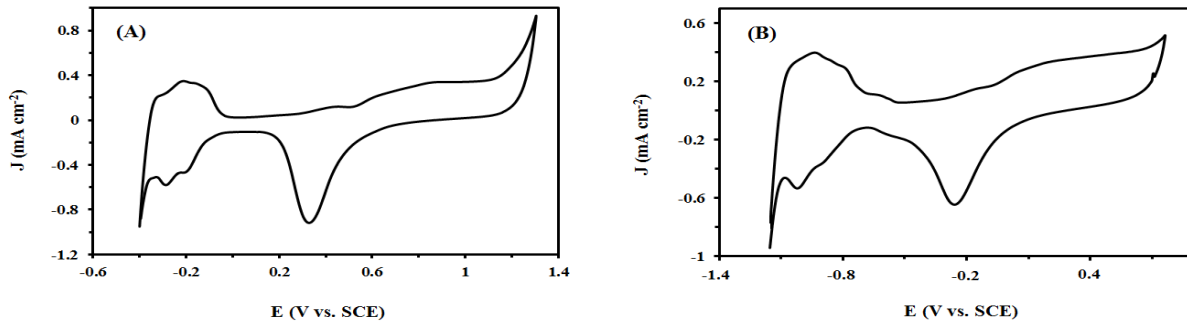


Fig. 1. Cyclic voltammograms of the Co@Pt/CCE catalyst in (A) 0.5 M H₂SO₄ electrolyte and (B) 0.5 M NaOH electrolyte at room temperature and at scan rate of 50 mV s⁻¹.

in alkaline was more negative than in the acidic media [35, 36].

The electrochemical active surface area (EASA) of the Co@Pt/CCE, which is an important factor in the characterization of an electrocatalyst, was measured by determining the coulombic charge associated with hydrogen adsorption/desorption. The anodic and cathodic peaks at the potential range from -0.4 to -0.1 V in the acidic media and -1.1 to -0.7 V in the alkaline media are due to the adsorption/desorption of hydrogen. The EASA was calculated from the following equation [10]:

$$\text{EASA (m}^2 \text{ g}^{-1} \text{ Pt)} = Q_{\text{H}} / [Q_{\text{ref}} \times \text{Pt loading}] \quad (1)$$

In which Q_{H} indicates the coulombic integrated charge associated with the hydrogen adsorption region (mC) and Q_{ref} has a corresponding value of 0.21 mC cm⁻², which is the charge for a monolayer adsorption of

hydrogen on surface of Pt. The EASA value for Co@Pt/CCE was 22.65 m² g⁻¹ and 27.32 m² g⁻¹ in the acidic and alkaline solutions, respectively. The origin of the high surface area in the alkaline solution was associated with the presence of OH_{ad}⁻ produced in the electroadsorption process with one electron exchanged between OH⁻ anions and the Pt surface [37].

3. 2. The electrocatalytic activity Co@Pt nanoparticles toward ethanol oxidation

To evaluate the electrocatalytic activity of Co@Pt/CCE in the acidic and alkaline media, cyclic voltammograms of ethanol oxidation were recorded in 0.5 M H₂SO₄ + 0.5 M ethanol solution and 0.5 M NaOH + 0.5 M ethanol solution at a scan rate of 50 mV s⁻¹. The currents were normalized to the EASA and are shown in Fig. 2. Looking up at the same time in both CVs reveals that; (I) The CV of

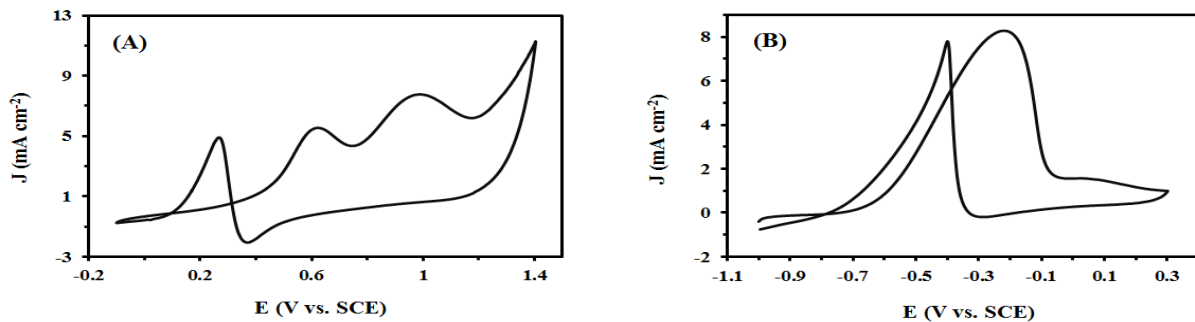


Fig. 2. Cyclic voltammograms of the Co@Pt/CCE catalyst in (A) 0.5 M ethanol + 0.5 M H₂SO₄ and (B) 0.5 M ethanol + 0.5 M NaOH at scan rate of 50 mV s⁻¹.

ethanol in the acidic media exhibited two oxidation peaks in the anodic going potential scan and one in the cathodic going sweep. The first peak in the CV for ethanol oxidation in the acidic media is explained by a two-path mechanism, with the formation of COads strongly bonded to the electrocatalyst substrate and also bulk oxidation. The second peak in the oxide region of the CVs in the acid solution was caused by the production of CO₂ and carboxylic acid [27]. In other words, for the electrooxidation of ethanol on the Pt-based electrocatalyst, the appearance of two peaks on the anodic sweep can be ascribed to the oxidation of the fuel by two kinds of chemisorbed oxygen species [38, 39]. In the negative-going potential sweep only one anodic peak appears and this is attributed to renewed oxidation of the fuel or related to ethanol adsorbates re-oxidation. It should be noted that this behavior is normal activity for ethanol and is similar to others reported works in acidic media [11, 24, 39]. While the CV of the same alcohol displays a single peak in both the anodic and cathodic going potential sweep, the oxidation peak current density of ethanol on the Co@Pt/CCE in the alkaline media is higher than that of the acidic media. The large peak in the reverse scan is ascribed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan. It can be concluded that the enhanced anodic peak current density and electrocatalytic activity on the Co@Pt/CCE catalyst in the alkaline solution might be due to the higher EASA. Many studies suggest that SO₄²⁻ adsorbed on the Pt surface would occupy the active sites leading to a decrease of active sites for ethanol adsorption, which explains the lower coverage shown in the acidic media [40].

The maximum catalytic activity was observed in the acidic electrolyte indicating that, in addition to OH_{ad}, co-adsorbing bisulfate anions may also play an inhibiting role in the kinetics of ethanol electrooxidation. In addition, the catalyst was more active at low over-potentials in the alkaline media than in the acidic media confirming the previous observation that at low over-potentials specific adsorption of bisulfate anions has an inhibiting effect either by blocking the adsorption of ethanol and/or

displacing OH_{ad} from the surface [35]. The accessibility of OH_{ad} at relatively low potentials might be the main reason for the higher activity toward the EOR in the alkaline electrolyte.

3. 3. Kinetic characterization and the scan rate effect

For the purpose of evaluation of the kinetic and mass transport properties of ethanol electrooxidation on the Co@Pt/CCE electrode, potentiodynamic polarization analysis and the relationship between the peak current density and the scan rate were employed. Tafel plots were used to examine the kinetic activity of the different modified electrodes. This type of plot has been widely used to understand the reaction mechanisms associated with rate-determining steps. Tafel areas in the polarization curves, recognized by the linear section from a plot of potential vs. log *J*, were analyzed to determine the Tafel slope, the exchange current density and the transfer coefficient. Tafel plots for the ethanol oxidation reaction on the Co@Pt/CCE electrode were obtained from the cyclic voltammograms in 0.5 M ethanol + 0.5 M supporting electrolyte in the potential interval from 0.1 to 0.3 V in the acidic media and -0.7 to -0.5 V in the alkaline media at a scan rate of 5 mV s⁻¹ as shown in Fig. 3.

Tafel behavior was analyzed under different conditions for the ethanol oxidation reaction in order to acquire insight concerning the electrochemical rate-determining steps at a number of different potentials. The rate-determining electron transfer step seems to vary with reaction conditions, type of supporting electrolyte, nature of the electrode surface, etc. The Tafel slopes for ethanol oxidation on the Co@Pt/CCE electrocatalyst were 134 mV dec⁻¹ and 111 mV dec⁻¹ in the acidic and alkaline media, respectively. The obtained Tafel slopes were close to the theoretical value of 120 mV dec⁻¹ ($\alpha = 0.50$), forecasted a one-electron transfer reaction as the rate-determining step. The value of the Tafel slope was lower in the alkaline electrolyte than the acidic electrolyte. This means that the charge-transfer kinetics of ethanol electrooxidation on the Co@Pt/CCE electrocatalyst in

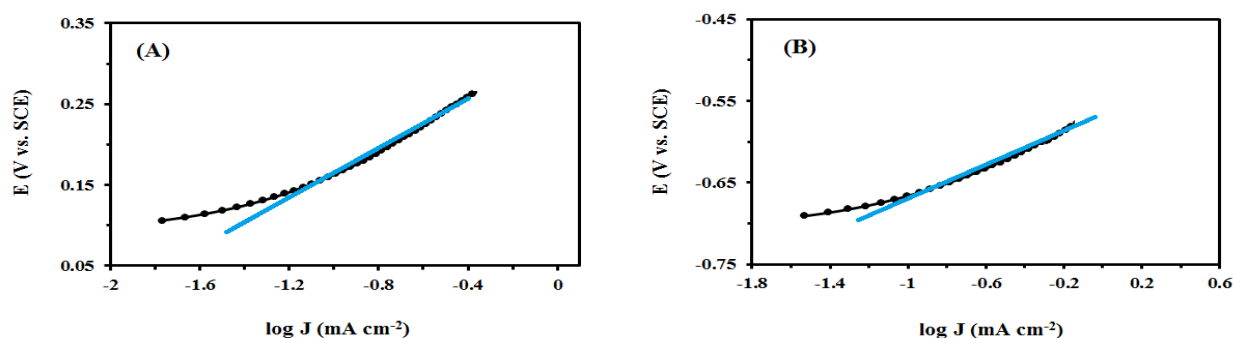


Fig. 3. Tafel plots of the Co@Pt/CCE catalyst in (A) 0.5 M ethanol + 0.5 M H₂SO₄ and (B) 0.5 M ethanol + 0.5 M NaOH at scan rate of 5 mV s⁻¹.

the alkaline solution is faster than the acidic solution. In addition, the values of $\alpha n'$ can be calculated. The values of $\alpha n'$ for the Co@Pt/CCE electrocatalyst were 0.44 and 0.53 in the acidic and alkaline medium, respectively. The intercept of the Tafel plot can be achieved by extrapolating the Tafel plot to the point where the overpotential equals zero. The intercept of the Tafel line is related to the $\log J_0$. The exchange current densities for ethanol oxidation were 3.9×10^{-5} mA cm⁻² and 31.6×10^{-5} mA cm⁻² in the acidic and alkaline electrolyte, respectively. A higher exchange current density for electrochemical reactions implies a faster electrode reaction, which is a main factor in effective electrocatalysts and suitable ethanol oxidation performance.

The charge-transfer kinetics of ethanol electrooxidation exhibited Tafel behavior for potentials in the rising area of the oxidation peak consistent with a one-electron

process in the rate-determining step. The rate-limiting step was recommended to be the electrochemical reaction between CO_{ad} and OH_{ad} at the edge of islands of OH, with competition between OH and CO adsorption for the released reaction sites. For catalytic kinetics, the Tafel plots for the electrooxidation of ethanol have been previously reported from cyclic voltammograms in the literature [41-43].

Variation of the anodic peak current density as a function of scan rate was given in Fig. 4. From this observation, it can be understood that the forward oxidation peak current density shifts positively with an increase in the scan rate. The anodic peak current densities are linearly proportional to the square root of the scan rate (see Fig. 5), which suggests that the kinetic of ethanol oxidation is much higher in the alkaline than in the acid solution, and the electrocatalytic oxidation of ethanol on the

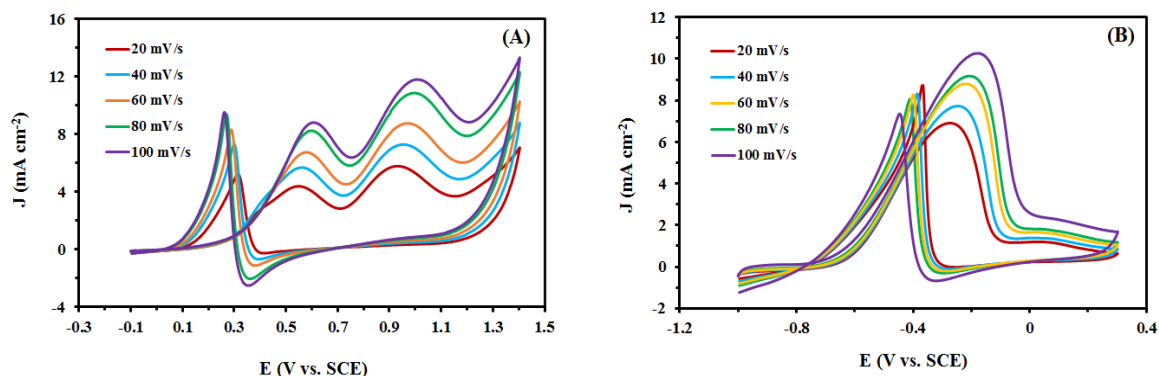


Fig. 4. Cyclic voltammograms of the Co@Pt/CCE catalyst in (A) 0.5 M ethanol + 0.5 M H₂SO₄ and (B) 0.5 M ethanol + 0.5 M NaOH at different scan rates (20, 40, 60, 80 and 100 mV s⁻¹).

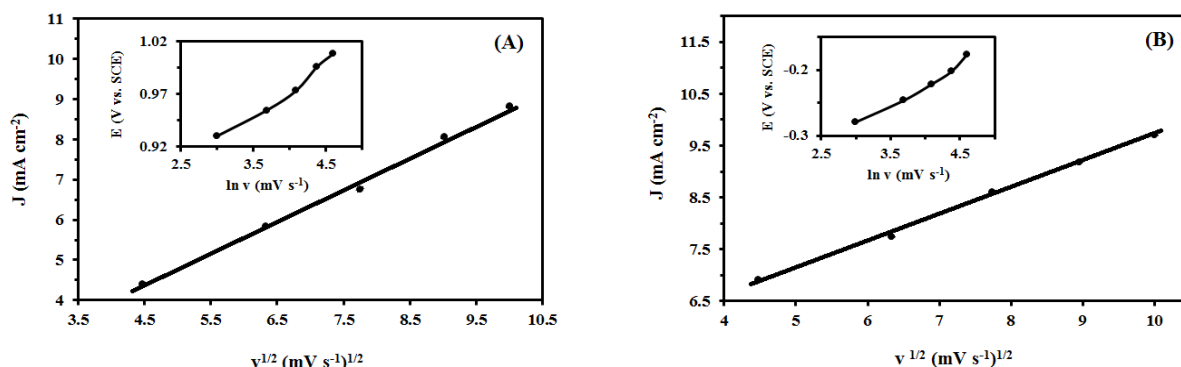


Fig. 5. Plot of the peak current density versus the square root of scan rate (The inset shows plot of E (V vs. SCE) versus the $\ln v$ (mV s^{-1})) in (A) 0.5 M ethanol + 0.5 M H_2SO_4 and (B) 0.5 M ethanol + 0.5 M NaOH.

Co@Pt/CCE is a diffusion-controlled process [44, 45]. In addition, the linear relationship between the peak current density and the square root of the scan rate confirmed that the oxidation of ethanol on the Co@Pt/CCE in both the acidic and alkaline media is an irreversible kinetic process. We can also see that the potential of different anodic and cathodic peaks vary with the increase of the scan rate. The relationship between the potential obtained from the forward CV scan and $\ln(v)$ is shown in the inset of Fig. 5. The results clearly reveal that the potential of the forward anodic peak increases when the scan rate increases and the anodic oxidation peak shifts to more positive potentials. Thus, there is linearly relationship between potential and $\ln(v)$ which indicates that the oxidation of ethanol is an irreversible electrode process [45].

3. 4. The effect of ethanol and electrolyte concentration

The importance of electrolyte and fuel concentration is also observed in this work. In order to assess the capacity of the Co@Pt/CCE catalyst against ethanol oxidation, the effect of different ethanol concentrations on the anodic peak current density was investigated. Different concentrations of ethanol in a certain concentration of electrolyte results in different cyclic voltammograms. The cyclic voltammetry responses of various ethanol concentrations are shown in Figs. 6 and 7. As can be clearly seen, by increasing the ethanol concentration, the peak current density increases and drops afterward in a concentration higher than 2 M in both the acidic and alkaline electrolyte. This

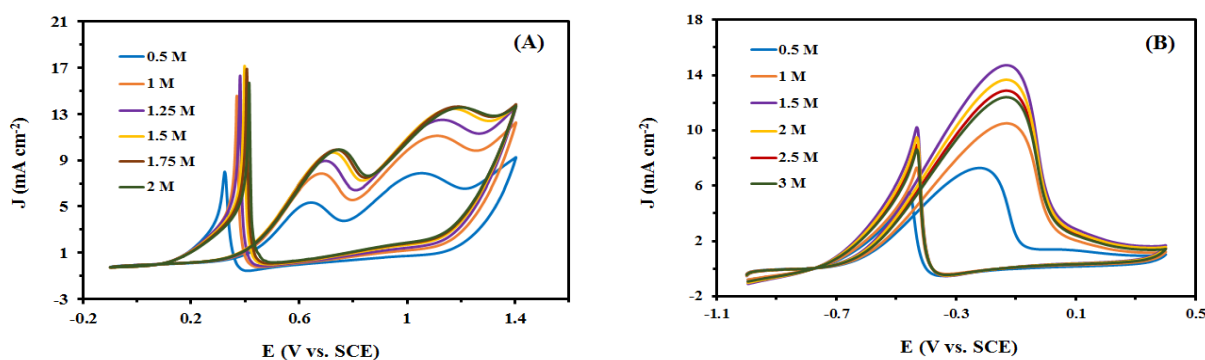


Fig. 6. Cyclic voltammograms of the Co@Pt/CCE catalyst in various fuel concentrations in (A) acidic media (0.5, 1, 1.25, 1.5, 1.75 and 2 M ethanol) and (B) alkaline media (0.5, 1, 1.5, 2, 2.5 and 3 M ethanol) at scan rate of 50 mV s^{-1} .

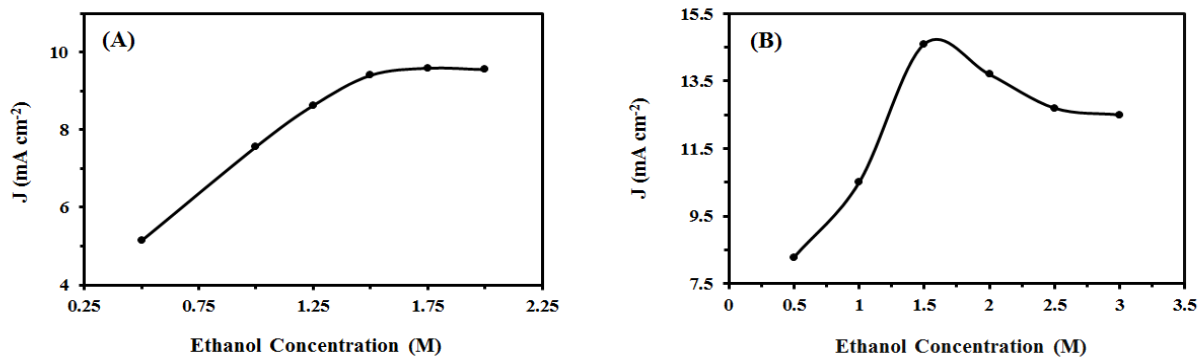


Fig. 7. Plot of the peak current density versus ethanol concentration in (A) acidic media and (B) alkaline media at scan rate of 50 mV s^{-1} .

effect might be due to the saturation of the Pt active sites by ethanol molecules and contamination of the electrocatalyst surface arising mainly from the CO_{ads} during the oxidation reaction.

The logarithmic plot of the peak current density of ethanol electrooxidation with different concentrations produces a straight line of a slope equal to the order of the reaction with respect to the ethanol concentration according to the relation [33]:

$$\text{Rate} \propto J = k C^n \quad (2)$$

$$\log J = \log k + n \log C \quad (3)$$

where J is the peak current density, k is the reaction rate constant, C is the bulk concentration and n is the reaction order. The slope of the curve of $\log J$ (mA cm^{-2}) versus $\log C$ (M) is 0.47 and 0.49 for ethanol in the acidic and alkaline electrolyte, respectively. Therefore, the reaction order of the ethanol oxidation reaction is about 0.47 and 0.49 on the Co@Pt/CCE electrode in the acidic and alkaline solution, respectively.

Electrocatalytic oxidation of ethanol on the Co@Pt/CCE catalyst in various H_2SO_4 concentrations is shown in Fig. 8 (A). For a certain content of ethanol, an increase of the H_2SO_4 concentration from 0.1 to 1.1 M leads to a decrease in the current density. This suggests that the acidic electrolyte is not as favorable as the alkaline electrolyte for the ethanol oxidation reaction. Cyclic voltammetry measurements

in different concentrations of NaOH were performed to examine the effect of the alkalinity of the solution on the oxidation reaction (see Fig. 8 (B)). The anodic peak showed an enhancement in current density when the NaOH concentration increased from 0.1 to 1.1 M. These results suggest that higher NaOH concentrations are desirable to obtain a good current density, and a low concentration of NaOH is not favorable for the ethanol oxidation reaction.

It is generally accepted that the electrooxidation of small organic compounds on metal electrodes occurs in the presence of reactive $\text{M}(\text{OH})_{\text{ads}}$ species formed by hydroxyl adsorption on the electrode surfaces. The pH effect is attributed to the competitive adsorption of oxygenated species with anions from the electrolyte. As a result, a more alkaline media is desirable for the oxidation reaction of such species [46].

3.5. Chronoamperometric study

One of the main problems preventing the development of direct alcohol fuel cells is the susceptibility of the reaction to self-poisoning, the main poisoning species being recognized as adsorbed CO. The adsorbed CO may also act as an intermediate, where some fraction of CO_{ads} can be further oxidized by oxygen-containing species. A chronoamperometric study was carried out for further evaluation of the catalytic activity and stability of the catalyst under a period of time in continuous operation. Chronoamperometric experiments were widely applied to examine the

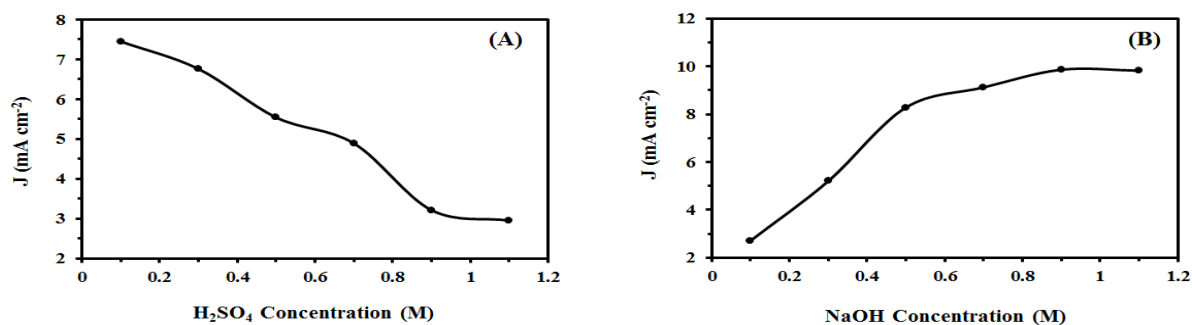


Fig. 8. Plot of the peak current density versus electrolyte concentration in (A) acidic media (0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 M H_2SO_4) and (B) alkaline media (0.1, 0.3, 0.5, 0.7, 0.9 and 1.1 M NaOH) at scan rate of 50 mV s^{-1} .

catalytic stability and reactive mechanism [47, 48]. Fig. 9 shows the chronoamperometric curves of 0.5 M ethanol + 0.5 M H_2SO_4 solution and 0.5 M ethanol + 0.5 M NaOH solution on the Co@Pt/CCE electrode at 0.6 V and -0.2 V for 1500 s, respectively. An initial fast current density decay in the chronoamperometry curves was possibly due to electrocatalyst poisoning by CO-like intermediate species generated during the continuous oxidation process. A further gradual decay of current density with time implies that the catalyst has a good anti-poisoning ability [49]. During the whole procedure, the Co@Pt/CCE catalyst in the alkaline electrolyte displayed a higher current density and lower rate of current density decay than that in the acidic electrolyte. On the other hand, the results exhibit that the presence of reactive $\text{M}(\text{OH})_{\text{ad}}$ species in alkaline solution improves the tolerance of Co@Pt

nanoparticles against poisoning species, such as CO and CO-like intermediates, thus enhancing the catalytic activity and the stability of Co@Pt nanoparticles. Finally, to compare the electrocatalytic performance of Co@Pt/CCE toward ethanol oxidation in an alkaline solution with other electrocatalysts in same conditions, electrochemical parameters obtained in this work and others studies are listed in Table 1. Table 1 confirms that Co@Pt/CCE exhibits better or comparable catalytic performance than other reported electrocatalysts toward ethanol oxidation in an alkaline solution. These results show that Co@Pt/CCE exhibits a promising catalytic behavior toward ethanol oxidation and also demonstrates that Co@Pt nanoparticles, by providing a bimetallic core-shell nanostructure and reducing the loading of expensive noble metals, improve Pt utilization efficiency.

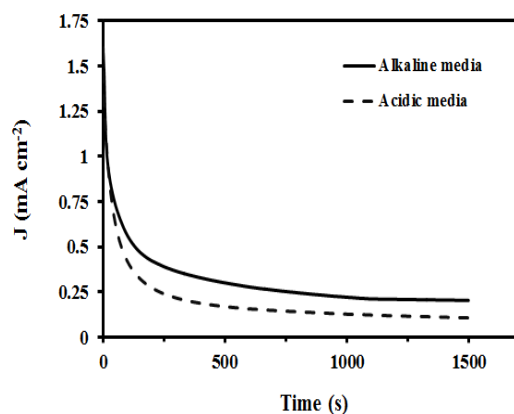


Fig. 9. Chronoamperometry curves for the Co@Pt/CCE catalyst in (A) 0.5 M ethanol + 0.5 M H_2SO_4 solution at 0.6 V and (B) 0.5 M ethanol + 0.5 M NaOH solution at -0.2 V.

4. Conclusion

In this study, the electrochemical manner of the modified CCE was studied for ethanol oxidation reaction in acidic and alkaline media using cyclic voltammetry and chronoamperometry techniques. The cyclic voltammetry response of the Co@Pt/CCE catalyst during EOR showed differences in acidic and alkaline solutions. The concentration of ethanol and the supporting electrolyte also affected the reaction. High electrocatalytic activity and stability were obtained in the alkaline solution and a higher alkalinity was favorable to the reaction. As a conclusion, the better

Table 1: Comparison of different electro catalysts in electro oxidation of the ethanol in acidic and alkaline medium.

Electrocatalyst	E_{onset}	$E_{\text{a Forward}}$	J_{acidic} (mA cm ⁻²)	J_{alkaline} (mA cm ⁻²)	$J_{\text{aforward}}/J_{\text{abacward}}$	Ref.
FeCo@Fe@Pd	-0.71	-0.28	-	3.93	1.24	24
PdSnAg	-0.52	-0.17	-	3.37	1.49	50
PdSnNi	-0.50	-0.20	-	2.23	1.36	50
PdNi	-0.48	-0.14	-	0.69	0.69	51
PdCo	-0.59	-0.16	-	8.76	0.86	51
Ru@PtPd	-0.56	-0.15	-	3.6	1.50	52
PdNiCeO	-0.4	0.15	-	5.3	1.4	53
Te@Au	-0.35	0.3	-	12	6	54
Pt/C	0.34	0.64	3.3	-	1.75	55
PtMn	0.32	0.66	5.3	-	1.78	55
PtRu/graphite	0.35	0.64	7.50	-	1.52	56
PtSn	0.4	0.8	0.08	-	0.9	57
Pt/C	0.96	0.64	1.85	-	0.6	58
Pt/C	0.41	0.9	1.75	-	0.61	59
Co@Pt	0.26	0.59	6.12	-	1.65	This work
Co@Pt	-0.56	-0.21	-	8.48	1.1	This work

EOR activity of Co@Pt/CCE in the alkaline solution is ascribed to faster ethanol adsorption and the availability of oxygen-containing species. Since the use of alkaline electrolyte also enhances the kinetics of the EOR, alkaline fuel cells may prove to be superior to acidic fuel cells, particularly with the use of Co@Pt/CCE electrocatalyst, as exhibit by the present study. Hence, the prepared Co@Pt core-shell nanoparticles have a potential application in electrochemical devices such as fuel cells. These nanoparticles have clear structural advantages in phrases of unique catalytic properties, simple and clean processing and saving expensive metals, which recommend their potential for use in fuel cells. We believe that the concept of a core-shell structure as well as the fabrication technique can not only be used for fuel cells but also potentially extended to other fields such as electro-chemical sensing and photo-electrochemistry.

Acknowledgment

The authors gratefully acknowledge the Research Council of Azarbaijan Shahid Madani University for financial support.

5. References

- [1] Lund H., "Renewable energy strategies for sustainable development", Energy, 2007, 32: 912.
- [2] Herring H., "Energy efficiency-a critical view", Energy, 2006, 31: 10.
- [3] O'Hayre R.P., Cha S.W., Colella W.G., Prinz F.B., "Fuel cell fundamentals", JOHN WILEY & SONS, INC, 2006.
- [4] Srinivasan S., "Fuel cells: from fundamentals to applications", Springer, 2006.
- [5] Wilberforce T., Alaswad A., Palumbo A., Dassisti M., "Advances in stationary and portable fuel cell applications", Int. J. Hydrogen Energy, In Press, 2016.
- [6] Carrette L., Friedrich K.A., Stimming U., "Fuel Cells: Principles, Types, Fuels, and Application", Chem. Phys. Chem, 2000, 4: 162.
- [7] Dyer C.K., "Fuel cells for portable applications", J. Power Sources, 2002, 106: 31.

- [8] Chan S.H., Low C.F., Ding O.L., "Energy and exergy analysis of simple solid-oxide fuel-cell power systems", *J. Power Sources*, 2002, 103: 188.
- [9] Akhairy M.A.F., Kamarudin S.K., "Catalysts in direct ethanol fuel cell (DEFC): An overview", *Int. J. Hydrogen Energy*, 2016, 41: 4214
- [10] Camacho B.R., Morais C., Valenzuela M.A., Alonso-Vante N., "Enhancing oxygen reduction reaction activity and stability of platinum via oxide-carbon composites", *Catal. Today*, 2013, 202: 36.
- [11] Divya P., Ramaprabhu S., "Platinum nanoparticles supported on a bi-metal oxide grown carbon nanostructure as an ethanol electro-oxidation electrocatalyst", *J. Mater. Chem. A*, 2013, 1: 13605.
- [12] Luo J., Wang L., Mott D., Njoki P.N., Lin Y., He T., Xu Zh., Wanjana B.N., Lim I.-Im S., Zhong Ch. J., "Core@Shell Nanoparticles as Electrocatalysts for Fuel Cell Reactions", *Adv. Mater.*, 2008, 20: 4342.
- [13] Oezaslan M., Hasché F., Strasser P., "Pt-Based Core-Shell Catalyst Architectures for Oxygen Fuel Cell Electrodes", *J. Phys. Chem. Lett.*, 2013, 4: 3273.
- [14] Adzic R., Zhang J., Mo Y., Vukmirovic M., "Platinum-coated non-noble metal-noble metal core-shell electrocatalysts", US Patent 9005331 B2, 2015.
- [15] Zhong C.J., Maye M.M., "Core-shell assembled nanoparticles as catalysts", *Adv. Mater.*, 2001, 13: 1507.
- [16] Zhang Q., Lee I., Joo J.B., Zaera F., "Core-Shell Nanostructured Catalysts", *Acc. Chem. Res.*, 2013, 46: 1816.
- [17] Lu X., Luo F., Song H., Liao Sh., Li H., "Pulse electrodeposition to prepare core-shell structured AuPt@Pd/C catalyst for formic acid fuel cell application", *J. Power Sources*, 2014, 246: 659.
- [18] Zhang M., Yan Z., Xie J., "Core/shell Ni@Pd nanoparticles supported on MWCNTs at improved electrocatalytic performance for alcohol oxidation in alkaline media", *Electrochim. Acta*, 2012, 77: 237.
- [19] Chaudhuri R.G., Paria S., "Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications", *Chem. Rev.*, 2012, 112: 2373.
- [20] Lin R., Cao Ch., Zhao T., Huang Zh., Li B., Wieckowski A., Ma J., "Synthesis and application of core-shell Co@Pt/C electrocatalysts for proton exchange membrane fuel cells", *J. Power Sources*, 2013, 223: 190.
- [21] Zhu H., Luo M., Zhang Sh., Wei L., Wang F., Wang Zh., Wei Y., Han K., "Combined method to prepare core-shell structured catalyst for proton exchange membrane fuel cells", *Int. J. Hydrogen Energy*, 2013, 38: 3323.
- [22] Habibi B., Ghaderi S., "Synthesis, characterization and electrocatalytic activity of Co@Pt nanoparticles supported on carbon-ceramic substrate for fuel cell applications", *Int. J. Hydrogen Energy*, 2015, 40: 5115.
- [23] Zhao Y., Wang Y., Dong L., Zhang Y., Huang J., Zang J., Lu J., Xu X., "Core-shell structural nanodiamond@TiN supported Pt nanoparticles as a highly efficient and stable electrocatalyst for direct methanol fuel cells", *Electrochim. Acta*, 2014, 148: 8.
- [24] Fashedemi O.O., Ozoemena K.I., "Comparative electrocatalytic oxidation of ethanol, ethylene glycol and glycerol in alkaline medium at Pd-decorated FeCo@Fe/C core-shell nanocatalysts", *Electrochim. Acta*, 2014, 128: 279.
- [25] Spendelow J.S., Lu G.Q., Kenis P.J.A., Wieckowski A., "Electrooxidation of adsorbed CO on Pt(111) and Pt(111)/Ru in alkaline media and comparison with results from acidic media", *J. Electroanal. Chem.*, 2004, 568: 215.
- [26] Pandey R.K., Lakshminarayanan V., "Electro-Oxidation of Formic Acid, Methanol, and Ethanol on Electrodeposited Pd-Polyaniline Nanofiber Films in Acidic

- and Alkaline Medium”, *J. Phys. Chem. C*, 2009, 113: 21596.
- [27] Chen S., Schell M., “A comparison of multistability in the electrocatalyzed oxidations of methanol and ethanol in acid and alkaline solutions”, *J. Electroanal. Chem.*, 1999, 478:108.
- [28] Spendelow J.S., Wieckowski A., “Electrocatalysis of oxygen reduction and small alcohol oxidation in alkaline media”, *Phys. Chem. Chem. Phys.*, 2007, 9: 2654.
- [29] Cohen J.L., Volpe D.J., Abruña H.D., “Electrochemical determination of activation energies for methanol oxidation on polycrystalline platinum in acidic and alkaline electrolytes”, *Phys. Chem. Chem. Phys.*, 2007, 9: 49.
- [30] Tsionsky M., Gun G., Giezer V., Lev O., “Sol-Gel-Derived Ceramic-Carbon Composite Electrodes: Introduction and Scope of Applications”, *Anal. Chem.*, 1994, 66: 1747.
- [31] Habibi B., Dadashpour E., “Carbon-ceramic supported bimetallic Pt–Ni nanoparticles as an electrocatalyst for electrooxidation of methanol and ethanol in acidic media”, *Int. J. Hydrogen Energy*, 2013, 38: 5425.
- [32] Habibi B., Delnavaz N., “Carbon-ceramic supported bimetallic Pt–Ni nanoparticles as an electrocatalyst for oxidation of formic acid”, *Int. J. Hydrogen Energy*, 2011, 36: 9581.
- [33] Habibi B., Mohammadyari S., “Palladium nanoparticles/nanostructured carbon black composite on carbon–ceramic electrode as an electrocatalyst for formic acid fuel cells”, *J. Taiwan Inst. Chem. E.*, 2016, 58: 245.
- [34] Schmidt T.J., Ross P.N., Markovic N.M., “Temperature-Dependent Surface Electrochemistry on Pt Single Crystals in Alkaline Electrolyte: Part 1: CO Oxidation”, *J. Phys. Chem. B*, 2001, 105: 12082.
- [35] Tripkovic A.V., Popovic K.D., Grgur B.N., Blizanic B., Ross P.N., Markovic N.M., “Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions”, *Electrochim. Acta*, 2002, 47: 3707.
- [36] Tripkovic A.V., Popovic K.D., Lovic J.D., “Kinetic study of methanol oxidation on Pt₂Ru₃/C catalyst in the alkaline media”, *J. Serb. Chem. Soc.*, 2007, 72: 1095.
- [37] Tripkovi A. V., Popovi K. Dj., Lovi J. D., Jovanovi V. M., Kowal A., “Methanol oxidation at platinum electrodes in alkaline solution: comparison between supported catalysts and model systems”, *J. Electroanal. Chem.*, 2004, 572: 119.
- [38] Vielstich W., “Fuel Cells: Modern Processes for the Electrochemical Production of Energy”, Wiley-Interscience, 1968.
- [39] Oliveira R.T.S., Santos M.C., Marcussi B.G., Tanimoto S.T., Bulhões L.O.S., Pereira E.C., “Ethanol oxidation using a metallic bilayer Rh/Pt deposited over Pt as electrocatalyst”, *J. Power Sources*, 2006, 157: 212.
- [40] Jing M., Jiang L., Yi B., Sun G., “Comparative study of methanol adsorption and electro-oxidation on carbon-supported platinum in acidic and alkaline electrolytes”, *J. Electroanal. Chem.*, 2013, 688: 172.
- [41] Suffredini H.B., Tricoli V., Vatistas N., Avaca L.A., “Electro-oxidation of methanol and ethanol using a Pt–RuO₂/C composite prepared by the sol-gel technique and supported on boron-doped diamond”, *J. Power Sources*, 2006, 158: 124.
- [42] He Q., Chen W., Mukerjee S., Chen Sh., Laufek F., “Carbon-supported PdM (M = Au and Sn) nanocatalysts for the electrooxidation of ethanol in high pH media”, *J. Power Sources*, 2009, 187: 298.
- [43] Bai Y., Wu J., Xi J., Wang J., Zhu W., Chen L., Qiu X., “Electrochemical oxidation of ethanol on Pt–ZrO₂/C catalyst”, *Electrochem. Commun.*, 2005, 7: 1087.
- [44] Wang H., Jusys Z., Behm R.J., “Ethanol Electrooxidation on a Carbon-Supported Pt Catalyst: Reaction Kinetics and Product Yields”, *J. Phys. Chem. B*, 2004, 108: 19413.

- [45] Liu J., Ye J., Xu Ch., Jiang S.P., Tong Y., "Kinetics of ethanol electrooxidation at Pd electrodeposited on Ti", *Electrochem. Commun.*, 2007, 9: 2334.
- [46] Jin Ch., Song Y., Chen Zh., "A comparative study of the electrocatalytic oxidation of ethylene glycol on PtAu nanocomposite catalysts in alkaline, neutral and acidic media", *Electrochim. Acta*, 2009, 54: 4136.
- [47] Abbaspour A.k., Norouz-Sarvestani F., "High electrocatalytic effect of Au-Pd alloy nanoparticles electrodeposited on microwave assisted sol-gel-derived carbon ceramic electrode for hydrogen evolution reaction", *Int. J. Hydrogen Energy*, 2013, 38: 1883.
- [48] Wang X-M., Xia Y-Y., "The influence of the crystal structure of TiO₂ support material on Pd catalysts for formic acid electrooxidation", *Electrochim. Acta*, 2010, 55: 851.
- [49] Zang J., Dong L., Jia Y., Pan H., Gao Zh., Wang Y., "Core-shell structured SiC@C supported platinum electrocatalysts for direct methanol fuel cells", *Appl. Catal. B Environ.*, 2014, 144: 166.
- [50] Zhu F., Wang M. He Y., Guanshui M., Zhang Zh., Wang X., "A comparative study of elemental additives (Ni, Co and Ag) on electrocatalytic activity improvement of PdSn-based catalysts for ethanol and formic acid electro-oxidation", *Electrochim. Acta*, 2014, 148: 291.
- [51] Wang X., Ma G., Zhu F., Lin N., Tang B., Zhang Zh., "Preparation and characterization of micro-arc-induced Pd/TM (TM =Ni, Co and Ti) catalysts and comparison of their electrocatalytic activities toward ethanol oxidation", *Electrochim. Acta*, 2013, 114: 500.
- [52] Gao H., Liao Sh., Liang Zh., Liang H., Luo F., "Anodic oxidation of ethanol on core-shell structured Ru@PtPd/C catalyst in alkaline media". *J. Power Sources*, 2011, 196 :6138.
- [53] Wei Y.-C., Liu C.-W., Kang W.-D., Lai C.-M., Tsai L.-D., Wang K.-W., "Electro-catalytic activity enhancement of Pd-Ni electrocatalysts for the ethanolelectro-oxidation in alkaline medium: The promotional effect of CeO₂ addition", *J. Electroanal. Chem*, 2011, 660: 64.
- [54] Jin H., Wang D., Zhao Y., Zhou H., Wang Sh., Wang J., "Fabrication of Te@Au core-shell hybrids for efficient ethanol oxidation", *J. Power Sources*, 2012, 215: 227.
- [55] Ammam M., Easton E. B., "Quaternary PtMnCuX/C (X = Fe, Co, Ni, and Sn) and PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloys catalysts: Synthesis, characterization and activity towards ethanol electrooxidation", *J. Power Sources*, 2012, 215: 188.
- [56] Dong L., Gari R. R. S., Li Zh., Craig M. M., Hou Sh., "Graphene-supported platinum and platinum-ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation", *Carbon*, 2010, 48: 781.
- [57] Jiang L., Hsu A., Chu D., Chen R., "Ethanol electro-oxidation on Pt/C and PtSn/C catalysts in alkaline and acid solutions", *Int. J. Hydrogen Energy*, 2010, 35: 365.
- [58] Bayer D., Berenger S., Joos M., Cremers C., J. Tubke, "Electrochemical oxidation of C₂ alcohols at platinum electrodes in acidic and alkaline environment", *Int. J. Hydrogen Energy*, 2010, 35: 12660.
- [59] Lamy C., Belgsir E.M, Leger J-M, "Electrocatalytic oxidation of aliphatic alcohols: Application to the direct alcohol fuel cell (DAFCs)", *J. Applied electrochem.*, 2001, 31: 799.