

RESEARCH PAPER

Kinetic Study of Ethanol and Methanol Electro-oxidation on Pd-vulcan XC-72R/Cu Electrocatalyst in Alkaline Media

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ARTICLE INFO

Article History:

Received 14 February 2019

Accepted 27 May 2019

Published 01 July 2019

Keywords:

Direct Alcohol Fuel Cell

Electro-Oxidation

Ethanol

Kinetics

Methanol

ABSTRACT

In this study, palladium nano-particles were electrodeposited galvanostatically on carbon black powder (Vulcan XC-72R). The catalytic activity for electro-oxidation of ethanol and methanol in alkaline media were studied by cyclic voltammetry and linear sweep voltammetry techniques. The results indicated that the electro-oxidation of ethanol and methanol strongly depends on adsorbed species on the electrocatalyst layer. Effects of ethanol, methanol and KOH concentration on the electrocatalytic properties of the synthesized electrocatalysts during electro-oxidation reactions were evaluated by linear sweep voltammetry with various scan rates. The overall rate equations for ethanol electro-oxidation and methanol electro-oxidation on Palladium /Vulcan in alkaline media were developed. It has been shown that the Pd-C particles with mass loading of 0.11 mg cm^{-2} have superior catalytic activity. Finally, two overall rate equations were developed for EOR and MOR.

How to cite this article

Zar M, Tabaian H, Omidvar H, Saberi Mehr A, Hosseinzadeh G.. Kinetic Study of Ethanol and Methanol Electro-oxidation on Pd-vulcan XC-72R/Cu Electrocatalyst in Alkaline Media. J Nanostruct, 2019; 9(3): 539-546. DOI: 10.22052/JNS.2019.03.015

INTRODUCTION

In recent years, the application of direct alcohol fuel cells (DAFCs) is highly regarded as a promising renewable energy source. Alcohols have significant advantages compared to hydrogen such as lower price and less fuel storage problems. Ethanol and methanol are the most common fuels for using in DAFCs. They can be easily produced from fermentation of biomasses and sugar-containing raw material [1-5].

Ethanol and methanol electro-oxidation reactions have more efficiency in alkaline than acidic media. Yet, the low rate of electro-oxidation reactions is one of the main problems in the application of direct alcohol fuel cells, which leads to an increase in their kinetic studies [6-7]. The output power densities of DAFCs are significantly influenced by the kinetics of anode electrode,

especially by the ethanol and methanol electro-oxidation reactions (EOR & MOR). There are many different catalysts that can be utilized to improve the kinetics of electro-oxidation reactions in DAFCs [8-9] and to reduce the overpotential of both the anode and cathode electrodes. Pt-based nanoparticles widely used as electrocatalyst in fuel cells but because of their high cost and scarcity, non-Pt metal catalysts have received special interest [10,11]. Among the various non-Pt catalysts, Pd-based nanoparticles, due to their lower cost and abundance have attracted the interest of researchers in recent years. Moreover, Pd-base catalysts represent higher activity and better steady-state performance compared to Pt-based catalysts in alkaline media for EOR and MOR [12, 13]. Another effective parameter to increase the reaction rate in fuel cells is the

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choice of electrocatalyst support. Vulcan XC-72R is a well-known carbonaceous catalyst support for DAFCs anode electrocatalyst with good electrical conductivity and catalyst-support interaction and most importantly high specific surface area (SSA ~ 250 m² g⁻¹) [14-16].

Most recently, studies on electro-oxidation of ethanol and methanol on Pt-based and non-Pt based catalysts especially Pd-based catalysts have done [17]. Liu et al. has studied the kinetics of ethanol electro-oxidation on Pd nanoparticles electrodeposited on Ti. They measured the diffusion coefficient of ethanol (4×10^{-5} cm².s⁻¹ at 298K), anodic transfer coefficient ($\alpha = 0.1$) and reaction order of OH⁻ and ethanol (0.2 and 1.0 respectively) and finally represented the overall rate equation for EOR on Pd/Ti electrode in alkaline media [18]. Tripkovic et al. found that the activity of Pt-based catalysts deposited on carbon black support for MOR strongly depends on the pH of the solution and temperature [19]. The kinetics of MOR at PtRu has investigated by Vidakovic et al. Using the absorption models such as Langmuir and Frumkin [20].

Highly dispersed Pd nanoparticles on carbon black were successfully synthesized by Hu et al. This study represented that Pd/CB catalyst shows unexceptionable properties for both EOR and MOR in alkaline media [21]. M. Jing et al. studied on MOR over carbon-supported Pt nanoparticles. Their results showed that the rate constant for methanol adsorption in alkaline media is significantly greater than that in acidic media. They also measured the reaction order and activation energy of MOR in acidic and alkaline media by using the CV diagrams and polarization curves of MOR [22]. Pd on Vulcan XC-72 nanocatalyst (2-4 nm) with high activity and good stability was synthesized by microwave heating-glycol reduction method for ethanol electrooxidation. F. Zhang et al. by using the cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy and single cell performance methods, studied on adsorbed intermediates on Pd/C during the ethanol electrooxidation. Their results showed that the adsorption behavior beings from the maximum catalysis of electro-catalysis and ends in the formation of the Palladium (II) oxide layer on the electrocatalyst surface [23].

The present article reveals that Pd-based electrocatalyst can be effective catalyst for ethanol and methanol electro-oxidation in alkaline media

for DAFCs. For improving the performance of direct alcohol fuel cells, it is essential to development of knowledge and studies on kinetic parameters. Furthermore the aim of this work is to calculate the main kinetic parameters including reaction order of ethanol, methanol, alkaline agent, rate constant and diffusion coefficient of ethanol and methanol during of EOR and MOR on Pd-based electrocatalyst. Finally, the presented whole rate equation for ethanol and methanol electro-oxidation in alkaline media, can be useful for best understanding the key role of kinetic parameters in DEFCs and DMFCs.

MATERIALS AND METHODS

PdCl₂, NH₄Cl, KOH, ethanol 99.9%, methanol 99.9% and Isopropanol 99.9% from Merck were prepared. Epoxy-Resin (C₃H₅₀[C₁₈H₁₉O₃]_nC₁₈H₁₉O₃), Cu (wire, 99%) and active carbon black powder (Vulcan XC-72R by Cabot Crop) used as support in the working electrode. All solutions were prepared with double-distilled water.

Preparation of Substrate layer

The carbon substrate for Pd nanoparticles electrodeposition was prepared by brushing method. In the first step, 2ml resin and 15ml isopropanol were mixed by mechanical stirrer and then 200 mg active carbon black powder (Vulcan XC-72R, Cabot Corp.) was added. For achieving a uniform ink, the solution was mixed for 15 min. The obtained mixture was put in an oven in different temperatures and times according to the Table 1. to reach a viscous past to coat on copper wire substrate (D= 0.4 mm, H= 70 mm). After uniform immersion of wire in mentioned ink, the copper wire again was put in an oven to dry the Epoxy-Resin. The process of drying was also done in different temperatures and times as indicated in Table 2.

Table 1. The steps of preparing the past-form carbon black powder ink

Step	Time (min)	Temperature (°C)
1	60-90	50
2	60-90	60
3	60-120	70

Table 2. The steps of drying the carbon black powder ink

Step	Time (min)	Temperature (°C)
1	10	110
2	20	120
3	20	150
4	30	170
5	30	180

Electrocatalyst Synthesis

Constant current method was accomplished to synthesize of electrocatalyst layer. 5 mA cm⁻² constant current density was applied within 2000s. The Pd loading was estimated to be 0.11 mg cm⁻² based on Faraday's law with 20% current efficiency. A solution containing 1mM PdCl₂ and 1M NH₄Cl was used as deposition bath. For this purpose, an electrochemical cell with undivided compartments consist of electrocatalyst as working electrode was used. It is estimated that the choice of Cu as substrate for support layer can lead to give the high current density of EOR and MOR in alkaline media and improve the kinetics of electro-oxidation reactions, because of its high electrical conductivity. In the other hand uniform distribution of Vulcan XC-72R on the copper surface might leads to increase the corrosion resistance of Cu.

Electrochemical measurement

Cyclic voltammetry and liner sweep test were performed in order to find the influences of alcohol and KOH concentrations on EOR and MOR by using the Autolab equipment (PGSTAT 302 N). During the all of tests, electrocatalyst, stainless steel and Ag/AgCl were used as working, counter and reference electrode, respectively. All experiments were performed in a conventional three electrode

electrochemical cell at room temperature.

The sweep rate during all tests was 5 mV/s. The start potentials in CV tests were selected based on Open Circuit Potential (OCP) of the electrocatalyst vs. Ag/AgCl and potential range were selected based on potentials related to ethanol and methanol oxidation [23-26].

Characterization instruments

The X-ray diffraction patterns of Pd nanoparticles were obtained using an X-ray diffractometer (XRD, Philips X'pert MPD.Pro) with a Cu K α radiation ($\lambda = 0.15406$ nm). The morphology and the particle size of the electrodeposited Pd nanoparticles were characterized by scanning electron microscopy (SEM, MIRA3 TESCAN) and transmission electron microscopy (TEM, Philips CM30 300 kV).

RESULTS AND DISCUSSION

Characterization of Pd nanoparticles

Fig. 1a shows the SEM image of the deposited Pd nanoparticles. As can be seen, the electrocatalyst surface consists of well distributed spherically Pd nanoparticles with an approximate average size of about 50 nm, furthermore, the prepared nanoparticles were agglomerated to some extent at the surface of substrate. Spherical shape of the deposited Pd nanoparticles clearly can be seen in the TEM image (Fig. 1b), the estimated

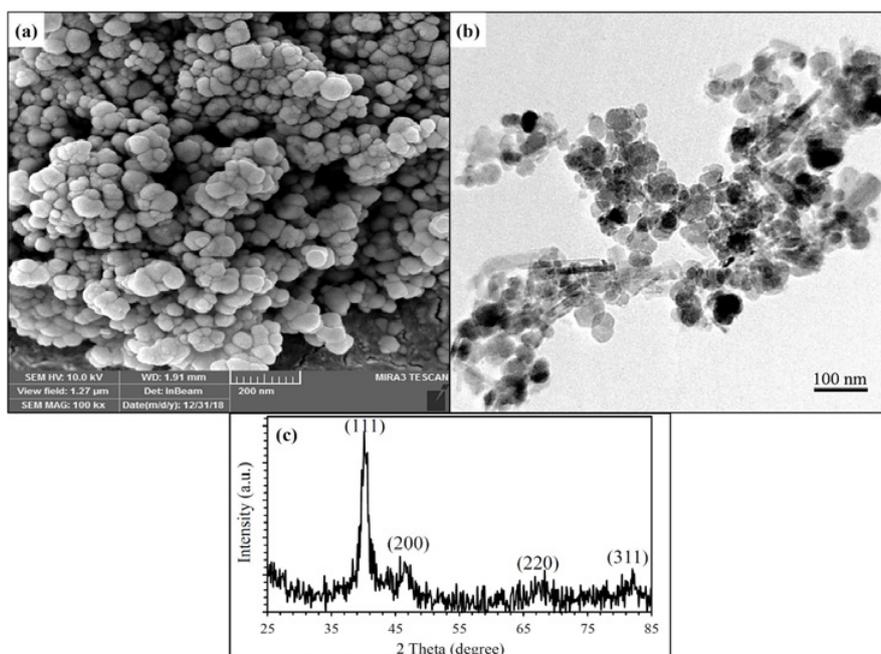


Fig. 1. (a) SEM image, (b) TEM image, and (c) XRD pattern of electrodeposited Pd nanoparticles produced at constant current density of 5 mA cm⁻² during 2000 s.

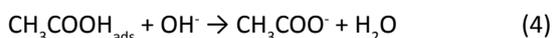
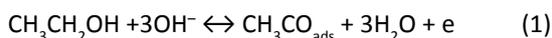
particle size based on TEM image is about 40 nm. The XRD pattern of the Pd nanoparticles is shown in Fig. 1c. The peaks located at $2\theta = 40.5, 46.4, 68.4$ and 82.5° are related to diffraction from (111), (200), (220) and (311) crystalline planes, respectively, which well matched with face centered cubic structure of Pd (JCPDS No. 05-0681). The broadening of XRD peaks (ie, Scherrer's broadening) indicates nonstructural nature of the prepared Pd nanoparticles.

Electrocatalytic Properties

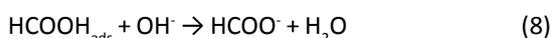
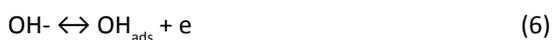
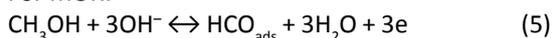
Effect of ethanol and methanol concentration

The reaction mechanism of ethanol and methanol have complex pathways that can be involved several adsorbed intermediates. According to the commonly reaction mechanisms for EOR and MOR in alkaline media, electro-oxidation of ethanol and methanol on Pd-based electrocatalysts in alkaline media are proposed to occur according to the following reactions [18, 24-27]:

For EOR:



For MOR:



For both EOR and MOR, the third stage is the slowest step during electro-oxidation and it is reported as rate determining step (rds). Moreover, CH_3COO^- and HCOO^- maybe oxidized at higher potentials to CO_2 [18, 24, 28, 29].

Fig. 2 shows the CV diagrams of ethanol and methanol electro-oxidation on Pd-vulcanX72CR/Cu electrocatalyst in 1.0M alcohol and 1.0M KOH solutions. The results indicate that Pd-Vulcan XC-72R/Cu has good catalytic activity for ethanol and methanol electro-oxidation and offers acceptable

oxidation current density in alkaline media compared to other Pd base electrocatalyst [9, 18, 24, 30]. As can be seen the electro-oxidation peak for ethanol and methanol oxidation occurred at -0.1 V and -0.2 V, respectively. Effects of methanol and ethanol concentration on the peak current density are illustrated in Fig.3. It is obvious that peak current density of EOR and MOR reach to maximum values by increasing concentration of ethanol and methanol, and decrease by further increase of alcohol content. For EOR process on the Pd-vulcanXC72R, the maximum current density occurs at 3.5 M ethanol concentration (71.70 mA/cm^2) and for MOR, it occurs at 2.0 M methanol concentration (17.35 mA/cm^2). This behavior is related to the adsorbed species that accumulate on the electrocatalyst surface [18, 22,23, 25]. Due to the excessive presence of alcohol on the electrocatalyst surface, there is no adequate sites for OH_{ads} on the electrocatalyst surface. Moreover, the catalytic activity of Pd-Vulcan XC-72R/Cu for EOR is much more than MOR in alkaline media.

Effect of KOH concentration

The concentration of alkaline agent is one of the most effective parameters on ethanol and methanol electro-oxidation in direct alcohol fuel cells. To study the effect of KOH concentration on EOR and MOR, linear sweep voltammetry tests were performed in different concentrations of KOH and 1.0M constant concentration of ethanol and methanol. Results are shown in Fig. 4. As can be seen no clear electro-oxidation peak can be observed for EOR in 0.001 M KOH and for MOR in 0.1 M KOH. The results show that electro-oxidation rate of ethanol and methanol

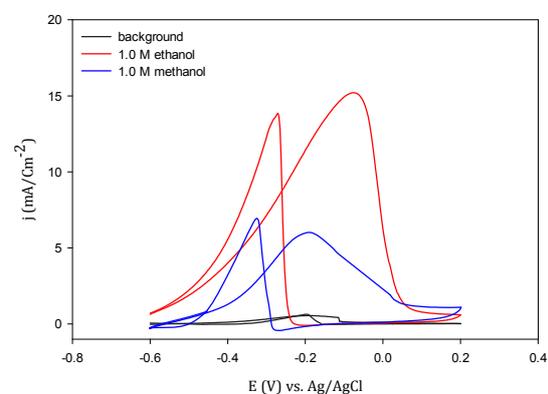


Fig. 2. Cyclic voltammetry of ethanol and methanol electro-oxidation on Pd-Vulcan XC-72R electrode in 1.0 M KOH solution at a scanning rate of 5 mV s^{-1} .

are highly influenced by the alkaline agent concentration. The Pd particles can operate as an activate catalyst during the EOR and MOR only when the concentration of OH⁻ is more than 0.001 M and 0.1 M, respectively. According to the Fig . 4.a the current density increases by increasing of the KOH concentration. For EOR, When KOH concentration increases to more than 2 M, the amount of OH_{ads} on the electrocatalyst surface quickly enhances and it leads to decrease the sufficient sites for CH₃CO_{ads} on the Pd-NPs surface. In the same way, Fig. 4b shows that when the concentrations of KOH rises above 1.0 M, the amount of HCO_{ads} is decreased on electrocatalyst surface.

Estimation of anodic transfer coefficient

Electro-oxidation current density of an electrocatalyst is a function of concentrations of the present reagents, as well as overpotential. The relationship between oxidation current density (j) and overpotential (η) is expressed by Tafel

equation (Eq. 9) as [31]:

$$j = j^\circ \exp\left(\frac{\alpha_a n F}{RT} \eta\right) \text{ or } \log j = \log j^\circ + \frac{\alpha_a n F}{2.303 RT} \eta \quad (9)$$

Where j is the electrode current density, n is electron transfer number, α_a is anodic transfer coefficient, F is the Faraday constant, R is the constant of gases and T is the temperature in Kelvin. j° in this equation is the exchange current density and can be expressed by Eq.10.

$$j^\circ = K \prod C_i^{m_i} \quad (10)$$

where K is the overall rate constant, C_i is the chemical concentration reagent i and m_i represents the reaction order of reagent i.

The anodic transfer coefficient can be calculated by plotting the over potential (η) versus the logarithm of current density [32]. Tafel plots of EOR and MOR are shown in Fig. 5 for different concentrations of KOH. The electron transfer number during of ethanol and methanol electro-oxidation reactions were assumed to be 2.8 and 1.3, respectively [31].

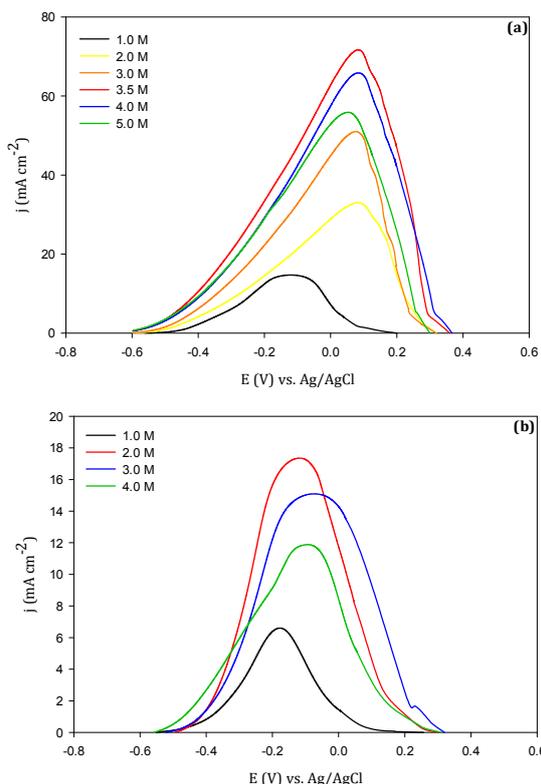


Fig. 3. Linear sweep voltammetry curves of ethanol and methanol electro-oxidation on Pd-Vulcan XC-72R electrode in solutions of 1.0M KOH and different concentrations of alcohols with different concentration of alcohols (a) ethanol (b) methanol. Scan rate is 5 mV s⁻¹.

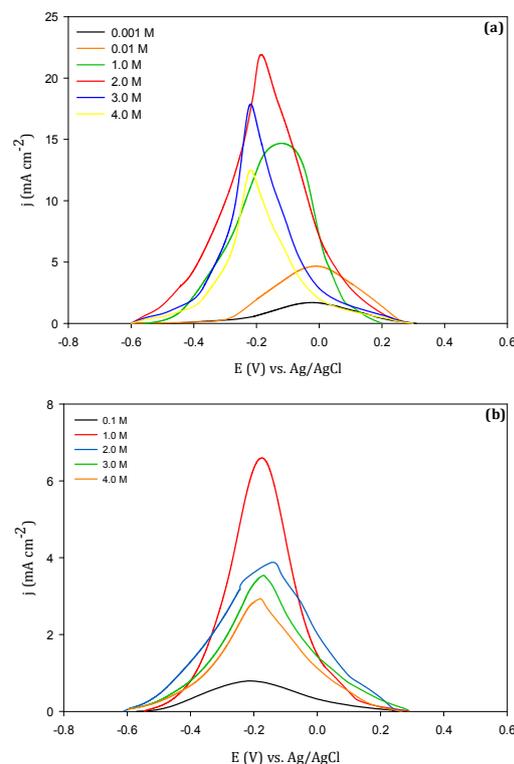


Fig. 4. Linear sweep voltammetry curves of ethanol and methanol electro-oxidation on Pd NPs electrode with different concentration of KOH, (a) 1.0 M ethanol (b) 1.0 M methanol.



Calculated slopes of Tafel plots for ethanol and methanol electro-oxidation were 280 mV dec^{-1} and 278 mV dec^{-1} , respectively. Accordingly, the average anodic transfer coefficient for EOR and MOR are listed in Table 3. In Most systems α turns out to lie between 0.3 and 0.7 and it can usually be approximated 0.5 in the absence of actual measurement [33]. Results of the present study are in the correct range.

*The kinetic equations for EOR and MOR
Measurement of reaction order for ethanol, methanol and KOH*

Reaction orders of ethanol, methanol and alkaline agent (KOH) are the most effective and determinative parameters of reactions kinetics of DAFCs. These values can be calculated at constant concentrations of other reagents and at constant values of over potential.

Fig. 6 shows the dependency of EOR and MOR

current densities on the ethanol and methanol concentrations in logarithmic coordinate in 1.0 M KOH at constant low potentials. According to equation (10) the reaction order of ethanol and methanol can be approximated by the average slop of lines in Fig. 6. The calculated reaction orders of ethanol and methanol are listed in Table 4. Fig. 7 shows the effect of KOH concentration on current density in logarithmic coordinate. Again, the reaction order of KOH during of EOR and MOR can be estimated, as shown in Table 5.

Substituting α , n and m_i values in Eq. 9 and 10, Eq. 11 and 12 are derived:

Table 3. Anodic transfer coefficient for EOR and MOR

Electro-oxidation reaction	EOR	MOR
α (Average)	0.3	0.6

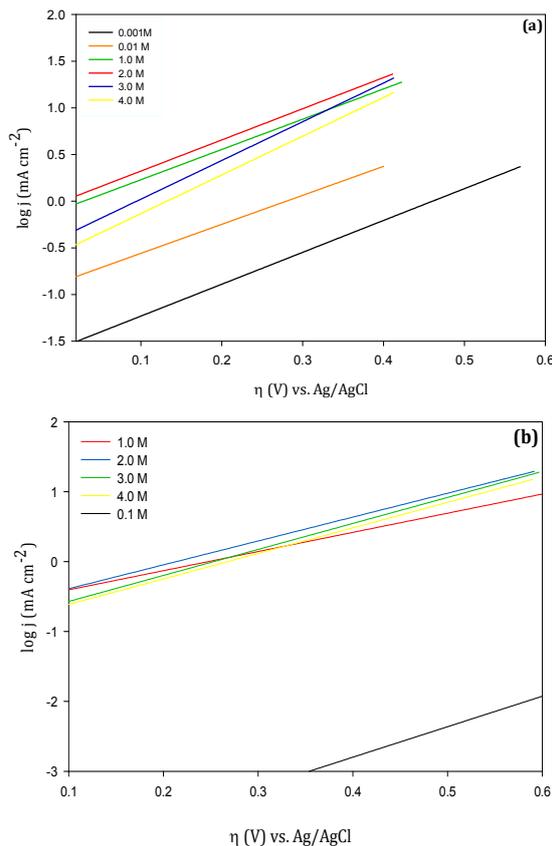


Fig. 5. Tafel plots for ethanol and methanol electro-oxidation on Pd-Vulcan XC-72R electrode with different concentration of KOH together with, (a) 1.0 M ethanol (b) 1.0 M methanol. Scanning rate had been 5 mV s^{-1} .

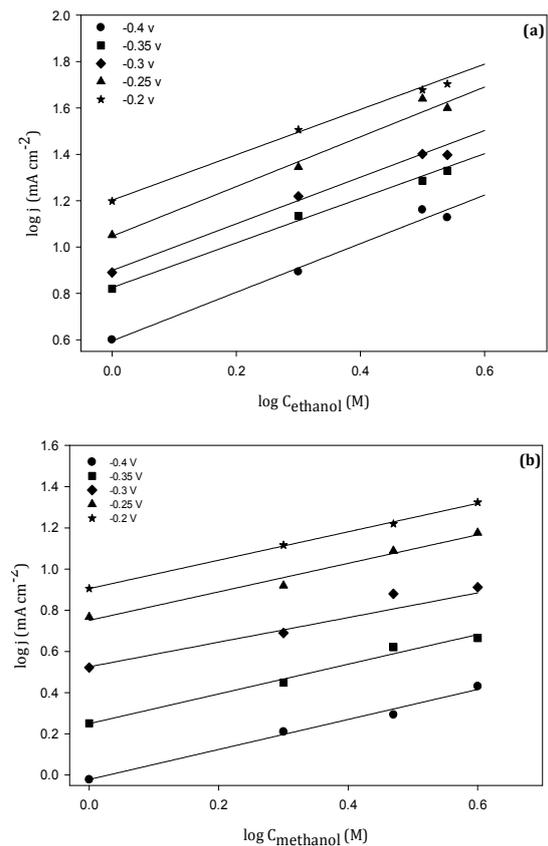


Fig. 6. Dependence of ethanol and methanol electro-oxidation currents density on the ethanol and methanol concentration in logarithm coordinate in 1.0 M KOH, (a) ethanol (b) methanol.

Table 4. Reaction order of EOR and MOR in 1.0 M KOH vs. alcohol concentration

E (V vs. Ag/AgCl)	-0.4 V	-0.35 V	-0.3 V	-0.25 V	-0.2 V	Ave.
EOR	1.05	0.96	1.00	1.07	0.98	1.0
MOR	0.73	0.72	0.68	0.69	0.69	0.7

Table 5. Reaction order of KOH in 1.0 M ethanol and 1.0 M methanol

E (V vs. Ag/AgCl)	-0.4 V	-0.35 V	-0.3 V	-0.25 V	-0.2 V	Ave.
KOH (for EOR)	0.50	0.52	0.48	0.50	0.49	0.50
KOH (for MOR)	0.30	0.31	0.31	0.28	0.32	0.30

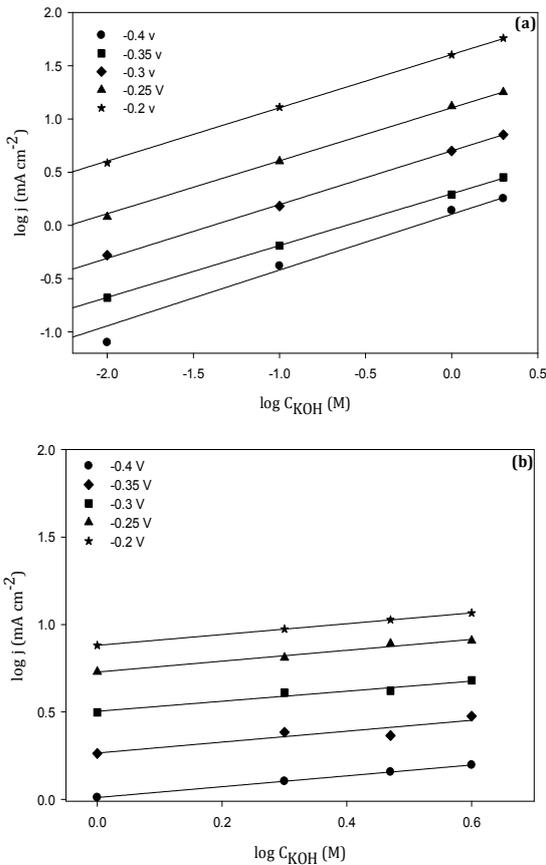


Fig. 7. Dependence of ethanol and methanol electro-oxidation current density on KOH concentration in logarithm coordinate in 1.0 M KOH, (a) EOR (b) MOR.

$$j_{ethanol} = K_{ethanol} C_{KOH}^{0.5} C_{ethanol} \exp\left(\frac{0.10}{T} \eta\right) \quad (11)$$

$$j_{methanol} = K_{methanol} C_{KOH}^{0.3} C_{methanol} \exp\left(\frac{0.094}{T} \eta\right) \quad (12)$$

The overall rate constant (K) can be calculated from the Eq. 11, 12 and Eq. 9 by .Calculated the average values of K were obtained as follows:

$K = 4.8 \times 10^{-3}$ m/s for EOR

$K = 1.2 \times 10^{-3}$ m/s for MOR

As can be seen, the overall rate constant for ethanol oxidation reaction is higher than methanol oxidation reaction. Finally, the overall kinetic equation for electro-oxidation of ethanol and methanol on PdNPs synthesized in this work can be given as following equation:

$$j_{ethanol} = 4.8 \times 10^{-3} C_{KOH}^{0.5} C_{ethanol} \exp\left(\frac{0.84F}{RT} \eta\right) \quad (13)$$

$$j_{methanol} = 1.2 \times 10^{-3} C_{KOH}^{0.3} C_{methanol} \exp\left(\frac{0.78F}{RT} \eta\right) \quad (14)$$

CONCLUSIONS

Based on the experimental results, Vulcan XC-72R supported Pd nanoparticles effectively catalyzed electro-oxidation of ethanol and methanol in the alkaline media. The efficient EOR and MOR activity on Pd-Vulcan XC-72R/Cu in alkaline media with 1 M KOH occurred in 3.5 M ethanol and 2 M methanol, respectively. Best performance of electrocatalyst for EOR and MOR in constant concentration of ethanol and methanol (1 M) consecutively occurred in 2 M KOH and 1 M KOH. At the end, two overall rate equations for EOR and MOR were developed.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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