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STUDY OF TYPE OF ELECTROLYTE EFFECT ON PLATINUM ELECTRO-CATALYST PERFORMANCE PREPARED BY CYCLIC VOLTAMMETRY ELECTRODEPOSITION METHOD FOR GLUCOSE OXIDATION REACTION

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Abstract

There are several methods to prepare electro-catalysts for low temperature fuel cells. Platinum is used as a common electro-catalyst for this purpose. Electrodeposition method is applied for preparing platinum on modified carbon paper as electrode directly. Many parameters effect on performance of prepared electrodes. At this work, the effect of type of electrolyte in electrodeposition solution was investigated for making electro-catalyst that is be used as anode in Glucose Alkaline Air Fuel Cell (GAAFC). Cyclic voltammetry ((1.2-0.6) V vs. Ag/AgCl sat. KCl, 100 mV/S) is used as electrodeposition method. Number of CV cycles is varied 10 to 50. Electrodeposition was performed in two precursor solution (0.5 M) containing phosphate and sulfate anions. Platinum concentration in solution was 3 mM. The prepared electro-catalysts were studied for Glucose Oxidation Reaction

(GOR) by CV analysis in 0.3 M glucose solution and 0.5 M KOH. Also, Electrochemical Impedance Spectroscopy (EIS) method was used. According our results, the type of anion in electrodeposition solution affects on properties of prepared platinum electro-catalyst for GOR. Optimized condition for number of CV cycles in phosphate and sulfate solutions is 10 and 40 respectively.

Keywords

Platinum Electrocatalyst, Cyclic Voltammetry, Fuel Cell, Glucose Oxidation Reaction, Electrodeposition Method.

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1. Introduction

With an increasing demand of contamination production and reducing the fossil fuels, scientists are focusing on more easily available, cheap and safer fuel and this bring the scientists to the new model of fuel cell which could works by glucose.(Basu & Basu, 2010) Studies on electro-catalytic oxidation of glucose are of high interest to the fuel cell researcher for various reasons.(Bockris et al., 1964; Chen et al., 2012; Delidovich et al., 2013; El-Refaei, et al., 2013; Habrioux et al., 2011) Glucose is abundant, cheap and non-toxic bio-fuel. There are no storing problems or explosion danger like hydrogen in hydrogen-oxygen fuel cell. The studies throughout the last few decades on electro-oxidation of carbohydrate was carried out and showed that noble metal catalyst based on platinum and the others in alkaline media improve the rate of electro-oxidation of GOR. (Arjona et al., 2012; Basu & Basu, 2011; Basu et al., 2013; Jin & Chen, 2007; Kerzenmacher et al., 2010; Kloke, et al., 2012; Yan et al., 2011; Zhang & Toshima, 2013)

Generally, GAAFCs can be divided into three types based on the type of electro-catalyst that is used: enzymatic, microbial, and metallic glucose fuel cells enzymatic glucose fuel cells are currently under development (Kerzenmacher et al., 2008), the confined stability of enzymes restricted their application in a long time. Theoretically, glucose can be completely oxidized to carbon dioxide and water by transferring 24 electrons per molecule glucose. GOR and the theoretical cell voltage U_0 would then be given in reaction3:

$$\text{Anode: } C_6H_{12}O_6 + {}_{24}OH^- \rightarrow 6CO_2 + 18H_2O + 24\,e^- \qquad G^\circ = -2.870\times106 \text{ J mol}-1 \quad (1)$$

$$\text{Cathode: } 6O_2 + 12H_2O + 24\,e^- \rightarrow 24OH^- \quad (2)$$

$$\text{Overall: } C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 18H_2O \quad U_0 = 1.24V\ [17] \quad (3)$$

There is several methods to preparing electro-catalyst. Catalysts for low-temperature fuel cells are typically in the nano-size range and are frequently formed or deposited on high-surface- area supports. Platinum and platinum-based catalysts can be made by chemical precipitation at low temperatures such as: Colloidal, Sol-gel, Impregnation, Electrochemical, Vapor Deposition, etc. (Bock, 2009)

Electrochemical deposition has been used to deposit nano particles on a wide variety of substrates, including glassy carbon, (Arjona et al., 2012) carbon paper (Gharibi et al., 2005; Pasta et al., 2012). carbon nano tube (Prilutsky et al., 2010; Shamsipur et al., 2010) this method affected by many parameters such as: solution concentration, applied potential, temperature and type of electrolyte(Zhang et al., 2011).Type of electrolyte have an important effect on electrodeposition process in a way that can be able to affects surface structure and particle shape of electrocatalyst.

The present article points out selected electrolytes to the prepare electro-catalysts for GOR by CV electrodeposition method, with this study we want to demonstrate that the type of electrolyte in electrodeposition method could effect on electro-catalytic activity of electro- catalyst for GOR in GAAFCs.

2. Experimental

2.1 Materials

Carbon powder Vulcan XC-72R was used as support and H_2PtCl_6 and H_2SO_4 from Merck Company were used as precursor. All aqueous solutions were prepared using ultrapure water during experiments.2-Propanol (>99% purity) (Quailed Fine Chemicals) was used as solvent for preparing Vulcan paste and carbon paper (Toray 90 T) was used as working electrode's- glucose(>99% pure) and KOH (>85% assay, flakes purified) (Merck) were used as fuel and electrolyte, respectively.

2.2 Electrode Fabrication

Substrate was fabricated by deposition of 3mg/cm^2 carbon Vulcan paste on carbon paper sheet with 1.13 cm^2 geometric area then it dried by heating in 200 ^{0}C$^.$for 45 minutes.

As prepared substrate expose to precursor solution included of H2SO4 and H3PO4 (0.5 M) and H2PtCl6 (3mM) (Merck, Germany) then 10, 20, 30, 40 and 50 CV scans (100 mV.s-1, 1.20 to −0.60 V vs. Ag/AgCl sat KCl) were performed under N2 atmosphere to study of electrolyte effect on the catalytic activity for GOR.

2.3 Electrochemical Characterization

Electrochemical experiments were performed in a separator free three-electrode cell. Ag/AgCl saturated with KCl electrode was used as reference electrode and for counter electrode platinum sheet electrode was used. In all experiment glucose and potassium hydroxide concentration was fixed in 0.3 and 0.5 M, respectively.

2.4 Physiochemical Characterization

The surface morphology of the deposited platinum electrocatalyst on the modified carbon paper substrate electrode was obtained using a field-emission SEM (KYKY-EM3200) and Atomic Force Microscopy (HIGH-SPEED AFM) made by Pardis Technology Park, Tehran, Iran.

2.5 Determining of Roughness Factor

In this work the charge measurement from stripping of the adsorbed hydrogen upd-H monolayer on the Pt-electrode (Q_H) was used to evaluate the ECSA for all Pt electrodes and expressed as roughness factor (RF) according to equation 4

$$RF=Q_H/Q_o.A \qquad (4)$$

Where Q_H is the measured charge of the hydrogen desorption, $Q_0$is the charge of a hydrogen monolayer adsorbed on polycrystalline platinum (210 μC cm^{-2}) and A is the geometric area of the electrode (Chen et al., 2011).

3. Result and Discussion

3.1 Cyclic Voltammogram of GOR in Alkaline Solution

Figure 1 shows a typical voltammogram of GOR. The cyclic voltammogram was carried out from -0.9 to 0.8 Vvs.Ag|AgCl (sat.KCl) reference electrode at $20mVs^{-1}$ scan rate in KOH 0.5 M and 0.3Mglucose solution in room temperature. Three oxidation regions (O1, O2, and O3) can be seen for GOR in positive direction scan. The result is in full agreement with glucose electro- oxidation given in the literatures (Basu, 2010; Chen et al., 2012; Zhang & Toshima, 2013). O1 and O2 regions appeared due to chemisorption’s and dehydrogenation of glucose in the hydrogen wave region in CV diagram. The peak O2 appeared at the potential region where the electrode surface is partially covered by adsorbed-OH. In this region, namely double layer region, adsorbed-OH catalyst surface can oxidize glucose also.

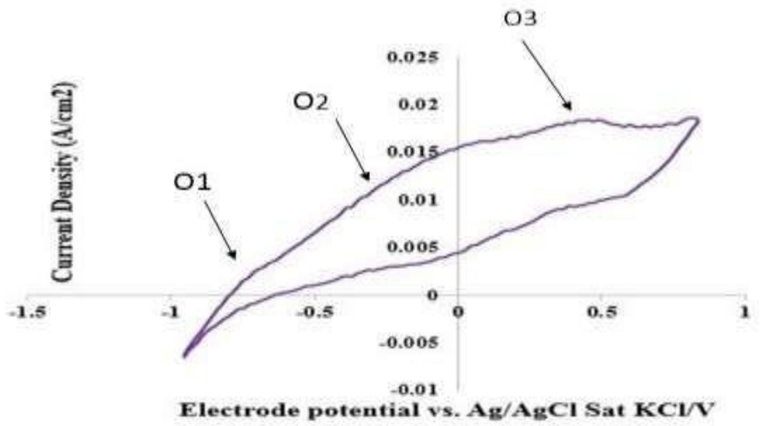

Figure 1: *Cyclic voltammogram of Platinum electrode at scan rate of 20 mV/s in the presence of 300mM glucose (measurement were performed in 0.5M KOH solution under a nitrogen atmosphere at 25 c).*

Peak O3 is observed at higher potential on already oxidized platinum surface. Gluconic acid, which was observed by FTIR and HPLC study (Basu, 2011) as great intermediate of GOR, may be produced due to oxidation of adsorbed intermediate from hydrolysis of glucono-γ- lactone, which can be formed from oxidation of adsorbed intermediate.

3.2 Dependence of Catalytic Activity of Platinum Electrocatalyst to the Number of Applied Cycles in Sulfate and Phosphate Electrolytes

Figure 2 shows to investigate the relation between catalytic activity of electro-catalysts to the number of applied cycles in different electrolyte, S1-S5 and P1-P5 electro-catalyst was prepared by applying 10 to 50 cycles in CV electrodeposition process. Current density was increased by increasing the number of cycles in S1 to S5 electro-catalysts, According to the literature comparison of catalytic activity for GOR in alkaline media carried out at -0.3 V vs. Ag/Cl (Basu, 2011). Correspond to table 1, by increasing the number of applied cycles anodic current density was increased. Data in Table 1 shows that by addition of applied cycle's roughness factor is increased and electrode cycles is maximized, after that RF is decreased

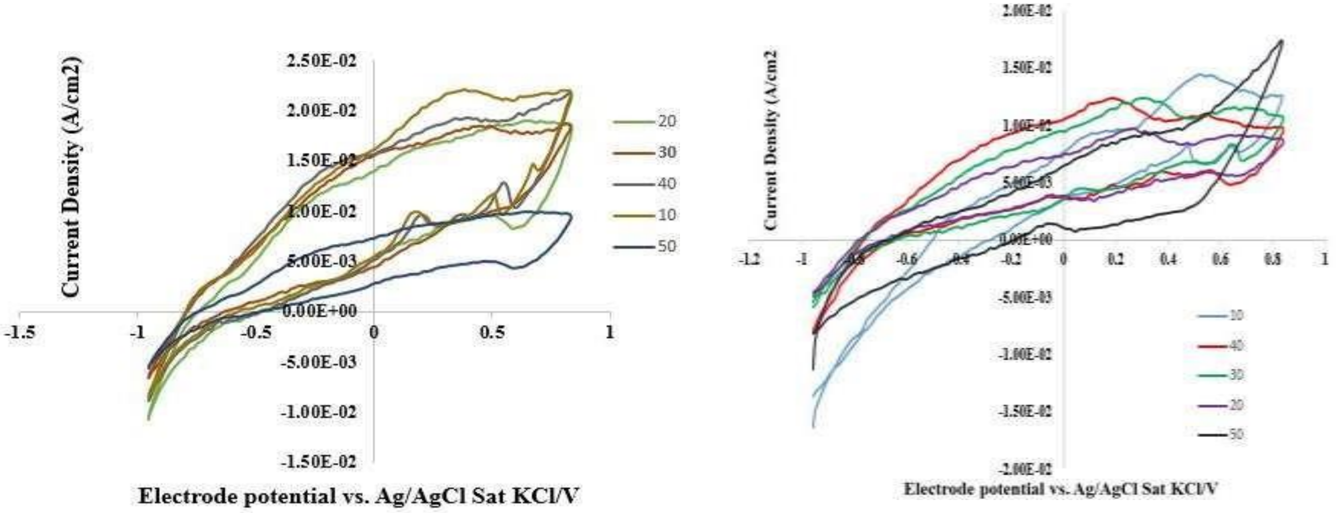

Figure 2: *Cyclic voltammogram of S1-S5 and P1-P5 electro-catalysts prepared in cycle deposition number of 10,20,30,40 and50 respectively and 3 mM precursor concentration (measurement were performed at scan rate of 20 mV/s in the presence of 300mM glucose in 0.5M KOH solution under a nitrogen atmosphere at 25^{o}C)*

P1-P5 electro-catalysts CV curves show that, by increasing the cycle number in deposition process. Catalytic response to GOR despite the small changes, close together. Performance of as-prepared electro-catalysts in phosphate is 40 percent more than sulfate electrolyte.

This observation shows that adding the cycle number in the presence of these electrolytes have a different catalytic behavior for GOR. Oxidations peaks in the cathodic scan from the end of anodic scan to near to 0.2 V may be refer to produced intermediate in anodic scan. These produced intermediates at the surface of S and P type of electrocatalyst are different, that leads to different peaks. This anodic peaks origination related to the different electrodes surface structure result in different cycle number deposition and then different catalytic behavior.

Corresponds to data in table 1 and table 2, we observed the highest oxidation current in S type electro-catalyst by applying the 40 cycles but in P type electro-catalyst this current obtained by 10 applied cycle. So phosphate anion could be able to prepare surface structure that reduced the duration and increase performance the electro-catalyst for GOR.

Comparison of current density in ohmic region shows that by increasing the applied cycles, positive incline of this region with increasing cycles can be leads to better performance. Following the

RF data could be typical reason to this result. These changes can because by varying the shape, size and distribution of the platinum particles.

Table 1: *Open Circuit Potential, Current Density and RF Data of S1-S5 Electrocatalyst*

Electrocatalyst	S1	S2	S3	S4	S5
Open circuit potential(V)	-0.65	-0.56	-0.78	-0.78	-0.78
Current density(mA/cm^2) at -0.3 V	6	7	7	10	9.3
Roughness Factor(cm^2)	270	295	385	450	400

Table 2: *Open Circuit Potential, Current Density and RF Data of P1-P5 Electrocatalyst*

Electrocatalyst	P1	P2	P3	P4	P5
Open circuit potential(V)	-0.81	-0.80	-0.83	-0.78	-0.80
Current density(mA/cm^2) at -0.3 V	15.00	14.80	15	15	7.5
Roughness Factor(cm^2)	685	680	640	650	670

3.3 EIS Characterization of the Optimized Anode in S and P Type of Electrocatalyst

EIS was used to understand the difference between S4 and P1 electro-catalyst by comparison the fitting parameter of Nyquist diagrams. Impedance spectra were recorded from 1000 to 0.01 Hz with excitation amplitude of 10 mV in KOH solution (0.5 M) and glucose 0.3M at OCV potential.

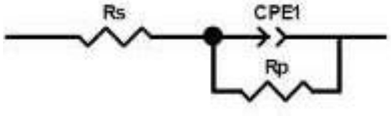

Figure 4: Eq*uivalent circuits compatible with the experimental impedance data in Figure 3 for GOR*

on S4 and P1 electrode

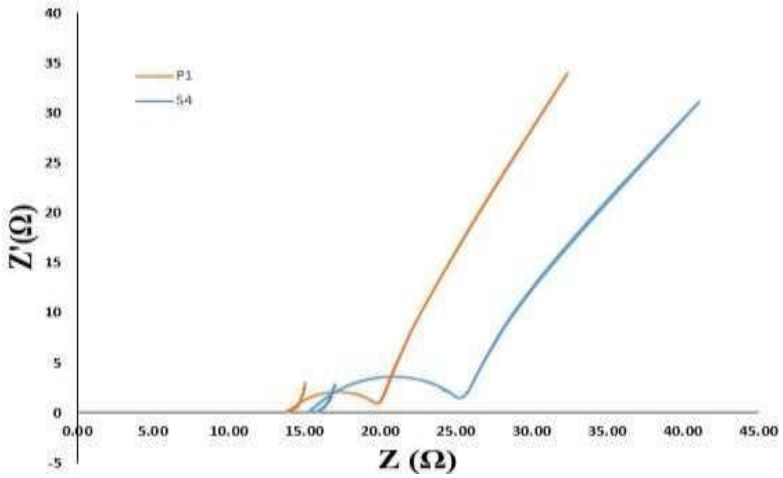

Figure 3: *Nyquist diagrams of S4 and P1 electrocatalyst in KOH solution (0.5 M) and glucose 0.3M at OCV potential.*

As can be seen in table 3 data extracted from Nyquist diagrams of S4 and P1 in figure 3. The charge transfer resistance of S4 is higher than P1and solution resistance of P1 is lower than S4. Rs difference between S and P may be refer to their natural features resulted in anion effect in electrodeposition process. More charge transfer resistance of S4 rather than P1 could be reduce the current density of it and decrease its performance.

Table 3: *Equivalent circuit parameters of GOR on S4 and P1 electrocatalyst in KOH solution obtained from Figure. 3*

Electrocatalyst	Rs	Rp	CPE-T	CPE-P
S4	17.30	26.5	0.07	0.85
P1	15.07	21.7	0.06	0.89

3.4 SEM and AFM Characterization

Figure 4, The SEM images taken at 40 KX magnifications indicates the uniformity in size and shape of catalysts. These images show that preparation of electrocatalysts by CV electrodeposition method can be produce a large amount of platinum nano particle at the surface of electrocatalyst and rough surface that was prepared more active site for GOR.

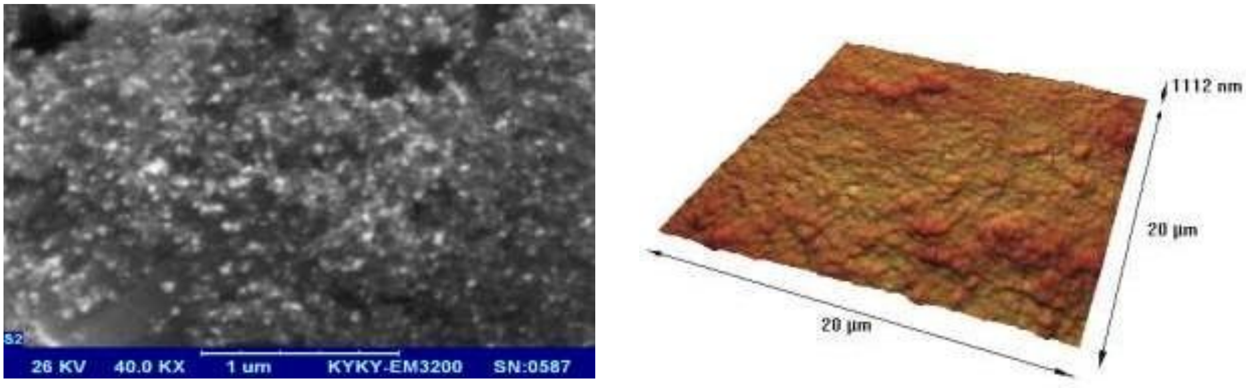

Figure 4: *SEM and AFM Micrographs of Electrode Surface*

4. Conclusion

In conclusion, we demonstrated that electrolyte effect in CV electrodeposition of Platinum is a versatile method for the preparation of platinum electrocatalyst with our desire catalytic activity. According our results, charge transfer resistance for GOR is affected by type of electrolyte in electrodeposition solution. Thus P type electrocatalysts have better performance for GOR than S type electrocatalysts. S and P type electro-catalysts have 270 to 400and 640 to 670roughness factors (RF), respectively. Therefore types of electrolyte in precursor solution have a more important role in achieving a better RF and then performance of electrocatalyst for GOR. The configuration of platinum electrocatalysts in P type electrodes intend to manner that can produce better situation for GOR.

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