



Trade Science Inc.

Research & Reviews In

Electrochemistry

Full Paper

RREC, 3(1), 2012 [16-19]

Effects of nano structure of platinum electrocatalyst on electrochemical behavior of new Nafion/Pt/GDL electrode

Mostafa Dehghani Mobarakeh

Energy Research Center, Renewable Energy Department, Research Institute of Petroleum Industry (RIPI),
P.O. Box 14665-1998, Tehran, (IRAN)

E-mail : dehghanim@ripi.ir

Received: 27th December, 2010 ; Accepted: 6th January, 2011

ABSTRACT

In this study, effects of structural properties of new Nafion/Pt/GDL electrode on electrochemical behaviors of electrodes were investigated. For this purpose a new gas diffusion electrode based on Pt-coated Nafion membrane was fabricated. Electroless method was used to deposit platinum on Nafion membrane. The electrochemical and structural properties of samples were evaluated by electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), scanning electron microscopy (SEM) and X-ray diffraction. In the optimum condition; 85 mV dec⁻¹ for Tafel slope, 2×10^{-3} A for exchange current density (i_0) and 8 Ω for charge transfer resistance (R_{ct}) were obtained. For this electrode the platinum particle size is 4 nm. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Oxygen reduction reaction;
Nafion membrane;
Platinum deposition;
Gas diffusion electrode;
Proton exchange membrane
fuel cell.

INTRODUCTION

Fuel cell systems must overcome economics obstacles to become commercially viable. For proton exchange membrane fuel cell (PEMFC), the cost of platinum catalyst has always hindered their commercialization. The kinetic of oxygen reduction reaction in the PEMFC requires the precious platinum catalyst due to its lower activity^[1,2]. Since platinum is a very rare and expensive metal, it is necessary to have low platinum in the electrode^[3-5]. In addition to the high cost of platinum, the problem related to the thick catalyst layer was another reason to fabricate new MEA with low loading of platinum. Catalyst layer with shorter thickness produce better performance due to lower diffusion barriers

and better catalyst addition^[6-9].

The electrocatalytic reduction of molecular oxygen on a platinum catalyst can be largely affected by catalyst particle size and surface structure^[10,11]. Bett et al^[12] found that Pt atoms at the corners, edges, and kink sites or dislocation showed less ORR activity than those on the crystallite faces. It was demonstrated that variables such as membrane modification, heat treatment, time of platinum deposition, different reducing agent and the concentration of platinum salt play important roles in the modification of the morphology of the Pt deposition, improvement in the catalytic activity of the Pt deposition^[13-16]. To alleviate these impediments, we developed a new approach to designing the low-Pt electrocatalysts for the electrode. This approach involves

pressing Pt-coated Nafion membrane on diffusion layer to prepare new electrode with low platinum loading. In this work platinum electrocatalyst was deposited on the Nafion surface instead of using Pt/C (10% or 20%) in catalyst layer in the conventional methods.

EXPERIMENTAL

Nafion treatment

Before the deposition of platinum on Nafion surface, the membranes were treated by immersing them at 80°C for more than 1h in 3% H₂O₂, deionized water and 0.5M H₂SO₄ solutions.

Platinum deposition

Platinum deposition of Nafion membrane was achieved by Impregnation /reduction method. In this method the treated Nafion membranes were immersed in different concentrations of H₂PtCl₆ solution. After the platinum deposition, the Pt-Nafion membrane was hot pressed on gas diffusion layer to make gas diffusion electrode. The loading of platinum for GDE1, GDE2 and GDE3 were 0.2, 0.28 and 0.12 mg cm⁻² respectively. TABLE 1 summarizes the conditions of chemical deposition of the analyzed GDEs discussed in this report.

TABLE 1 : Platinum deposition conditions of GDEs

Sample	[H ₂ PtCl ₆]/M	Time of deposition	Platinum Deposition Temperature
GDE1	0.05	10 min	40 °C
GDE2	0.01	30 min	70 °C
GDE3	0.005	30 min	70 °C

The platinum precursor was H₂PtCl₆ · 6H₂O and the reductant was NaBH₄/NaOH.

Analysis

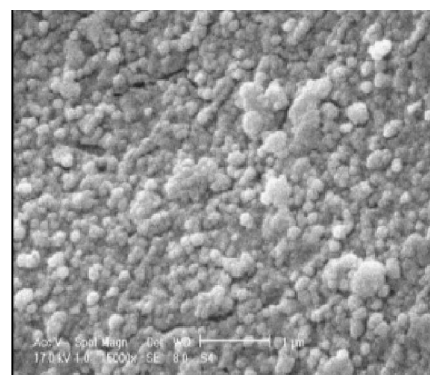
The morphology of new GDEs was characterized via Scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical behaviors of the GDEs were investigated by electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurement in 2 M H₂SO₄.

RESULTS AND DISCUSSION

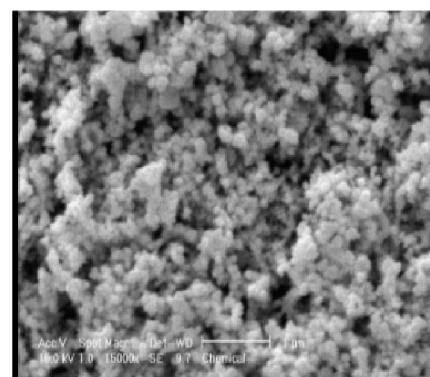
SEM results

The characteristics of platinum coated on the Nafion

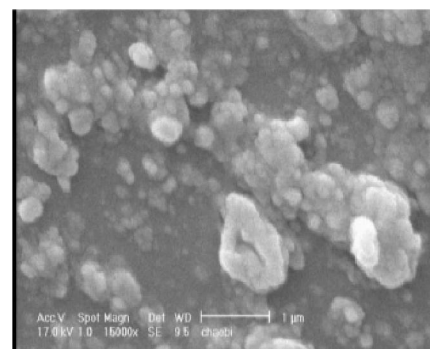
membrane were examined by means of scanning electron microscopy (SEM). Figure 1 shows scanning electron micrographs for GDEs.



(a)



(b)



(c)

Figure 1 : SEM images of GDE1 (a), GDE2 (b) and GDE3(c)

It was believed that some of the cracks have been probably caused by the residual stress between the Pt layer and Nafion membrane. After removing of the Nafion membrane from water, and drying it, shrink of the membrane occurs. As a result, some cracks were developed eventually in the Pt-films. Figure 1 b shows scanning electron micrograph for GDE2. Scanning electron microscopic analyses indicate good adhesion between the metallic electrode and the Nafion polymer.

Full Paper

From Figure 1.b it can be observed that the platinum particles are uniformly distributed on the membrane which it shows the uniformity of activation of the membrane surface.

XRD results

XRD diffractogram of GDE2 has been shown in Figure 2. The XRD patterns revealed the metallic polycrystalline platinum peaks. This electrode shows a strong peak at $40^\circ (2\theta)$ corresponding to Pt (111). The characteristic diffraction peaks of the FCC Pt highlighted the successful reduction of Pt precursor to metallic form. Amorphous band at ca. 18° related to the crystalline peak of Nafion. Considering the Pt (111) peak, it can be seen that this peak is wide, thus indicating that the procedure is good enough to form nanoclusters of metallic platinum. The Scherer formula is used to assess the particle size.

$$t = n\lambda/b\cos\theta \quad (1)$$

n = constant coefficient, λ = wavelength, b = peak breadth

From the extent of the line broadening of (111) at 2θ of 40° , the average platinum particle size of this sample was estimated to be about 4 nm.

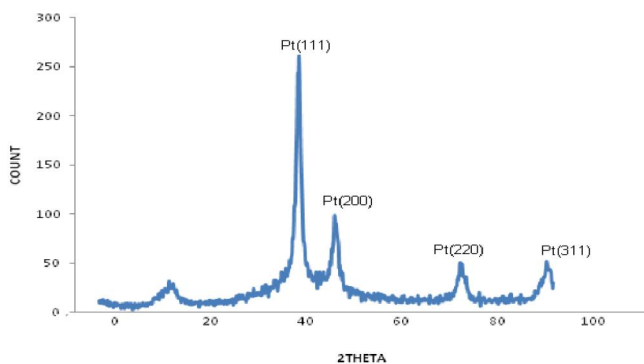


Figure 2 : XRD patterns of GDE2

The size of particle can be controlled by manipulating the synthesis temperature. By increasing the temperature, a smaller particle size achieved^[5]. From the XRD diagrams of GDE1 and GDE3, the platinum particle size for GDE1 and GDE3 were calculated to be 6 and 8 nm respectively, also XRD results are in good agreement with SEM results. Both techniques suggest that high temperature and long deposition time have good effect on chemical characteristics of new electrode. The surface of GDE2 shows better structural characteristics in related to other electrodes.

Research & Reviews On

Electrochemistry
An Indian Journal

Electrochemical measurements

In order to investigate the electrochemical characteristics of electrodes, the A.C impedance spectrum of each electrode was obtained at potential of 0.3V. AC Impedance measurements were carried out in the presence of O_2 . The Nyquist plots of electrodes are shown in Figure 3.

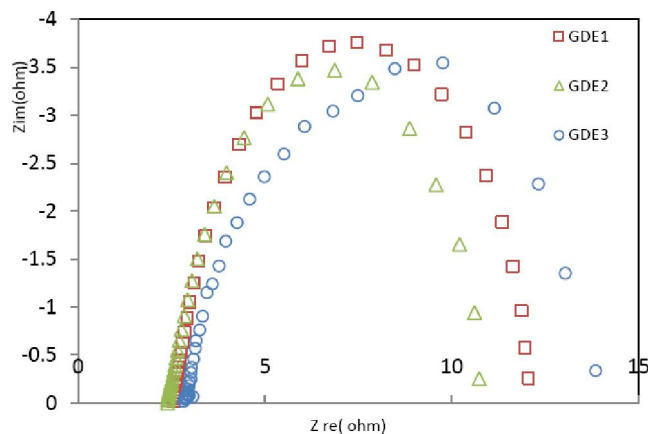


Figure 3 : Nyquist plots of impedance response from 30 kHz to 10 mHz. at 0.3 V in $2M H_2SO_4$.

As can be seen, the spectrum of each electrode takes the form of a single semi-circular curve. However the diameter of the semi-circle for GDE2 is lower than other electrodes, which means that this electrode has lower charge transfer resistance (R_{ct}) and better performance than other electrodes. The charge transfer resistance (R_{ct}) for this optimum electrode is 8 ohm.

Figure 4 shows the polarization curves for GDEs. As can be seen in this graph, GDE2 has higher current in the -220 mV than other electrodes. This result confirms that of the impedance technique.

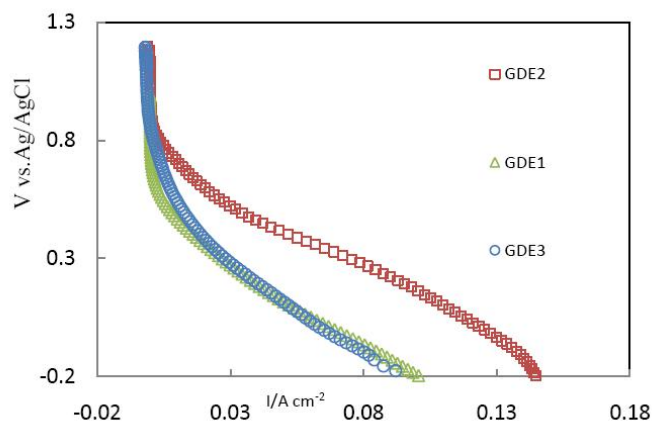


Figure 4 : Polarization curves for electrodes, with scan rate $5 mV s^{-1}$ in $2M H_2SO_4$.

The kinetic parameters of the ORR for electrodes can be obtained from the polarization data. The kinetics data were obtained using the semi-empirical equations:

$$E = E_0 - b \log i - R_i \quad (1)$$

$$E_0 = E_r + b \log i_0 \quad (2)$$

Where E_r is the reversible potential for the electrode; i_0 the exchange current density for the ORR; b the Tafel slope; i the current density and R represents the total contributions of polarization components. The kinetics parameters for GDEs are listed in TABLE 2.

TABLE 2 : Kinetics parameters for ORR

Electrode	b (m v dec ⁻¹)	R_{ct} (Ω)
GDE1	91	8
GDE2	108	11
GDE3	110	13

According to results of TABLE 2, GDE2 with lower Tafel slope and R_{ct} , has the highest electrochemical activity toward the ORR among the three electrodes. The OCV (open circulate voltage) value for this optimum electrode is 0.819 V.

CONCLUSION

In the present study new GDE (based on Pt/Nafion membrane) have been fabricated. Electrochemical results showed that, GDE2 has the highest electrochemical activity toward the ORR among the three electrodes. The results showed that the deposition time and the temperature have significant effects on electrochemical behavior of Nafion/Pt/GDL electrode. These data suggested the enhancement of electrode performance with increasing platinum deposition temperature. The SEM and XRD findings showed that platinum layer can be attached to Nafion membrane closely and firmly with strong peak correspond to (111) crystalline face. The results illustrate that placing a Pt monolayer on a Nafion membrane is an attractive way of designing better O_2 reduction electrocatalysts with very low Pt contents.

ACKNOWLEDGEMENT

The author would like to place on record, their appreciation for the support rendered by Iran Renewable

Energy Initiative Council, on the research leading to the present article.

REFERENCES

- [1] E.Antolin; J.Appl.Electrochem., **34**, 563-576 (2004).
- [2] N.Rajalakshmi, Hojin Ryu, K.S.Dhathathreyan; Chemical Engineering Journal, **102**, 241-247 (2004).
- [3] Dong-Hoon Son, Raj Kishore Sharma, Yong-Gun Shul, Hansung Kim; Journal of Power Sources, **165**, 733-738 (2007).
- [4] B.Smitha, S.Sridhar, A.A.Khan; Journal of Membrane Science, **259**, 10-26 (2005).
- [5] Sanjeev M.Rao, Yangchuan Xing; Journal of Power Sources, **185**, 1094-1100 (2008).
- [6] J.Zhang, M.B.Vukmirovic, K.Sasaki, F.Uribe, R.R.Adzic; J.Serb.Chem.Soc., **70**, 513-525 (2005).
- [7] Hexiang Zhong, Huamin Zhang, Gang Liu, Yongmin Liang, Jingwei Hu, Baolian Yi; Electrochemistry Communications, **8**, 707-712 (2006).
- [8] S.Lister, G.Mclean; J.Power Sources, **130**, 61-67 (2004).
- [9] M.D.Bennett, D.J.Leo; Smart Mater.Struct., **12**, 424-436 (2003).
- [10] Dong-Hoon Son, Raj Kishore Sharma, Yong-Gun Shul, Hansung Kim; Journal of Power Sources, **165**, 733-738 (2007).
- [11] Sanjeev M.Rao, Yangchuan Xing; Journal of Power Sources, **185**, 1094-1100 (2008).
- [12] Cicero W.B.Bezerra, Lei Zhang, Hansan Liu, Kunchan Lee, Aldal ´ ea L.B.Marques, Edmar P.Marques, Haijiang Wang, Jiujun Zhang; Journal of Power Sources, **173**, 891-908 (2007).
- [13] Koslov, S.Alexander, Palaniamy, Thirumalai, Narasimhan, Dave; Electroless Autocatalytic Platinum Plating. United States Patent, 6391477, (2002).
- [14] Z.X.Liang, T.S.Zhao; Journal of Physical Chemistry C, **111**, 8128-8134 (2007).
- [15] Raul Diaz, Jordi Arbiol, Fausto Sanz, Joan R.Morante; Chem.Mater., **14**(8), 3277-3283 (2002).
- [16] Sally-Ann Sheppard, Sheelagh A.Campbell, James R.Smith, Grongar W.Lloyd, Thomas R.Ralph, Frank C.Walsh; The Analyst, (1998).