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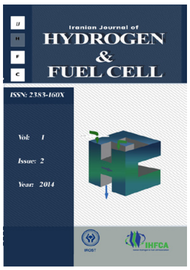

Single walled carbon nanotube in the reaction layer for oxygen reduction reaction in gas diffusion electrodes

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Abstract

In this paper, the effect of surface area in the reaction layers of gas diffusion electrodes for oxygen reduction reaction (ORR) was investigated. Various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 1 and 1.5%wt of reaction layer) of single walled carbon nanotube (SWCNT) were inserted in the reaction layer. The results were studied in a three-electrode half-cell system configuration, which connected to a potentiostat-galvanostat system via linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronoamperometry (CHA) and impedance analysis. The results indicated that the addition of SWCNT, by changing in surface area of catalyst layer can improve the ORR kinetics parameters. The best performance is obtained for an electrode with 0.4% SWCNT.

1. Introduction

Currently, a variety of fuel cells are in different stages of development. They can be classified in two diverse categories according to the type of fuel and oxidant, whether the fuel is processed inside (internal reforming) or outside (external reforming) the fuel cell, the type of electrolyte, the temperature of operation, whether the reactants are fed into the cells by internal or external manifolds, etc. The operating temperature and useful life of the fuel cell dictate the physicochemical and thermo mechanical properties of the materials used in the cell components. The capabilities of proton exchange membrane (PEM) fuel cells rely on their simplicity. Polymer electrolyte fuel cells (PEMFCs) have attracted great attention due to their high power density, low temperature operation and environmentally friendly technology. Nano sized Pt catalysts are used in the cathode and anode of PEMFCs. A high dispersion is required to elevate catalytic activity and reduce the amount of expensive precious metals used. Cost and durability are two

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issues in proton exchange membrane fuel cells, which are intimately related. Costs reduction strategies usually consider decreasing the amount of the most expensive elements or substituting some components by cheaper or more durable materials. Particularly, PEMFC electrodes constitute a large amount of the cost of the module, contributing to more than 40% on its whole expense [1]. One of the milestones for this technology consists of looking for alternative materials to enlarging PEMFC catalysts lifetime.

Carbon supports for PEMFC catalysts must combine a number of properties such as electron conductivity, corrosion resistance, surface properties and low cost [2]. High surface area supports with high stability against corrosion, and providing strong interaction with the metal are good candidates for the synthesis of stable small nanoparticles with high metal specific surface area [3, 4].

The gas diffusion electrode consists of an electrode support and an electrocatalyst layer. The electrode support is made from porous carbon paper, while the electrocatalyst layer consists of platinum-dispersed carbon powders joined by Polytetrafluoroethylene (PTFE) particles. Like the electrode support, the electrocatalyst layer is also porous to gases. The electrode support supplies reactant gases such as hydrogen and oxygen to the electrocatalyst layer, the electrochemical reactions occur in the electrocatalyst layer [7]. The performance of fuel cell electrodes can be improved either by using a more active electrocatalyst or by improving the structure of the gas diffusion electrode [8]. Platinum on carbon (Pt/C) catalysts are widely used both in electrochemical power sources and in electrolysis. For example, gas-diffusion electrodes made from Pt/C catalysts are employed in fuel cells to reduce the quantity of noble metal used [9].

Among the various kinds of carbons, carbon nanotubes are very attractive, because they have unique physicochemical characteristics such as good intrinsic conductivity, a pore structure without micro pores, durability under corrosive conditions and mechanical toughness thus have potential uses in a variety of power generation and storage devices, including proton exchange membrane fuel cells [10]. Because of its properties, in this paper, SWCNT inserted in catalyst layer to change surface area and the effect of these additions is studied.

The electrochemical reduction of oxygen on platinum plays an important role in energy conversion since the associated over potential corresponds to a voltage loss of 200–300 mV at operational current densities [11-15]. The rate of ORR has a significant effect on the performance of electrodes and changing in surface area may improve the performance.

Naranayanamoorthy and his coworkers [16] doped carbon black supported platinum catalyst with a small quantity of single walled carbon nanotube and evaluated the composite in a liquid electrolyte. Moreover, carbon nanotubes supported catalyst proved to possess better activity than a typical carbon material supported catalyst [17-20].

Peng Wu et al. [21] added Multi-walled carbon nanotube (MWCNT) to the anode of direct methanol fuel cells (DMFC) and showed that the MEA with 0.5wt% CNT has the best performance.

Sang- Min park et al. [22] introduced Vapor–grown carbon fiber (VGCF) to the anode of (DMFC) and changed the amount of (VGCF) up to 6 wt. %. A catalyst layer with 2 wt.% VGCF loading showed the best cell performance.

Nishicawa et al. [23] studied the effect of carbon black content in catalyst layer and they found that uncatalyzed carbon black (U-CB) into cathode catalyst layer enhanced the performance at high current densities and the optimum value ratio of U-CB/Pt-CB was found to be 0.1.

In the present study, initially gas diffusion electrodes (GDEs) were fabricated by addition of single walled carbon nanotube to reaction layer and then the effect of different amounts of SWCNT addition studied.

2. Material and Metodes

2.1. Preparation of gas diffusion electrodes

Commercially available cathode electrocatalyst was used to prepare the PTFE bonded porous GDE. 20% platinum on carbon was obtained from Electro Chem (EC). The catalyst dough was formed by mixing PTFE solution (EC), distilled water, isopropyl alcohol (Aldrich 99%) and 0.1, 0.2, 0.3, 0.4, 0.5, 1 and 1.5 % wt. of single-walled carbon nanotubes (Aldrich). The loading of platinum and PTFE in reaction layer were 0.3 mg/cm^2 and 30% of total mass ratio. The mixture sonicated for 30 min to create a highly dispersed mixture and the resulting dough was rolled to the desired size. After evaporating the solvents, a uniform paste was obtained which spread uniformly over the carbon paper (0.64cm^2) and then sintered at 473K for 1 h in inert atmosphere.

2.2. Electrochemical analysis

The oxygen reduction reaction (ORR) was evaluated in the cathode in which the current density measured with respect to potential using a half-cell measurement apparatus comprised a three-electrode system. An Ag/AgCl electrode was employed as the reference electrode, Pt electrode constructed from Pt plate as the counter electrode and the GDE described above as the working electrode. The GDE contained catalyst and a gas-diffusion layer and was set in a holder and then placed in sulfuric acid (2.5 mol dm^{-3}) at room temperature.

The scanning rate, scan increment and step/drop time used in the experiments were 1 mV s^{-1}, 2 mV and 2 s, respectively. The voltage scanned from -0.2 to 0.8 V vs. an Ag/AgCl electrode. The results were studied in a three-electrode half-cell system in a potentiostat (Zahner) with linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronoamperometry and impedance spectroscopy.

2.2.1. Linear sweep voltammetry analysis (LSV)

Tafel plots in LSV measurements used to determine the symmetry factor (α) and exchange current density (i_0) at the rate-determining step.

In 1905, Tafel plotted overvoltage against log of current density and found that for most values of the overvoltage, the graph approximates to a straight line. Such plots are now known as 'Tafel plots'. Most values of the overvoltage are given by the Tafel equation as:

$$\eta = \frac{2.3RT}{n\alpha F}\log\frac{i}{i_0} \qquad (1)$$

where R is the gas constant, T the temperature, n the number of exchanged electrons, α the symmetry factor, and i and i_0 are the current density and exchange current density, respectively [24].

At zero exchange current density (i_0) no reaction can occur. This exchange current density is crucial to the control of the performance of fuel-cell electrodes. It is vital to make the value of i_0 as high as possible since increasing the value of i_0 reduces the voltage drop.

Exchange current densities are analogous to rate constants in chemical reactions. Unlike rate constants however, current densities are concentration dependent. Variations due to concentration are not very significant when compared with the range of variations in the rate constants [24]. Tafel plots are used to determine the values of the symmetry factor (α) and i_0. The slope and intercept of a Tafel plot give α and i_0, respectively.

2.2.2. Cyclic voltammetry analysis (CV)

Results of CV graphs under nitrogen atmosphere give the electrochemical surface area. The determination of electrochemically active surface area (ECSA) of electrodes provides a quantitative measure of the effectiveness of electro catalyst. ECSA value of electrocatalyst is measured in terms of the number of electrochemically active sites per gram of the catalyst [25]. ECSA is measured through following equation:

$$ESCA = \frac{Q_H}{Q_F L_P} \qquad (2)$$

In this equation, denotes the surface area of CV curve, is columbic charge of Pt (0.21 mc.cm^{-2}) and the amount of Pt which is loaded on the carbon paper (here 0.3 mg.cm^{-2}).

Cyclic voltammetry (CV) measurements were conducted on gas diffusion electrodes at 298 K to investigate the effect of the addition of SWCNT on the electrochemical active surface area [26]. To obtain voltammograms for electrodes, nitrogen gas was initially fed to the electrolyte for 30 min and then fed to the electrolyte and electrodes during the tests. The potential was scanned between -0.2 and 0.8 V (Ag/AgCl) at sweep rate of $1mVs^{-1}$. Relative electrochemical active surface area (ECSA) can be extracted from the area of hydrogen oxidation peaks in cyclic voltammograms [27].

2.2.3. Chronoamperometry analysis (CHA)

Diffusion coefficient of oxygen is measurable using CHA analysis. To this aim, the potential was adjusted over 1.4 V for 60 s and 0.6 V (vs. Ag/AgCl) for 10 s. After 10 s the Catrel Cotrell equation could be applied to determine the $nCD^{1/2}$ value which showed oxygen permeability:

$$i = nfAC(\frac{D}{t\pi})^{\frac{1}{2}} \qquad (3)$$

2.2.4. Electrochemical Impedance Spectroscopy (EIS) analysis

In order to perform a quantitative evaluation of resistance against the ORR, the AC impedance method was applied. Impedance measurement was investigated at 0.3 V vs. Ag/AgCl potential for obtaining electronic resistance. This potential is in ohmic resistance region. The AC potential amplitude and the frequency range were 5 mV and 50 mHz to 100 KHz, respectively. Impedance analyzer was used to get the Nyquist diagrams and extract the electronic resistance of electrodes [29]. An equivalent circuit [30] was used to obtain Nyquist diagrams for comparing the electrodes resistance.

3. Results and Discussion

In order to study the influence of values of carbon nanotube addition on the performance of fabricated electrodes, various electrochemical methods were used. Here, the platinum loading was the same in fabricated electrodes.

3.1. Exchange current density

Fig.1 shows the values of exchange current density in low current density area versus additive amounts of carbon SWCNT also the kinetic parameters of different electrode are shown in table 1.By adding SWCNT to the reaction layer of gas diffusion electrode, the exchange current density was changed.

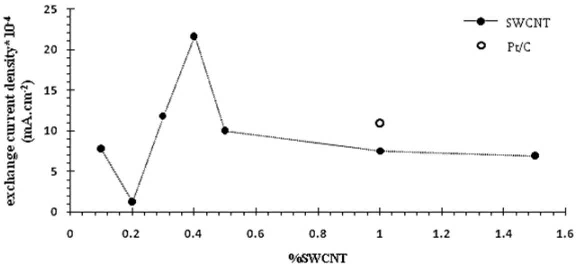

Fig.1. Exchange current density vs. percent of carbon nanotube in reaction layer at 298 K.

In reaction layer surface area i.e. 0.4% wt. of SWCNT, the highest value for the rate constant of oxygen reduction reaction is observed. The results show that, the existence of SWCNT in the reaction layer improves the exchange current density of ORR in comparison to the situation in which no SWCNT was applied.

3.2. Symmetry factor

The relationship between symmetry factor for oxygen reduction reaction and percent of single walled carbon nanotube in catalyst layer is shown in Fig. 2. The value of symmetry factor is the proportion of applied electrical energies harnessed in changing the rate of electrochemical reaction. Its value depends on the reaction involved and the electrode material, but it must be in the range 0-1.

Results show that α changed between 0.51 and 0.83 for ORR which depends on the amount of single walled carbon nanotube used in the catalyst layer. As a whole, in the optimized condition (0.4% wt .CNT) tendency of gas diffusion electrode for ORR is increased.

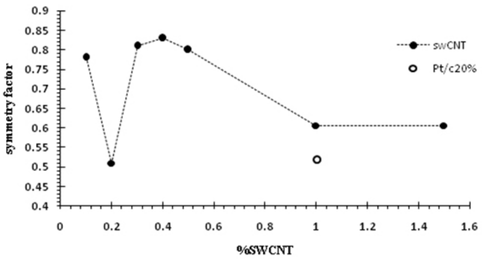

Fig. 2. Symmetry factor vs. carbon nanotube in the reaction layer for oxygen reduction reaction.

3.3. Electrochemical active surface area

As shown in Fig. 3, for the catalyst layer with SWCNT, the ECSA shows a maximum value at 0.4% (wt.). Using SWCNT in the reaction layer physically, significantly influences the electrochemical surface area. Therefore, the effective presence of SWCNT in the reaction layer is achieved at 0.4% (wt.). Further increase of SWCNT in the reaction layer declines electrochemical surface area.

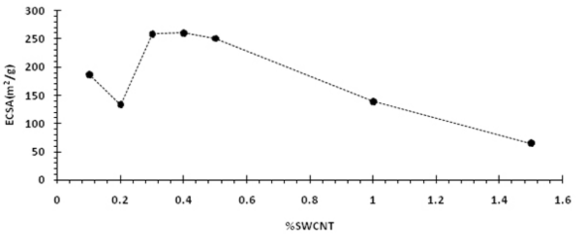

Fig. 3. ECSA variation vs. carbon nanotube content (%) in GDE for ORR.

3.4. The effect of presence of single walled carbon nanotube in the reaction layer on oxygen permeability

The results of CHA indicate that physical addition of 0.4 % wt. single walled carbon nanotube provides the highest value for oxygen diffusion in the reaction layer (See Table 2). The presence of carbon nanotube in reaction layer improves diffusion of oxygen with respect to situation in which carbon nanotube was not used as an additive in the reaction layer.

Tabele 1. kinetical parameters of oxygen reduction reaction at various amounts of carbon nanotube in reaction layer.

Carbon nanotube electrocatalysts	Tafel slop(LCD)	Exchange current density(i_0)$\times10^{-4}$	Symmetry factor(α)	current density in 300mv	Current density in 500mv	Current density in 700mv
0.1	0.08	7.8	0.78	137.11	81.02	31.47
0.2	0.12	1.2	0.51	30.53	1.95	0.61
0.3	0.07	11.8	0.81	230.00	132.45	47.25
0.4	0.07	21.7	0.83	273.44	158.28	57.58
0.5	0.07	10	0.80	150.98	122.86	72.53
1.0	0.10	7.5	0.61	134.89	78.81	31.61
1.5	0.22	6.9	0.61	96.33	56.36	21.02
Pt/C20%	0.12	11	0.52	209.22	120.14	41.80

3.5. AC impedance spectroscopy

To gain more information about the effect of SWCNT on ORR, the AC impedance spectrum of each electrode was obtained. The electronic conductivity of each electrode respect to SWCNT content is extracted from EIS data (table 3). Also as shown in Fig. 4, the gas diffusion electrode with 0.4%wt SWCNT has lowest charge ransfer resistance compared to other electrodes. The electronic conductivity of each electrode respect to SWCNT content is extracted from EIS data (table 3).

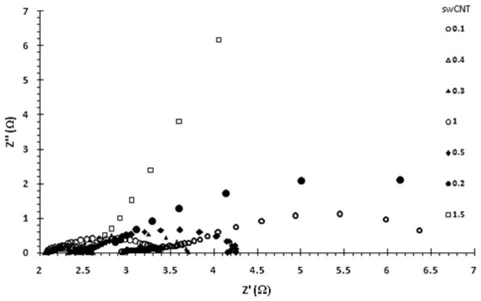

Fig. 4. Nyquist plots of the impedance responses from 100 kHz to 50 mHz for the GDEs including different amounts of SWCNT at 0.3V vs. Ag/AgCl, at 28 °C.

4. Conclusion

In this research, various amounts of single walled carbon nanotube were added to the catalyst layer of a gas diffusion electrode. According to observations reached from Tafel curve, cyclic voltammetry and chronoamperometry, it can be concluded that the

Table 2. Oxygen permeability in various amounts of carbon nanotube in reaction layer.

SWCNT	$ncD^{1/2} \times 10^{-5}$
0.1	173.45
0.2	79.23
0.3	257.06
0.4	263.36
0.5	192.21
1.0	133.36
1.5	92.68
Pt/C20%	71.00

Table3. Electronic resistance of electrodes with different amounts of SWCNT

%SWCNT	Electronic resistance of electrodes(Ω)
0.1	0.09
0.2	0.1
0.3	0.1
0.4	0.5
0.5	1.22
1	0.34
1.5	5.04

performance of whole electrodes are enhanced for oxygen reduction reaction by addition of SWCNT, and the best performance was found for 0.4% addition. It seems that the optimization of reaction layer surface area in the presence of activated carbon as additive intend to improving ORR kinetically at gas diffusion electrode.

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