

Performance of polypyrrole-impregnated composite electrode for unitized regenerative fuel cell

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Abstract

We have proposed a novel deposition method of thin Pt catalysts onto Nafion membranes impregnated with polypyrrole (PPy) for unitized regenerative fuel cells (URFCs). We demonstrated that the polypyrrole impregnated into Nafion membrane not only offered electronic conduction pathways necessary to sink electrons generated from the chemical reduction of platinum chloride, but also enhanced the direct loading of Pt particles onto the Nafion surface.

The distribution and thickness of Pt particles deposited on the PPy/Nafion composite membrane was observed by energy dispersive X-ray spectrometry. Atomic force microscopy and scanning electron microscopy were implemented to investigate the morphology of PPy/Nafion composite membrane surface and the influence of Pt loading onto the Pt/PPy/Nafion electrode surface morphology, respectively. The performance of fuel cell and water electrolysis was discussed in the reference to an I - V curve.

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1. Introduction

Fuel cells have attracted much attention as clean energy sources because of their high fuel conversion efficiency and environmental compatibility. In the application of proton exchange membrane fuel cells (PEMFC), a regenerative fuel cell (RFC) system is an energy storage device using hydrogen as the energy medium. RFCs have the advantage in long-term energy storage, because they are free from self-discharge. The simple way to obtain hydrogen and oxygen with high purity is water electrolysis. A regenerative fuel cell using hydrogen as energy storage medium was combined with two separated units for fuel cell and water electrolysis operation. A simpler and more compact system can be realized for the URFC. For the development of URFC, an important consideration is how to unitize the two functions of fuel cell and water electrolysis in a membrane electrode assembly. Previous efforts for URFC have been focusing on the selection of catalysts or an optimization of the operation condition so as to enhance the performance [1–4].

A conventional membrane electrode assembly (MEA) for a PEMFC is comprised of a Pt/C catalyst layer and a gas diffusion electrode [5–7]. But the conventional membrane

electrode assembly is not available for water electrolysis, because the gas diffusion electrode in the PEMFC inhibits the diffusion of reactants and products. For this reason, most of the MEAs used in URFC are constructed of two-layer structure electrodes consisting of membrane and catalyst layers. Also, most of the work to date in fabrication of catalysts onto solid polymer electrolytes utilized a roll-press method. However, the catalyst loading was high (about 8–10 mg/cm²) in the roll-press method, thus another approach was necessary for preparation of the electrode for the URFC in order to reduce the catalyst loading [1–4,8].

The aim of this study was to develop a direct deposition of Pt catalyst onto the Nafion membrane for the URFC. For this purpose, we have proposed a novel deposition method of thin catalyst layers on a Nafion membrane modified with polypyrrole (PPy). Among intrinsic conducting polymers, polypyrrole has attracted much attention as an advanced material because of its good environmental stability, facile synthesis and high conductivity. Pyrrole can easily be reacted by cation oxidizing species, and the resulting polymer is produced in the oxidized state with a cation center which is doped with electrolyte anion in order to neutralize electrical properties of the polymer backbone. Therefore, the combination of Nafion and polypyrrole is easily achieved. Ion (cation and/or anion) motion in polypyrrole has turned out to be more dependent on the size of the anions than on the

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nature of the anions [9–12]. Although some researches have reported on the modification of a Nafion membrane using a conducting polymer for fuel cells, there have been few investigations on the direct deposition of Pt catalyst onto Nafion modified with polypyrrole. We expected that polypyrrole could combine with the sulfonate groups of Nafion and that the resulting PPy/Nafion composite membrane could offer the electronic conduction pathway necessary to sink the electrons generated from the chemical reduction of platinum chloride. Despite using a conventional reduction method for the platinum precursor [13,14], the electrocatalyst of Pt was more easily fabricated on a Nafion membrane modified with polypyrrole compared with on a plain Nafion membrane. This method was not only simple, safe and more economical, but also achieved better performance for the URFC. By taking advantage of those properties we, herein, have proposed a novel preparation method for the electrode with a thin film catalyst for the URFC.

2. Experimental

2.1. Preparation of PPy/Nafion composite membrane

Polypyrrole-impregnated Nafion (PPy/Nafion) composites were prepared by the following procedure. The Nafion membrane was placed in a two-compartment cell. Both surfaces of the Nafion membrane were treated with 0.1 M FeCl_3 solution for 15 min, followed by washing with de-ionized water before polymerization. A 0.2 M solution of pyrrole monomer was simultaneously injected into the reaction chamber for 15 min. The Nafion membrane had a black color. The resulting PPy/Nafion composite membrane was soaked in a 0.5 M H_2SO_4 solution before Pt deposition.

2.2. Pt/PPy/Nafion electrode

The Pt catalysts on the PPy/Nafion composite membrane were prepared by reducing H_2PtCl_6 using NaBH_4 , and the amount of Pt deposited was controlled by the volume of 10 mM H_2PtCl_6 solution used. A solution of 10 mM H_2PtCl_6 was placed in one compartment of the cell and a solution of 0.5 M NaBH_4 was inserted into the other compartment. The volume of H_2PtCl_6 solution in the Pt deposition was varied from 0.5 to 2 ml. The deposition was carried out at room temperature for 1 h. After the Pt catalyst was deposited on one side of the PPy/Nafion surface, the opposite face of the Pt/PPy/Nafion was also deposited in the same method. After the reaction was completed, the resulting electrode was always soaked in 0.5 M H_2SO_4 for 24 h and then in de-ionized water for 1 h. The amount of Pt loading on the membrane was determined by inductively coupled plasma (ICP; ELAN 500, Perkin-Elmer, Inc.).

The surface of the Pt/PPy/Nafion electrode was observed by means of scanning electron microscopy (SEM, JSM-6700F, JEOL). Also, the thickness and the distribution

of the catalyst layer of the Pt/PPy/Nafion electrode were confirmed by energy dispersive X-ray spectrometer (EDS, Oxford 7421, Oxford Link ISIS). AFM (NanoScope III scanning probe microscope) was used for the morphological investigation of the membrane surface.

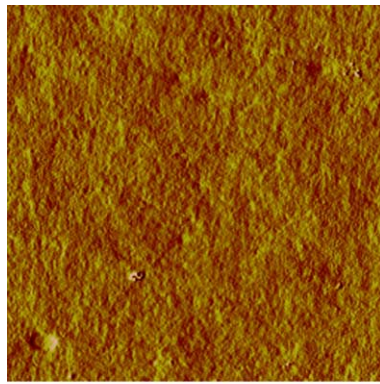
2.3. Cell test for URFC performance

The URFC performance test was conducted in both modes, of PEMFC and water electrolysis, using a single cell with an active area of 4 cm^2 . In the PEMFC mode, pure hydrogen and oxygen gases were provided to the fuel cell through a mass flow controller (Teledyne Hastings-Raydist Co.) from a storage tank. The streams of hydrogen and oxygen were humidified at 85 and 80 °C, respectively. The fuel cell tests were performed under ambient pressure at 75 °C. The performance of the single cell was carried out using a personal computer and an electronic load (HP-6060B, Hewlett Packard Co.) interfaced through a general purpose interface board (GPIB) and data acquisition/control software written in-house. In the water electrolysis mode, the cell was operated with pure water pumped into the electrode chamber from the water reservoir and direct current was supplied by a dc power supply (6410A, Hewlett Packard). Water was supplied to the bottom of the both sides of electrodes of the test cell, and the gases generated were released from the top of the test cell. Water was circulated by peristaltic pump at a rate of 100 ml/min for both electrodes.

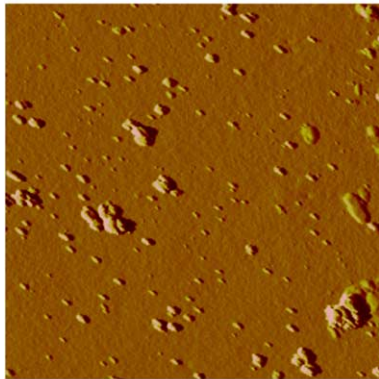
3. Results and discussion

3.1. Morphological analysis

The Pt catalyst layer on the PPy/Nafion membrane, as a function of Pt loading, was fabricated by controlling the volume of 10 mM H_2PtCl_6 solution used. When the Pt/Nafion electrode was fabricated in the absence of polypyrrole, the Pt particles formed on the Nafion surface were easily peeled off. In the presence of polypyrrole, we found that the Pt particles were deposited on PPy/Nafion membrane and the yield of Pt loading was in the range of 40–56%. According to the ICP data, the amount of Pt particles deposited on the membrane was 0.14, 0.20 and 0.38 mg/cm^2 at 0.5, 1.0 and 2.0 ml volume of 10 mM H_2PtCl_6 , respectively. These results suggested that the surface of the composite membrane that is polymerized with pyrrole served as an electronic conduction pathway owing to the electronic properties of the polypyrrole, therefore, the polypyrrole would play the role of an electronic sink for the reduction of the platinum precursor similar to the preparation of a conventional Pt/C catalyst. As mentioned earlier, the deposition of Pt on PPy/Nafion was easier than the method of using bare Nafion. The surface of the Nafion membrane impregnated with polypyrrole was observed by atomic force microscope (AFM). Fig. 1 shows the AFM images of the bare Nafion and PPy/Nafion composite



(a)



(b)

Fig. 1. AFM images of (a) Nafion 117 and (b) PPy/Nafion composite membrane surface.

membranes. When the pyrrole was polymerized on the Nafion membrane, the surface of the PPy/Nafion composite membrane had a flatten morphology compared with the bare Nafion membrane. This indicated that the polypyrrole was formed on the surface of the Nafion by the oxidation of pyrrole. The SEM images of the surface of the Pt/PPy/Nafion electrode are shown in Fig. 2. The porous structure and the aggregation of the Pt particles are uniformly observed on the Pt/PPy/Nafion electrode, and the average size of the Pt particles is less than $1\ \mu\text{m}$. In water electrolysis, isolated Pt particles could not be provided with an electronic conductor to each other from the external dc power supply. Therefore, the continuously linked Pt particles were more effective catalysts compared to isolated Pt particles. Also, if the Pt surface was more porous and the size of the Pt particle was much smaller, the surface area of Pt particle would be enlarged. As a result of morphological analysis, we expected that the Pt/PPy/Nafion electrode prepared having the amount of Pt loading of $0.38\ \text{mg}/\text{cm}^2$ exhibited most performance for water electrolysis. However, the morphological estimation from SEM was not consistent with the catalysts utility for the fuel cell mode, because the three-phase region was a more important effect for the PEMFC. It should be mentioned that the fuel and oxidant must react at the interface region between the electrolyte and the catalyst layer in the fuel cell

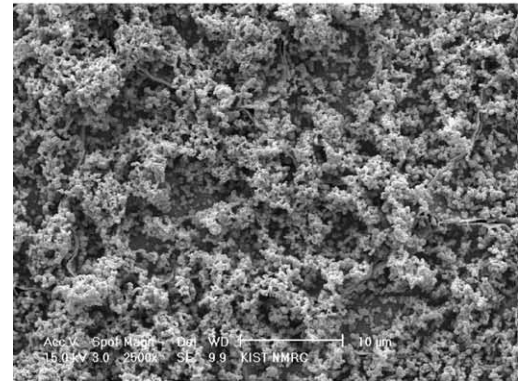
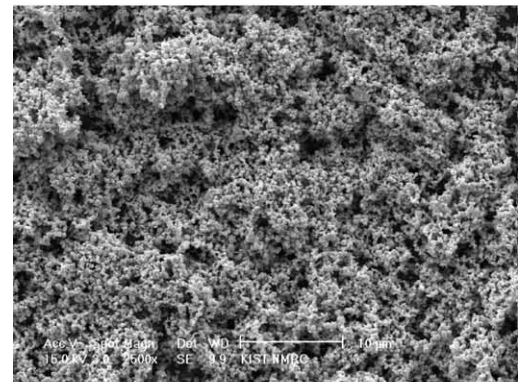
(a) $0.14\ \text{mg}/\text{cm}^2$ (b) $0.20\ \text{mg}/\text{cm}^2$ (c) $0.38\ \text{mg}/\text{cm}^2$

Fig. 2. Scanning electron micrographs of Pt/PPy/Nafion electrode surface with different Pt loading.

mode. Therefore, the catalyst layer should be porous enough to allow the reactant gases access into the three-phase region.

In order to investigate the location of the Pt deposit, the result of the EDS analysis is presented in Fig. 3. The images of the cross-section of the Pt/PPy/Nafion electrode assembly without diffusion layers are shown. A lump of Pt particles found in the membrane represents debris generated when the composite electrode was cut for EDS analysis. The thin catalyst layer on the PPy/Nafion composite membrane surface

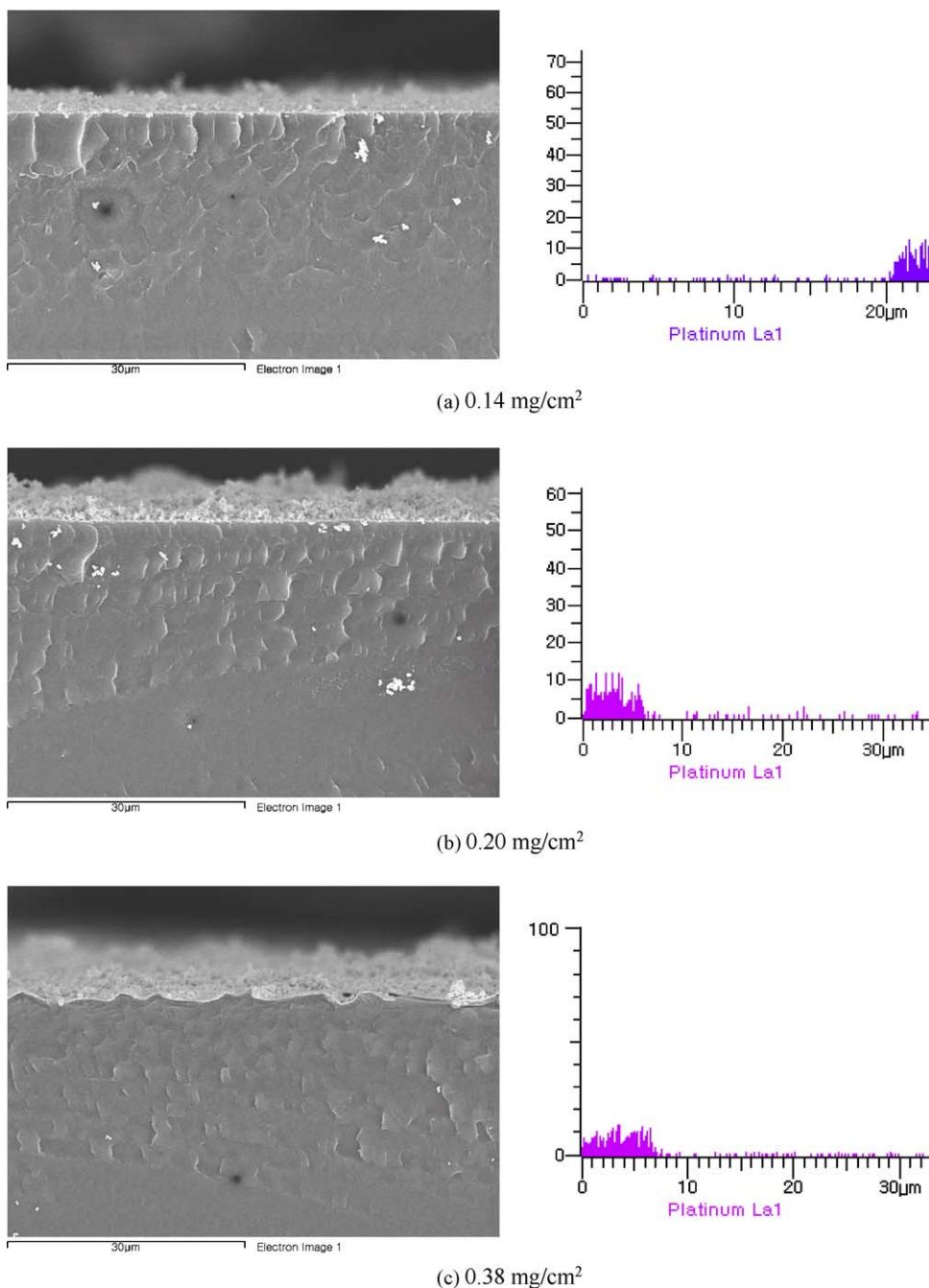


Fig. 3. Mapping of Pt distribution along the cross-section of Pt/PPy/Nafion electrode with different Pt loading.

is shown in Fig. 3. The thickness of the catalyst layer was found to be approximately 3–7 μm , with different amounts of Pt loading. After the surface region of the PPy/Nafion membrane was covered with Pt particles, granular Pt particles were progressively formed the direction perpendicular to the surface. When the fuel cell and the water electrolysis were conducted at high current density, the adhesion between the catalyst layer and the membrane was an important factor to consider for the purpose of reducing contact resistance. Also, because most of the current was generated in the interface between the catalyst layer and the membrane, at

high current density, the electrocatalyst layer must be tightly bound on the membrane. From the morphological analysis, we confirmed that the adhesion of the Pt particles was improved by polypyrrole, and the Pt deposition method using polypyrrole was valuable for fabrication of electrocatalysts onto the Nafion surface.

Fig. 4 shows typical cyclic voltammograms of the Pt/PPy/Nafion electrode in 0.5 M H_2SO_4 solution at room temperature. The measurement was conducted in the potential range from -0.3 to 1.2 V versus Ag/AgCl at a scan rate of 40 mV/s. The cathodic and anodic peaks observed

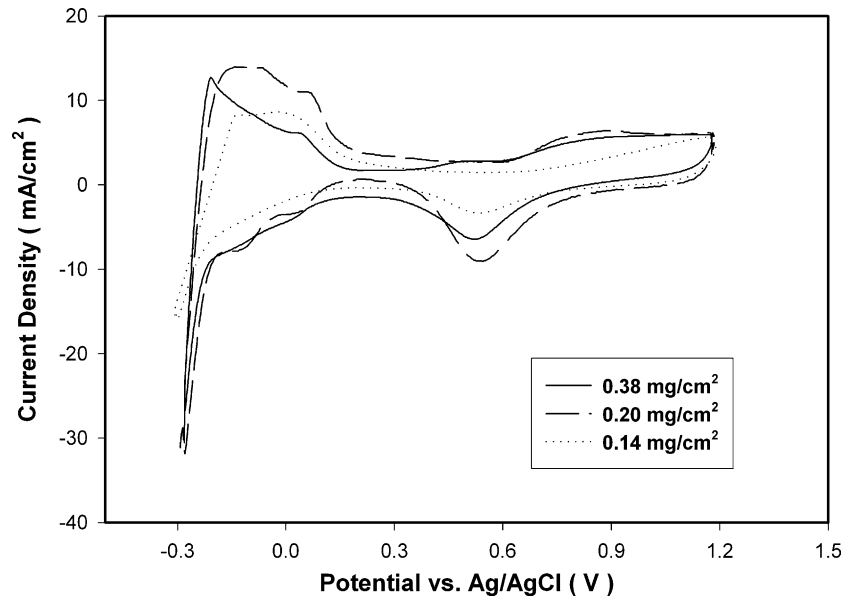


Fig. 4. Cyclic voltammograms of Pt/PPy/Nafion electrode prepared with various Pt loading (scan rate 40 mV/s).

between -0.3 V and 0.0 V versus Ag/AgCl corresponded to the adsorption and desorption of hydrogen ions on the Pt catalyst, respectively. From the CV, we found that the catalyst of the Pt/PPy/Nafion electrode behaved as an electrochemically active site. Using the electrochemical adsorption charge in Fig. 4, the roughness factor and the active surface area of the Pt/PPy/Nafion electrode were calculated in Table 1. The roughness factor was the ratio of the actual adsorption charge on the Pt/PPy/Nafion electrode to the theoretical adsorption charge on smooth platinum. The active surface area was represented as the ratio of the roughness factor to the Pt loading. As mentioned in Table 1, the surface area was relatively high for each Pt/PPy/Nafion electrode in spite of the low Pt loading. Therefore, it can be considered that the direct deposition of Pt catalyst on Nafion impregnated polypyrrole is a promising method to reduce the amount of loading on the electrocatalysts for URFC.

3.2. Single cell performance of Pt/PPy/Nafion electrodes for URFC

Fig. 5 shows the fuel cell performance curves of single cells obtained for a MEA with various loadings of Pt. The performance of the fuel cells as a function of Pt loading was evaluated in the presence of hydrogen and oxygen gas

with an active area of 4 cm² at 80 °C. The performance of the single cell was increased as the Pt loading was increased. In particular, a single cell with a Pt loading of 0.38 mg/cm² showed higher performance than with the other MEAs. When the cell voltage was 0.695 and 0.313 V, the current density was 190 and 636 mA/cm², respectively. Even though the performance of a single cell was increased as the Pt loading was increased, the active Pt catalyst within the three-phase region were not proportionate to the Pt loading, quantitatively. Therefore, in order to enhance the utility of the Pt catalyst on the Nafion membrane, further

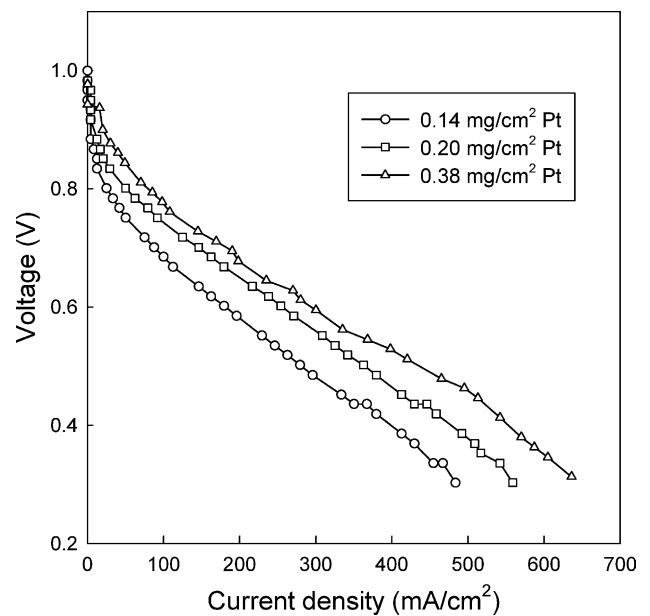


Fig. 5. I - V polarization curves for MEA of Pt/PPy/Nafion with different Pt loading.

Table 1
The electrochemical properties of Pt/PPy/Nafion electrode using polypyrrole

Pt loading (mg/cm ²)	Electricity (mC/cm ²)	Roughness factor	Surface area (m ² /g)
0.14	24.00	114.29	81.64
0.20	39.10	185.24	92.62
0.38	58.45	278.33	73.24

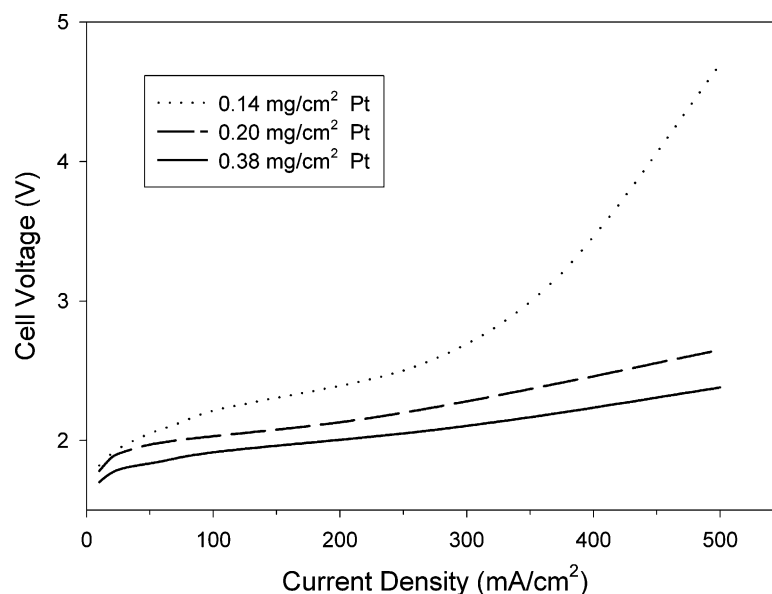


Fig. 6. Effects of different Pt loading on water electrolysis (the cell operated with purified water at 60 °C and atmospheric pressure).

investigations will be needed to establish the optimal condition for the Pt/PPy/Nafion electrode fabrication.

I–*V* curves for water electrolysis of URFC are presented in Fig. 6. As the Pt loading was increased, the performance of the water electrolysis followed the same trend. The single cell with 0.38 mg/cm² Pt loading showed higher water electrolysis performance than the other cells. When the current density was 2.38 A/cm², the voltage of the water electrolysis was 0.5 V at ambient pressure and 60 °C. Compared with the fuel cell performance, the water electrolysis performance was more dependent on the amount of Pt loading. In principle, the general approach to optimize the two functions of fuel cell and water electrolysis was to control the Pt loading catalysts for the URFC. Based on the results, the Pt/PPy/Nafion electrode with 0.38 mg/cm² was most suitable for URFC in this study.

4. Conclusion

We have proposed a novel method of direct deposition of Pt catalysts on Nafion membrane modified with polypyrrole for the URFC. We demonstrated that the polypyrrole could play a role as an electronic sink material for Pt catalyst deposition and the subsequent chemical reduction of the platinum precursor was easily reacted on the modified Nafion membrane. We confirmed that the resulting MEA had a very thin catalyst layer, and the adhesion of the Pt catalyst on the polypyrrole-modified membrane was considerably enhanced from the morphological analysis. Although more investigations are required to unitize the two functions of fuel cell and water electrolysis, this study showed that direct deposition

of Pt catalysts on Nafion-impregnated polypyrrole is a promising method to reduce the loading amount of electrocatalysts and to prepare a thin catalyst layer for the URFC.

Acknowledgements

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