Electrodepositing Pt by Modulated Pulse Current on a Nafion-Bonded Carbon Substrate as an Electrode for PEMFC

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Polymer electrolyte membrane fuel cell (PEMFC) electrodes were platinized by modulated pulse current electrodeposition. The aim of this study is to look for a way that keeps the advantages but circumvents the disadvantages of electrodeposting Pt for PEMFC electrodes. The capacitance effect of the double layer on the wave pattern of the pulse current was fully considered when choosing the current parameters. An uncatalyzed carbon electrode, on which a layer of Nafion-bonded carbon (NBC) was dispersed in advance, served as a substrate for electrodeposition. The platinized electrode by electrodeposition was assessed by the techniques of cyclic voltammetry, linear-sweep voltammetry, X-ray diffraction, transfer electron microscopy, and so on. The preliminary results show the following: (1) Pt deposition current efficiency in well-modulated pulse current electrodeposition has been markedly improved even to as high as 69.9% compared with 13% in the direct current electrodeposition. (2) It is difficult at the present time to get an electrode with high Pt loadings and good Pt dispersion by pulse electrodeposition because the hydrogen evolution is unavoidable. (3) It is uncertain for Pt deposition current efficiency even though the electrodeposition was conducted under the exact same technique because of the erratic generation and breaking of hydrogen bubbles.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) hold great promise for use as an environmentally friendly power source for automobiles.[1] One of the key requirements in making PEMFC commercially viable is to reduce the cost by reducing the amount of precious metal catalyst necessary to provide high-power-density operation at low temperature. It is, in general, agreeable that lowering the loading of noble-metal catalysts and improving their utility are the keys to the success of this technology, among others. For a given Pt loading, it is always expected that almost all Pt catalyst particles are effective in the electrochemical reactions. However, this is not always possible, especially in the case of perflurosulfonete ionomer (PFSI) electrolytes, which cannot reach every desired site, where Pt catalysts are present.[2] Effective Pt catalyst particles, however, are those that are not only in contact with PFSI but also have two conducting channels, that is, the electron channel via carbon particles to current collector and the proton channels via PFSI particles to the Nafion membrane.

Much effort has been devoted to develop electrodes with high utilization of noble-metal catalysts. These include the improvement in preparation process of catalyst ink,[2–4] extending the wet area of the catalytic region by adding a semihydrophobic carbon powder layer between the Teflon-coated carbon paper and the catalyst layer,[5] and sputter deposition of the metal catalyst directly onto the surface of Nafion-bonded carbon paper,[6] as well as electrodepositing noble-metal catalysts in desired locations.[7–13]

Among all, electrodeposition of noble-metal catalysts on the Nafion-bonded carbon electrode (NBC) in an aqueous solution opens a promise in increasing the utility of metal catalysts practically. It is because electrodeposition in aqueous bath can selectively deposit platinum catalysts only onto the electrode regions where both ions and electrons are accessible because only in those regions there are electron-transport channels and metal-ion-transport channels resulting from the hydrophilicity of the Nafion particles. Electrodeposition with pulse current, direct current, and cyclic voltammetry has been employed to deposit platinum onto a preformed uncatalyzed carbon substrate in the anodes and cathodes of H_2-fed PEMFCs.[7–13] Stab and Urban patented[14] an invention of the electrodeposition of noble-metal or noble-metal/metal electrocatalysts for use in direct methanol fuel cells (DMFCs). Unfortunately, with the conduction of Pt electrodeposition, further deposit of Pt would be likely deposited on already existing Pt particles, which leads to a larger size of deposited Pt particles if a relatively high Pt loading is required, for example, 0.5 mg·cm^{-2}. Usually, the Pt particle sizes from electrochemical deposition fall in the range of 20–70 nm[15–17] unless the Pt loading is ultralow, for example, 0.05 mg·cm^{-2}.[12] In consideration of the small size of widely used commercial catalysts Pt/C by the Johnson–Matthey Co. ca. 2–4 nm, there would be no advantages for a catalyst with Pt particle size of 20–70 nm even though every Pt particle was fully

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Electrodepositing Pt by Modulated Pulse Current

J. Phys. Chem. C, Vol. 111, No. 42, 2007 **15457**

utilized. In addition, the current efficiency for Pt electrodeposition is extremely low in a simple acidic aqueous solution, in which the hydrogen evolution is unavoidable.[11,12] Even worse, the current efficiency for Pt electrodeposition will be further worsened with Pt particles deposited on the NBC because the hydrogen evolution is sped up by Pt particles. The hydrogen bubble forming on the NBC may prevent the deposition solution from entering into the NBC, which consecutively interrupts the process of deposition. Meanwhile, serious hydrogen evolution will not only damage the structure of the NBC but also cause increased pH level locally, which may further lead to hydrolysis of Pt salts.

Recently, Tian et al.[18] reported that Platinum nanocrystals with unusual tetrahexahedral shapes were obtained by an electrochemical square-wave potential treatment of electrodeposited Pt nanospheres supported on a smooth glassy carbon electrode. The single tetrahexahedral nanocrystal is enclosed by 24 high-index facets such as {730}, {210}, and/or {520} surfaces that have a large density of atomic steps and dangling bonds. These high-energy surfaces are stable thermally (to 800 °C) and chemically and exhibit much enhanced (up to 400%) catalytic activity per unit surface area for electrooxidation of small organic fuels such as formic acid and ethanol. However, for catalytic activity per unit weight of Pt, the overall activity of these larger tetrahexahedral Pt nanocrystals is less than that of the 3-nm commercial Pt nanoparticles. This is due to the large size of the tetrahexahedral Pt nanocrystals because they are transformed from Pt nanospheres as large as 750 nm. Meanwhile, this excellent work did not involve how efficiently to prepare the Pt nanoparticles on a porous substrate.

Thus, it is necessary to manage to get a small Pt particle and to restrain hydrogen evolution in electrodeposition. Our previous research[19] showed that a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), can effectively inhibit the hydrogen evolution reaction (HER) on the Pt electrode. The current efficiency for Pt electrodepostion increases from 8.7% to 71.2% with introduction of 0.05 M CTAB into the Pt deposition bath. Unfortunately, the presence of CTAB can also inhibit the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). It means that a trace of remains of the CTAB in the electrode platinized electrodeposition with the aid of the CTAB would be detrimental for the HOR and ORR, the two final objectives of the electrode platinized electrodeposition.

Pulse electrodeposition exhibits marked advantages over direct current electrodeposition in the control of deposit grain size, surface morphology, and preferred orientation if the pulse parameters are carefully chosen and adjusted to the particle structure desired. In pulse electrodeposition, three parameters influence the deposit properties: peak current density (j_p), current on time (T_{on}), and current off time (T_{off}). Different from traditional slab electrode, the charge (t_c) and discharge time (t_d) of the double layer are usually very long in a porous electrode because of its large capacitance. Thus, when metal was deposited on the porous electrode substrate by the pulse current, the capacitance effect of the double layer on the wave pattern of pulse current must be taken into consideration of choosing j_p, T_{on}, and T_{off}. Generally, there are three cases about the effect of electrode double-layer capacitance on the wave pattern of pulse current as shown in Figure 1.[20] Especially, in the case of Figure 1c, both the charge time (t_c) and discharge time (t_d) of the electrode double-layer capacitance are greater than current on time (T_{on}) and the current off time (T_{off}); the real current response, that is, the Faraday current, would be close
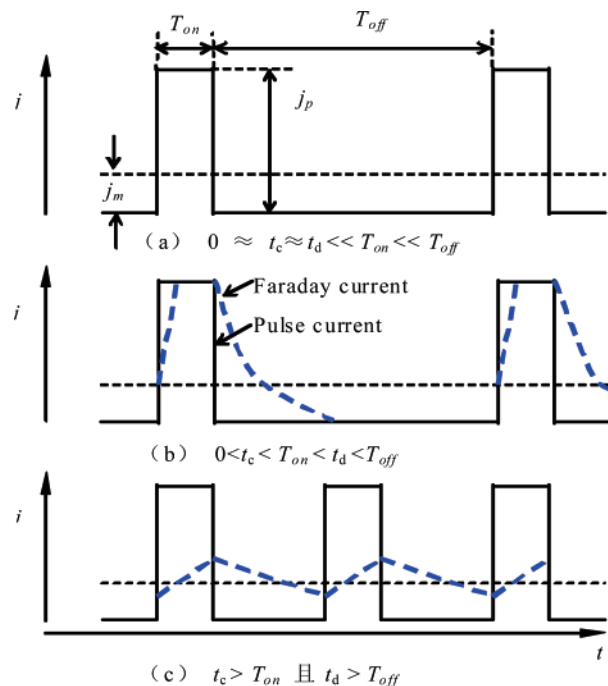

Figure 1. Effect of electrode double-layer capacitance on the wave pattern of pulse current (solid line, imposed pulse current; dashed line, response Faraday current).

to a quasi-direct current just with a certain fluctuation. In other words, the current just rises and falls surrounding the average current density (j_m). Thus, the superiority of pulse electrodeposition cannot work at all. However, too long current on time would possibly consume Pt complex ions before the current comes to an end. In this case, the surplus charge of pulse current would be used to electrolyze water, which is detrimental as mentioned above. Although electrodeposition with pulse current has been employed to deposit platinum onto a preformed uncatalyzed porous carbon substrate in preparation of PEMFCs anodes and cathodes,[8,9,14] the capacitance effect of the double layer on the wave pattern of pulse current was not taken into consideration when choosing the pulse current parameters.

The aim of this study is to look for a way that keeps the advantages but circumvents the disadvantages of electrodeposting Pt for PEMFC electrodes. The capacitance effect of the double layer on the wave pattern of the current was fully considered when choosing the current parameters, j_p, T_{on}, and T_{off}, which were modulated according to the capacitance effect of the double layer in order to obtain an optimum platinum loading, Pt particle size, and high dispersion onto a preformed uncatalyzed porous carbon substrate.

2. Experimental Section

2.1. Preparation of Nafion-Bonded Carbon Electrode (NBC). The Nafion-bonded carbon electrode, henceforth named as NBC, consists of two different carbon layers, hydrophobic and hydrophilic. As shown in Figure 2, first, the carbon paper (Tony Co, Jap.) was dipped in 30% Teflon for 30 min, dried in air, and sintered at 340 °C for 30 min; and then the ink containing carbon powder (Vulcon XC-72) and 10% PTFE (the dry weight ratio of PTFE to carbon powder was kept at 1:3) ultrasonically dispersed in isopropyl alcohol was coated on the Teflon-treated carbon paper and dried at 340 °C to form a hydrophobic layer. Subsequently, the hydrophilic ink containing carbon powder (Vulcon XC-72) was treated with nitric acid in refluxing conditions for 2 h and 5% Nafion ultrasonically
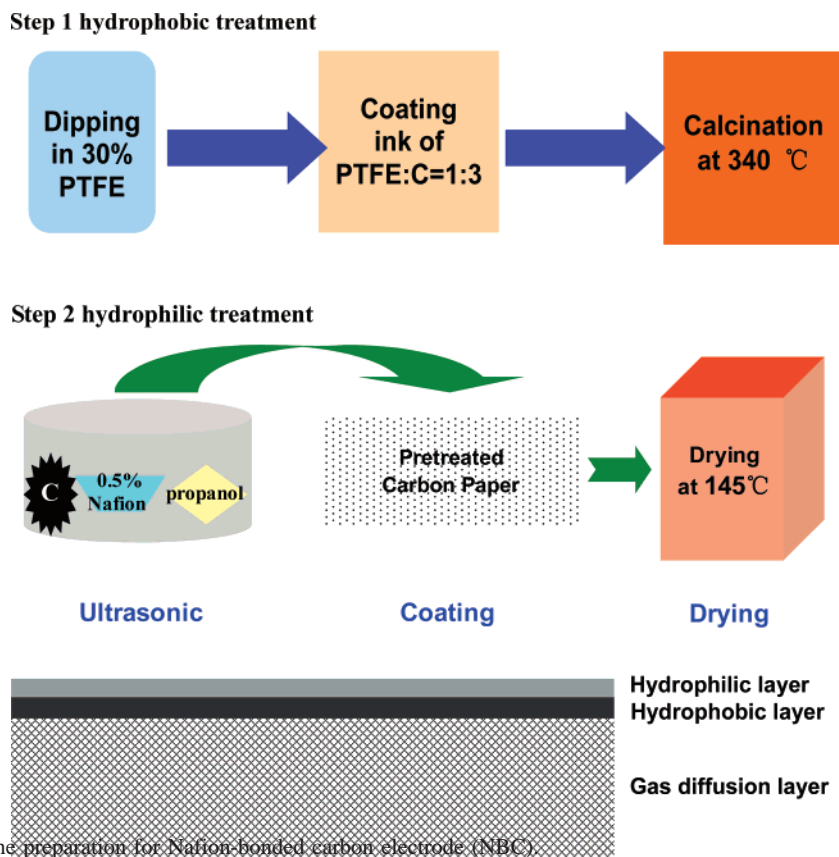
Step 1 hydrophobic treatment

Dipping in 30% PTFE → **Coating ink of PTFE:C=1:3** → **Calcination at 340 ℃**

Step 2 hydrophilic treatment

0.5% Nafion **propanol** → **Pretreated Carbon Paper** → **Drying at 145℃**

Ultrasonic　　　**Coating**　　　**Drying**

Hydrophilic layer
Hydrophobic layer

Gas diffusion layer

Figure 2. Schematic of the preparation for Nafion-bonded carbon electrode (NBC).

dispersed in isopropyl alcohol was applied on the hydrophobic layer. Finally, the Nafion-bonded carbon electrode (NBC) was dried at 145 °C for 20 min.

2.2. Loading Metal Catalysts by Electrochemical Deposition. The electrochemical deposition of Pt was carried out in a two-electrode cell system. The NBC was employed as the working electrode, and The Pt wire was employed as a counter electrode. The electrochemical deposition of platinum was performed on the NBC in a bath containing 10 g·L^{-1} of H$_2$-PtCl$_6$ and 60 g·L^{-1} of HCl at 65 °C. Rectangular galvanostatic pulses modulated by changing peak current densities, length of current on times, and current off times were applied to deposit Pt. The electrodeposition was performed on Autolab potentiostat/galvanostat PGSTAT 30 with GPES software.

2.3. Characterization of the Catalyst Electrode. Linear-sweep voltammetry (LSV) and cyclic voltammetry (CV) were used to characterize the electrochemical performance of the catalyzed electrode prepared by the pulse electrodeposition method. All electrochemical experiments were performed in a three-electrode cell at room temperature. The cell consists of a working electrode prepared by pulse electrodeposition methods, a Pt wire counter electrode, and a saturated potassium chloride silver chloride electrode (SSCE) (0.20 V vs SHE), which served as a reference electrode. All potentials are quoted with respect to the SSCE reference electrode (0.20 V vs SHE), unless otherwise stated.

2.4. XRD and TEM Test. The XRD test was carried out on SHIMADIU XRD-6000 (Japan). Cu Ka ($k = 0.15418$ nm) serves as the radiation source. The X-ray diffraction spectra were obtained at a scan rate of 4°/min^{-1} in a range of 2θ from 30° to 80°. The theoretical average particle size was estimated using Scherrer's equation.[21] Although there are several XRD peaks that can be used for the estimation of the particle size, only the full width at half-maximum corresponding to the (111) plane at $2\theta = 39.7°$ was used to determine the average Pt particle

size because the data at a low diffraction angles would lead to smaller errors in estimation of particle size than those at high angles according to literature.[22] The electrodeposited Pt particle together with the carbon carrier and Nafion polymer was scratched down from the NBC and ultrasonically suspending in isopropyl alcohol and observed on a PHILIPS TECNAI 10 transmission electron microscope (TEM).

2.5. Pt Content Test. Spectrophotometry with a color-developing agent of SnCl$_2$ was used to determine the Pt content in a catalyzed electrode.[23] First, the catalyzed electrode after performance tests was calcinated in air at a temperature of 700−800 °C to remove the carbon carrier and polymer; then the residue was dissolved by aqua regia to form a Pt-ion-containing solution in which 8 mL of 37% HCl, 10 mL of 20% NH$_4$Cl, and 5 mL of 20% SnCl$_2$ hydrochloric acid solution (the volume ratio of HCl to water is 1:1) were added. Finally, a spectrophotometer (TU-1900/TU-1901, Beijing Puxi, China) with a double beam of lights served to determine the Pt content by detecting the absorbency of the platinum-containing solution.

3. Results and Discussion

3.1. Effect of the NBC Preparation on Pt Electrodeposition. The ideal electrodeposition of Pt on the NBC is to a large extent decided by the properties of the NBC, such as porosity, thickness, hydrophobic/hydrophilic behavior, and so on. These properties of the NBC are in turn decided by the carbon and Nafion loadings as well as their ratio to each other. Thus, it is necessary to configure the NBC carefully. Unless otherwise stated, the carbon and Nafion loading are quoted with respect to the amount in the hydrophilic layer.

The electrochemical performances of the pulse-electrodeposited-Pt electrode with different carbon loadings in the NBC are shown in Figure 3. For all NBC substrates, the Pt electrodeposition was conducted at 100 mA cm^{-2} of pulse peak current,

Electrodepositing Pt by Modulated Pulse Current

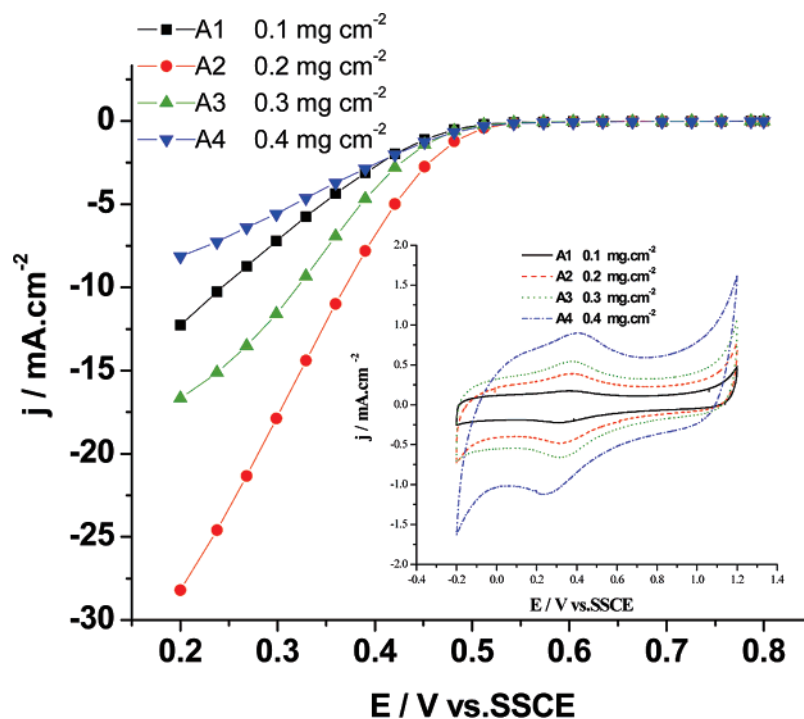*J. Phys. Chem. C, Vol. 111, No. 42, 2007* **15459**

Figure 3. LSV curves of the pulse-electrodeposited-Pt electrode at different carbon loadings in O_2-saturated 0.5 M H_2SO_4 at a sweep rate of 2 mV s^{-1}.

300 μs of current on time, and 1200 μs of current off time. The total charge for electrodeposition was fixed at 0.3 C cm^{-2}. The best performance observed as carbon loadings was 0.2 mg·cm^{-2}. The results show that the carbon loadings exert an important effect on the Pt electrodeposition. With the increase of carbon loadings, the thickness of the NBC increases consequently. This leads to double-layer capacitance increase of the NBC, which is embodied by increasingly widened CV cycles in the inserted CV curves of Figure 3. The best performance of the pulse-electrodeposited-Pt electrodes was observed on a NBC with a median carbon loading and accordingly a median value of capacitance as illustrated in the inserted CV curves of Figure 3. At low carbon loadings, the active sites in NBC are not enough for more Pt electrodeposition taking place concurrently, and Pt electrodeposition would be likely deposited on limited active sites, which leads to only a few Pt particles with large sizes. This would decrease the surface area of the Pt catalysts and worsen the electrochemical performance of the final electrode. When the carbon loadings increase to 0.4 mg cm^{-2}, the influence of double-layer's charge/discharge on Pt electrodeposition cannot be ignored any more. It was supposed that the situation as indicated in Figure 1c would take place in this case. That is, the real current for electrodeposition just rises and falls surrounding the average current density (j_m). The superiority of pulse electrodeposition doesn't work at all in this case.

The influence of the ratio of Nafion to carbon powder on the deposited Pt particle size was revealed in XRD patterns as shown in Figure 4. The measured average Pt particle sizes with different ratios of Nafion to carbon powder are summarized in Table 1. For all cases, the pulse electrodeposition was conducted under the conditions of 67 mA cm^{-2} peak current density, 300 μs current on time, and 1200 μs current off time, 0.2 mg cm^{-2} carbon loadings, and the electrodeposition charges were fixed at 0.3 C cm^{-2}. The XRD patterns shown in Figure 4 clearly indicate that there is a critical value of Nafion content in NBC in the light of looking for the smallest Pt particle. With a low Nafion content such as 1:50 and 1:30, the Pt deposition may
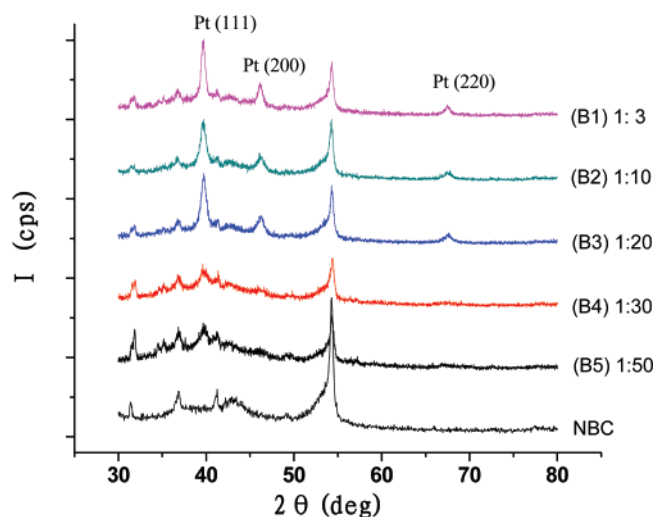

Figure 4. XRD spectra of Pt/C catalysts prepared at different ratios of Nafion to carbon powder.

TABLE 1: Average Pt Particle Size Prepared with Different Ratios of Nafion to Carbon (Parameters in Pulse Electrodeposition: On Time, 300 μs; Off Time, 1200 μs; Peak Current Density, 67 mA·cm^{-2}; Total Charge Density, 0.3 C·cm^{-2})

electrode	weight ratio of Nafion to carbon	average Pt particle diameter/ nm	Pt loadings/ mg cm^{-2}	current efficiency/ %
B1	1:3	14.23	0.086	56.6
B2	1:10	14.03	0.079	51.7
B3	1:20	10.97	0.087	57.4
B4	1:30	6.94	0.084	55.2
B5	1:50	7.28	0.081	53.2

occur in the whole NBC and the average Pt particle size calculated by Scherrer's equation is as small as ca. 7 nm. The average Pt particle size increases with the increase of Nafion content in the NBC. Too high Nafion content in the NBC would
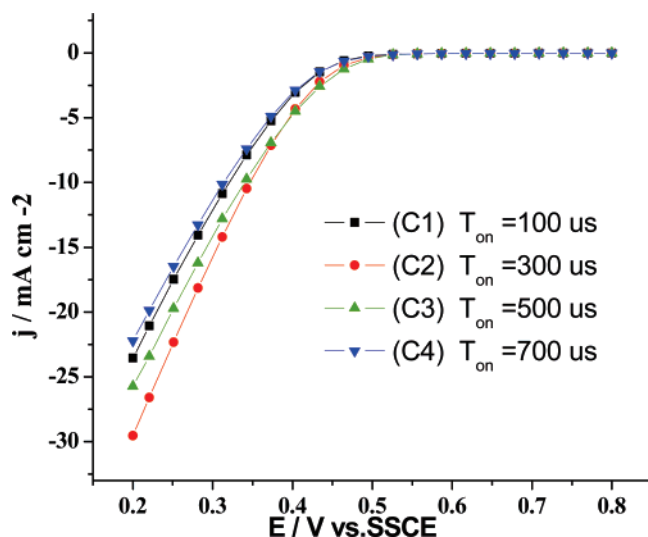
Figure 5. LSV curves of the electrodes prepared at different on times in O_2-saturated 0.5 M H_2SO_4 at a sweep rate of 2 mV s^{-1}.
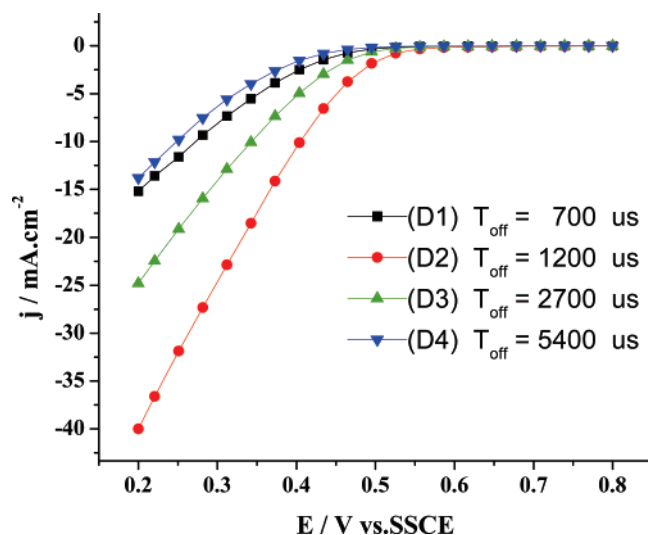

Figure 6. LSV curves of the electrodes prepared at different off times in O_2-saturated 0.5 M H_2SO_4 at a sweep rate of 2 mV s^{-1}.

form a Nafion polymer film on the electrode surface,[24] which prevents the Pt complex ions from entering inside the electrode. This leads to the Pt electrodeposition occurring only on the NBC surface. Too low Nafion content in the NBC, however, cannot guarantee enough mechanical strength of the NBC. The optimum ratio of Nafion to carbon powder is 1:30.

3.2. Effects of Pulse Parameters on Pt Electrodeposition. The performance of the Pt electrode catalyzed by pulse electrodeposition is greatly influenced by the pulse parameters T_{on}, T_{off}, j_p, and j_m. There is the following relationship among T_{on}, T_{off}, j_p, and j_m.

$$j_m = (T_{on}/(T_{on} + T_{off}))j_p \qquad (1)$$

Obviously, if the three of them were determined then the other one would be consequently determined by eq 1. Figure 5 shows the influence of current on time of electrodepostion current on the performance of the electrodes for the ORR in O_2-saturated 0.5 M H_2SO_4. The all-pulse electrodeposited electrodes from C1 to C4 were prepared under the same conditions of 67 mA cm^{-2} peak current density, 1200 μs current off time, and 0.3 C cm^{-2} total electrodeposition charges except the current on time, T_{on}. At 100 μs of the current on time, T_{on}, the charge time (t_c)
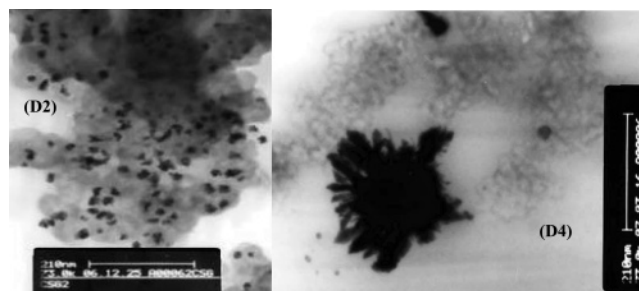

Figure 7. TEM images of Pt/C catalyst prepared according to D2 and D4 of Table 3.

TABLE 2: Influence of Pulse On Time on Pt Loadings and Current Efficiency when Electrodeposition Charges Were 0.3 C·cm^{-2}

electrode	T_{on}/ μs	T_{off}/ μs	j_p/ mA cm^{-2}	j_m/ mA cm^{-2}	Pt loadings/ mg cm^{-2}	current efficiency/ %
C1	100	1200	67	5.15	0.042	27.8
C2	300	1200	67	13.40	0.083	54.6
C3	500	1200	67	19.70	0.067	44.2
C4	700	1200	67	24.68	0.047	31.2

and discharge time (t_d) of the capacitance on the interface of NBC/deposition bath may be greater than the T_{on} and T_{off}. Thus, a similar situation as described in Figure 1c possibly took place. The Pt pulse electrodeposition actually becomes a quasi-direct current electrodeposition. It will have all disadvantages in the company of the direct current electrodeposition, such as large crystal size, low current efficiency, serious concentration polarization, considerable hydrogen evolution, and so on. With increase of current on time, the effect of double-layer charge/ discharge gets weakened, and the advantage of pulse elec-trodeposition will emerge. When the current on time reaches to 700 μs, however, because of the limited mass transfer of Pt complex ions, the hydrogen evolution would dominate the late electrodeposition of each pulse peak. The current efficiency for Pt electrodeposition would also decrease. The best performance of the electrode prepared at 300 μs in Figure 5 is obviously due to the highest current efficiency for Pt electrodeposition and therefore the highest Pt loadings of all prepared electrodes as listed in Table 2.

Figure 6 shows the influence of current off time of elec-trodepostion current on the performance of the electrodes for the ORR in O_2-saturated 0.5 M H_2SO_4. All electrodes were prepared under the same conditions of 67 mA cm^{-2} peak current density, 300 μs current on time, and 0.3 C cm^{-2} total electrodeposition charges except the current off time, T_{off}. The best performance was observed at 1200 μs current off time. The results indicate that it is important to keep a proper current off time for efficient Pt deposition because it is during the current off time that concentration polarization of the Pt complexes in the porous NBC is eliminated. If the current off time is short or even shorter than t_d, then, first, the concentration of Pt complex ions in the porous NBC cannot be completely recovered to its initial state, , second, the hydrogen evolution would take place, and finally, the situation described in Figure 1c would occur. If the current off time is too long, however, then it would be long enough for tiny Pt deposits to dissolute and then recrystallize to form large Pt deposits. This speculation is evidently confirmed by TEM images in Figure 7 of Pt/C catalysts prepared at different current off times, where too long of a current off time, for example, 5400 μs, leads to a few large Pt particles as shown in Figure 7 (D4), whereas a proper length of current off time, for example, 1200 μs, helps us to obtain
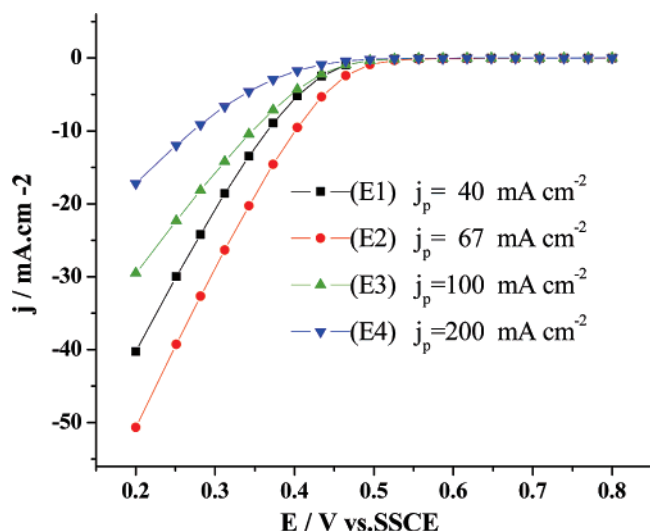
Electrodepositing Pt by Modulated Pulse Current

J. Phys. Chem. C, Vol. 111, No. 42, 2007 **15461**

Figure 8. LSV curves of the electrodes prepared at different peak current densities in O_2-saturated 0.5 M H_2SO_4 at a sweep rate of 2 mV s^{-1}.
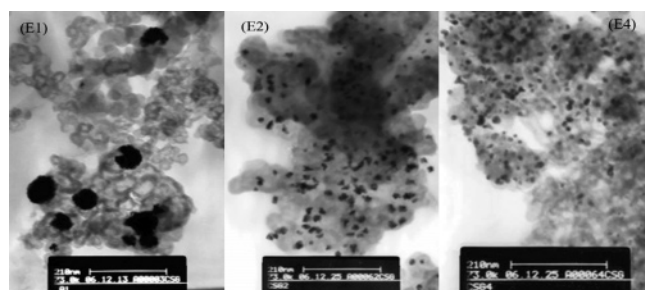

Figure 9. TEM images of Pt /C catalyst prepared according to E1, E2, and E4 of Table 4.

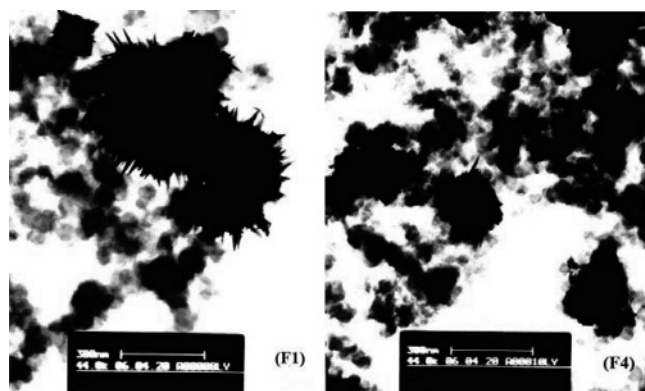**Figure 10.** TEM images of Pt/C catalyst prepared according to F1 and F4 of Table 5.

highly dispersed small Pt particles as shown in Figure 7 (D2). It is the difference in size of the Pt particles obtained at different current off times that causes the difference in electrocatalysis as demonstrated in Figure 6 even though the Pt loadings may be the same for all investigated electrodes. The data listed in Table 3 support the above analysis in respect to Pt loadings and current efficiency measurements.

Figure 8 shows the influence of peak current density in electrodepostion on the performance of the electrodes for the ORR in O_2-saturated 0.5 M H_2SO_4. All pulse electrodeposited electrodes from E1 to E4 in Figure 8 were prepared under the same conditions of 300 μs current on time, 1200 μs current off time, and 0.3 C cm^{-2} total electrodeposition charges except the peak current density. The TEM images of deposited Pt particles
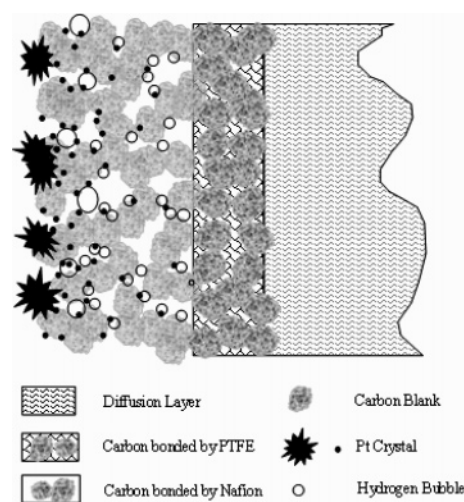

Figure 11. Schematic of the process occurring during deposition.

on electrodes E1, E2, and E4 are shown in Figure 9. The Pt loadings, particle sizes, and current efficiencies associated with electrodes E1, E2, and E4 are summarized in Table 4. Electrode E2 prepared at the peak current density of 67 mA cm^{-2} shows superior electrochemical performance to the others. The highest current efficiency for Pt electrodeposition and therefore the highest Pt loadings as well as not too large Pt particles of electrode E2 are responsible for its best performance. Because the peak current density was over 200 mA cm^{-2}, the electrochemical performance of the Pt catalyzed electrode is exceptionally poor although the deposited Pt particle in this case is of the smallest size. As known, a large peak current density is favorable for the formation of crystalline seeds with reference to the crystal growth and leads to many fine crystals. Conversely, a small peak current density is favorable for crystal growth with reference to the formation of crystalline seeds. Therefore, a large peak current density leads to many fine crystals but a small peak current density leads to a few big crystals. As illustrated in Figure 9, the Pt particle size decreased with the increase of peak current density. At a small peak current densities, Pt electrodeposition occurs only in a limited number of crystalline seeds, on which all deposition current was focused. Thus, the real deposition current density is much greater than the apparent. This may lead to a local concentration polarization of Pt complex ions around these limited crystalline seeds and in turn cause a decrease in the current efficiency and Pt loadings. As the peak current density rises to 200 mA cm^{-2}, the Pt complex ions all around the NBC cannot sustain such a large deposition rate. The surplus charge on each pulse peak was used to electrolyzing water. It also leads to a decrease in the current efficiency and the Pt loadings. Thus, the current efficiency and the Pt loadings in either case, too large peak current density or too small peak current density, are not high.

3.3. Effects of Deposition Charges on Pt Electrodeposition. Until this moment, the deposition charges have been controlled below 0.3 C cm^{-2} and the deposited Pt loadings were not over 0.3 mg cm^{-2}. As mentioned in the beginning, the deposited Pt will serve as following deposition seeds and the catalysts of the HER. This will lead to a large Pt particle and fractions of deposition charges consumed in the HER, and finally lowering the current efficiency for Pt deposition. In this section, the deposition charges were deliberately raised to 2.4 C cm^{-2} from the foregoing 0.3 C cm^{-2} in order to evaluate whether there is a possibility to get an electrode with high Pt loadings and good Pt dispersion by pulse electrodeposition. The results are summarized in Table 5 and demonstrated in Figure 10, in which

TABLE 3: Pt Particle Sizes, Loadings and the Current Efficiency when Electrodeposition Charges Were as High as 0.3 C·cm^{-2}

electrode	$T_{on}/$ μs	$T_{off}/$ μs	$j_p/$ mA cm^{-2}	$j_m/$ mA cm^{-2}	Pt loadings/ mg cm^{-2}	Pt particle size estimated by TEM images/ nm	current efficiency/ %
D1	300	700	67	20	0.050	n/a	32.7
D2	300	1200	67	13.4	0.106	12−17	69.9
D3	300	2700	67	20	0.084	n/a	55.2
D4	300	5700	67	20	0.081	∼200	53.2

TABLE 4: Influence of Pulse Peak Currents on Pt Loadings, Particle Size, and Current Efficiency when Electrodeposition Charges Were 0.3 C·cm^{-2}

electrode	$T_{on}/$ μs	$T_{off}/$ μs	$j_p/$ mA cm^{-2}	$j_m/$ mA cm^{-2}	Pt loadings/ mg cm^{-2}	Pt particle size estimated by TEM images/ nm	current efficiency/ %
E1	300	1200	40	8	0.063	40−60	41.3
E2	300	1200	67	13.4	0.106	12−17	69.9
E3	300	1200	100	20	0.091	n/a	59.8
E4	300	1200	200	40	0.065	5−14	43.1

TABLE 5: Pt Particle Sizes, Loadings, and the Current Efficiency when Electrodeposition Charges Were as High as 2.4 C·cm^{-2}

electrode	$T_{on}/$ μs	$T_{off}/$ μs	$j_p/$ mA cm^{-2}	$j_m/$ mA cm^{-2}	Pt loadings/ mg cm^{-2}	Pt particle size stimated by TEM images/ nm	current efficiency/ %
F1	300	700	67	20	0.227	70−600	18.7
F2	300	1200	100	20	0.245	n/a	20.1
F3	300	2700	200	20	0.275	n/a	22.6
F4	300	5700	400	20	0.214	40−200	17.6

only images of Pt particles from electrodes F1 and F4 of Table 5 are displayed. Compared with Pt particles obtained at the low deposition charges as shown in Table 4 and Figure 9, where the Pt particles are well-dispersed and the Pt particle size is quite small, the Pt particles obtained at the high deposition charges are as large as 600 nm and Pt particles are not uniformly dispersed. It seems that almost all weight of all Pt loadings is focused on one or two big Pt particles. In addition, the current efficiency for Pt deposition at the high deposition charges is generally lower than that at the low deposition charges. These results further confirm that it is difficult at present time to get an electrode with high Pt loadings and good Pt dispersion by pulse electrodeposition because of the fact that the hydrogen evolution is unavoidable. As long as the hydrogen evolution is unavoidable, the following drawbacks would have been in company with the Pt electrodeposition as illustrated in Figure 11: (1) the uncertain current efficiency for Pt deposition resulting from hydrogen bubbles being erratically generated and broken even though the electrodeposition was conducted under the exact same technique, for example, electrodes C2 in Table 2 and D2 in Table 3; (2) nonuniform Pt deposits across the NBC owing to the hydrogen bubble preventing the electrodeposition bath from entering inside of the electrode. Fortunately, such a gradient distribution of Pt deposits across the catalyst layer by pulse electrodeposition is beneficial to Pt utilization after hot pressed into a membrane electrode assembly (MEA). According to Antoine and co-workers' report,[25] for a porous active layer, ionic ohmic drop becomes a rate-limiting step in a MEA and performance of the MEA are improved because the catalyst particles are located close to the proton-exchange-membrane side. The MEA with the highest Pt loadings close to the proton-exchange-membrane side and then gradually decreasing Pt loadings across the catalyst layer to the lowest Pt loadings close to the gas-diffusion layer displays the best power output and the highest Pt utilization. The influence of catalyst gradients on active-layer performances is demonstrated in Figure 12.[25]

In short, there would be the possibility of application of the modulated pulse current electrodeposition into mass production of Pt-catalyzed electrodes if a low Pt loading in the PEMFC is required. Hydrogen evolution and drawbacks along with hydrogen evolution, however, block the method from mass application in the case where the high Pt loading is required because the hydrogen evolution is sped up with electrodeposition of Pt and erratic cracks of hydrogen bubbles lead to the uncertain current efficiency for Pt deposition.

3.4. Comparison between Electrodeposited Pt Electrodes and Nafion-Bonded Pt/C Electrodes. The comparison between the best electrode prepared by modulated pulse current electrodeposition and the electrode by the Nafion-bonded Pt/C catalysts (Jonhson−Matthey) is illustrated in Figure 13. The compositions of the two electrodes are precisely the same except for the Pt loadings and the way Pt was loaded. The difference in Pt loadings has been eliminated by the normalization of Pt loadings in the two electrodes. In the potential range of 0.4 to 0.8 V versus SSCE, the performance of the electrode prepared by the Nafion-bonded Pt/C catalysts (Jonhson−Matthey) is slightly better that by modulated pulse current electrodeposition. With the potential shiftting toward the negative direction after 0.4 V versus SSCE, in other words, with increase of overpotential, the performance of the electrode prepared by modulated pulse current electrodeposition gets increasingly better and finally exceeds the performance of the electrode by the Nafion-bonded Pt/C catalysts (Jonhson−Matthey). This implies that the electrode prepared by modulated pulse current electrodeposition has a good output performance at a large current density. It may be sound to expect that the electrode prepared by modulated pulse current electrodeposition completely exceeds one by the
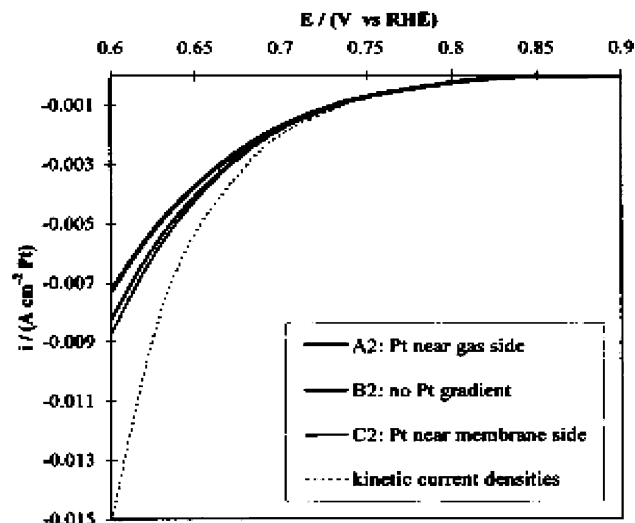
Electrodepositing Pt by Modulated Pulse Current

J. Phys. Chem. C, Vol. 111, No. 42, 2007 **15463**

Figure 12. Simulated $I-E$ curves for GDE porous active layers with different catalyst gradients.[25]
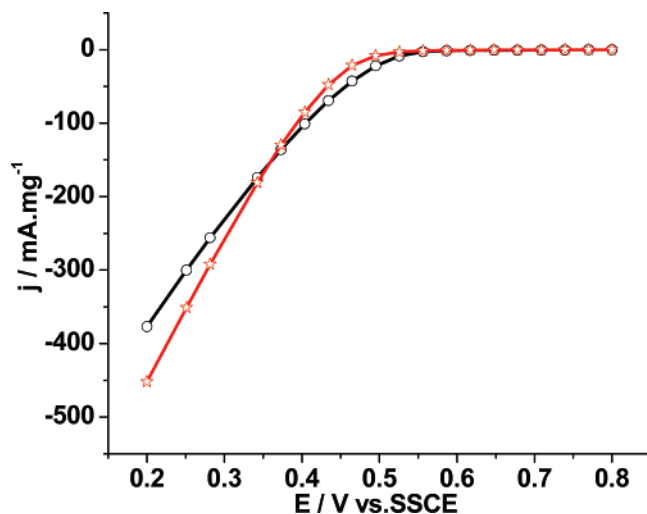

Figure 13. LSV curves of the 40 wt % Johnson−Matthey Pt/C catalyzed carbon electrode (circle) and the electrode fabricated by the pulse electrodeposition (star) in O_2-saturated 0.5 M H_2SO_4 at a sweep rate of 2 mV·s^{-1} (parameters in pulse electrodeposition: on time, 300 μs; off time, 1200 μs; peak current density, 67 mA·cm^{-2}; total charge density, 0.3 C·cm^{-2}).

Nafion-bonded Pt/C catalysts if the Pt particle size can be further reduced in electrodeposition.

4. Conclusions

The polymer electrolyte membrane fuel cell (PEMFC) electrodes were platinized by modulated pulse current electrodeposition. The Pt deposition current efficiency in well-modulated pulse current electrodeposition has been markedly improved to as high as 69.9% compared with 13% in direct current electrodeposition. The NBC with a ratio of Nafion to carbon of 1:30 and carbon loadings at 0.2 mg·cm^{-2} is most suitable for electrodepositing Pt. It is also critical of pulse current parameters for the performance of Pt deposits. For instance,

because the current on time and current off time were fixed at 300 and 1200 μs, respectively, and the total charge density was fixed at 0.3 C cm^{-2}, the electrode prepared at a peak current density of 67 mA cm^{-2} exhibits the best performance of all prepared electrodes. However, it is still difficult at the present time to get an electrode with high Pt loadings and good Pt dispersion by modulated pulse electrodeposition because hydrogen evolution is unavoidable. Pt deposition current efficiency is uncertain in electrodeposition of Pt even though the electrodeposition was conducted under the exact same technique because of hydrogen bubbles being randomly generated and broken. Meanwhile, the smallest particle size of the deposited Pt deposits is as large as 5−14 nm, which is too large for application, especially, compared with the already existed commercial Pt/C products of Johnson−Matthey Co. UK.

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