Development of Nanostructured Electrodes for Fuel Cells Using Pulse Electrodeposition

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A new method based on pulse electrodeposition technique was developed for preparation of MEA's. In this approach, platinum is directly deposited on the surface of the carbon electrode. The method ensures most of the platinum to be in close contact with the membrane. Using this method it is posble to increase the Pt/C ratio up to 75 wt% near to the surface of electrode resulting in a 5 μm thick catalyst layer. The MEA prepared by pulse electrodeposition technique exhibits a current density of 0.33 A/cm^2 at 0.8 V with platinum loading of 0.25 mg of Pt/cm^2. The results indicated that pulse deposition could be an attractive technique to replace the conventional powder type MEA preparation methods and help achieve industry goals of reducing catalyst cost and increasing efficiency in PEM fuel cells

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Introduction

One of the major impediments to the commercialization of PEM fuel cell technology is the low activity and high content of supported Pt electrocatalyst used for oxygen reduction [1-3]. In order to increase the utilization of the noble catalyst, different methods to manufacture MEA (membrane electrode assembly) for PEM fuel cell have been developed over the last decade.

Traditionally, platinum salts are reduced chemically by using a reducing agent. Platinum particles reduced in the solution are in colloidal form. These particles are subsequently adsorbed by a high surface area carbon to make a Pt/C powder [4].The ratio of Pt in carbon can be controlled by the initial concentration of Pt salts. However, it is difficult to keep the particle size under 5 nm when the Pt ratio in the Pt/C powder is over 40wt%. The oxygen reduction activity is directly dependent on the surface area available for reaction and hence on the particle size. Increase in particle size results in the decrease of activity and utilization of platinum. Further, this limitation of Pt/carbon in carbon also imposes a limitation on decreasing the catalyst layer thickness. Since the ion exchange membrane used in PEM fuel cell is a solid type, the contact between membrane and Pt becomes a critical factor in order to obtain a high performance [5,6]. For this reason, current approaches aimed at lowering the Pt loading focus on localizing Pt where the electrocatalytic reaction takes place. This has been achieved through sputtering method on the electrode [7]. However, this technique is not a volume production method. It requires expensive vacuum equipment and cannot be used for fabrication of large structures with complex shapes.

As a direct deposition technique, electrodeposition has attracted attention due to its ease of preparation and low cost requirement. Taylor *et al* [8] developed an electrochemical catalyzation (ECC) technique to improve the utilization of Pt catalyst. In this technique, a Nafion solution was impregnated into the uncatalyzed carbon electrode and platinum was electrodeposited from a commercial plating bath. Platinum ions diffuse through a Nafion thin layer formed on the surface of uncatalyzed carbon electrode and are electrodeposited only in regions with ionic and electronic conductivity. Recently, Antoine and Durand [9] impregnated carbon with H_2PtCl_6 and electrochemical pulsed are applied to deposit Pt in Nafion active layer. It guarantees a smaller active layer thickness and high platinum mass fraction up to 40wt%. However, in terms of Pt concentration distribution, it has a uniform profile in the catalyst layer like a power type process.

In this study, a new approach based on pulse electrodeposition to prepare MEAs is suggested. Pulse plating has traditionally been shown to produce deposits with lower grain sizes and particle sizes as compared to DC plating [10,11]. For MEAs, this method has the potential to create Pt particles smaller than 5 nm while generating a high Pt/C ratio at the membrane-electrode interface. Further, this technique ensures that most of the platinum is in close contact with the membrane. By placing smaller particle of platinum on the surface of the electrode, the MEA prepared by this method should show higher performance with smaller amount of Pt than conventional electrodes.

Experimental

To localize Pt at the membrane carbon interface it is critical to prepare a proper carbon blank electrode. This was done through the following steps. Carbon black (Vulcan Xc-72, Cabot Corp.) was treated at 600^{o}C for 3 hours to remove organic matter. Next, the pretreated carbon was mixed with PTFE and isopropyl alcohol in a supersonic mixer. Finally, this mixture was applied on wet proofed carbon cloth and dried at 300°C. In order to form a hydrophilic layer, a glycerol was added to the mixture and sprayed on the electrode. The uncatalyzed carbon electrode was cut to a proper size and installed in a sample holder for electrodeposition. The size of the electrode available for deposition was varied from 5 to 25 cm^2 by adjusting the size of the sample holder. Electrodeposition was performed on the carbon blank electrode using a Pt plating bath containing 10 g/L of H_2PtCl_6 and 60g/L of HCl at room temperature. Platinum gauze was used as a counter electrode. A pulse generator controlled both the pulse wave and the deposition current density. The amount of platinum electrodeposited on the electrode was estimated by the weight difference before and after electrodeposition. After electrodeposition, the electrodes were heated at 300°C in H_2 gas for 2 hours. And then, the electro-catalyzed electrode was impregnated with 5wt% of Nafion solution by spraying and then dried at 80°C for 2 hours. The amount of Nafion loading was controlled to 0.8 mg/cm^2. The commercial E-TEK electrode (single sided ELAT 20wt% Pt/C, 0.4 mg/cm^2) was used as the anode for all tests. A total of 1.2 mg/cm^2 Nafion solution was also applied to E-TEK anode electrode by brushing and spraying. Nafion-impregnated electrodes and membrane (Nafion 112) were bonded to form a MEA by hot pressing at 130°C for 3 min with a pressure of 140 atm. The reaction gases were supplied through a humidifier and a mass flow controller from hydrogen and oxygen tanks. The reactant gases flow according to the cell performance (1.5 stoic for H_2, 2 stoic for O_2). The cell was operated under ambient pressure.

Electron probe microanalysis (EPMA, Cameca instrument incorporated, model MBX) and back-scattering electron imaging were employed to measure the thickness of the electrocatalyst layer and to determine the concentration profile of Pt across the cross-sectioned MEA. The particle size of Pt prepared by pulse electrodeposition was determined by using transmission electron microscopy (TEM, Hitachi H-8000 model). Energy dispersive analysis by X-ray (EDAX) coupled with environment scanning electron microscope (ESEM) was used to obtain the surface morphology of electrode and to determine the ratio of Pt in carbon.

Results and Discussion

In an electroplating process, metal ions are transferred to the cathode and adatoms are formed by the charge transfer reaction and finally incorporated into the crystal lattice. This phenomenon occurs by building up existing crystals (growth of crystals) or creating new one (nucleation). These two steps are in competition and can be influenced by the surface diffusion rate of adatom and the rate of charge transfer reaction. High surface diffusion rates, low population of adatoms caused by slow charge transfer reaction and low overpotential leads to the growth of crystals, while conversely low surface diffusion rates, high population of adatoms, and high overpotential increases the rate of nucleation [12]. The nucleation rate [13] is given by

$$J = K_1 \exp\left[\frac{-bs\varepsilon^2}{zekT\eta}\right] \qquad [1]$$

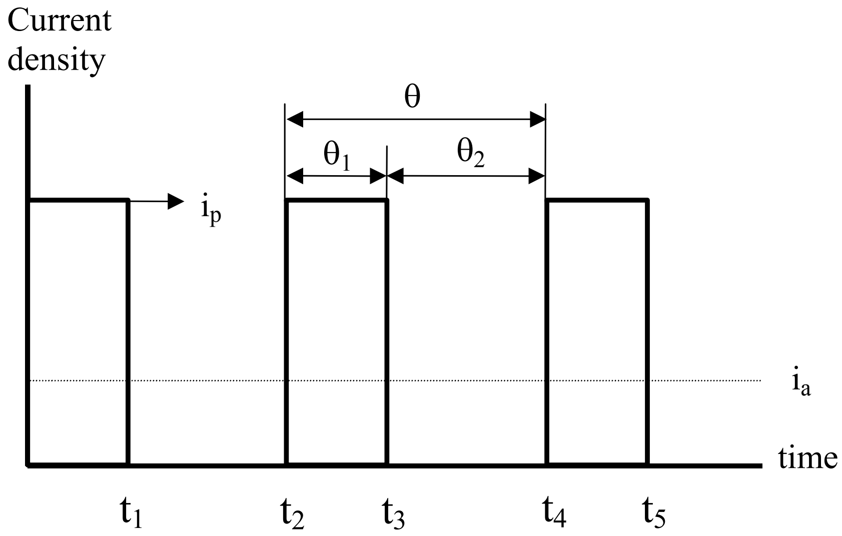

Figure 1: Current waveform and pulse deposition parameters.

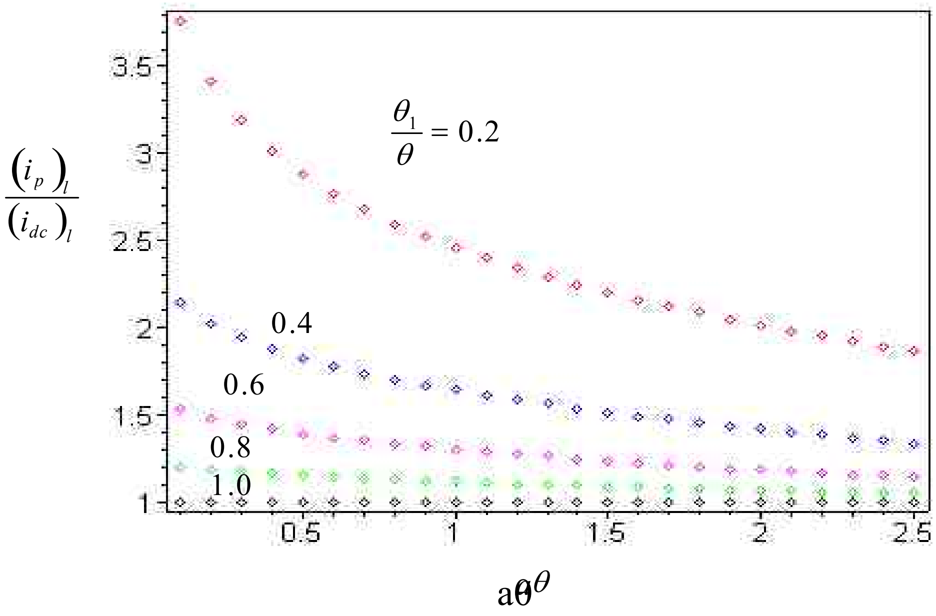

Figure 2: The ratio of limiting current density between pulse electrodeposition and direct current electrodeposition with respect to pulse period and duty cycle.

where K_1 is the rate constant, b is the geometric factor depending on the shape of the 2D cluster ($b=P^2/4S$, where P is the perimeter and S is the surface area), s is the area occupied by one atom on the surface of the nucleus, ε is the edge energy, k is the Boltzmann constant, z is the electronic charge of the ion, e is the charge of the electron, T is the temperature. The overpotential, η, is given by the Tafel expression,

$$\eta = \alpha + \beta \log i \qquad [2]$$

where α and β are constants and i is the current density. From the above equations it can be seen that as the applied current density increases the overpotential increases, which in turn according to Eq. 1 increases the nucleation rate.

When compared to direct current (D.C) deposition, pulse electrodeposition enables higher cathodic current density to be applied at the electrode interface due to higher concentration of metal ions at the surface of electrode. A simple diffusion model was suggested in literature to interpret theoretically the pulse and D.C. deposition processes [14, 15]. The current wave form of pulse deposition is shown in Fig. 1. Pulse electrodeposition has three independent variables, namely, on time (θ_1), off time (θ_2) and peak current density (i_p). The duty cycle is defined as follows

$$\text{Duty cycle (\%)} = \frac{\theta_1}{\theta_1 + \theta_2} \times 100 \qquad [3]$$

The ratio of the limiting current density in pulse electrodeposition $(i_p)_{.l}$ and D.C. plating $(i_{dc})_{.l}$ was determined by Cheh [14] and is given below.

$$\frac{(i_p)_l}{(i_{dc})_l} = \frac{1}{1 - \dfrac{8}{\pi^2} \displaystyle\sum_{j=1}^{\infty} \frac{1}{(2j-1)^2} \cdot \frac{\left(\exp\left[(2j-1)^2 a\theta_2\right] - 1\right)}{\left(\exp\left[(2j-1)^2 a\theta\right] - 1\right)}} \qquad [4]$$

where a = $\pi^2 D / 4\delta^2$ ($\sec^{-1}$) is the diffusion parameter. This ratio for various values of aθ (pulse period) and θ_1/θ (duty cycle) are plotted in Fig. 2. The result shows that the limiting current density of pulse electrodeposition is always higher than D.C. electrodeposition. And the electrodeposition can be carried out at a higher current density by decreasing the pulse periods or by decreasing the duty cycle. According to equation 2, the larger the current density, the higher is the overpotential. Thus, the nucleation rate increases resulting in a finer crystal grain.

Figure 3 illustrates the structure of membrane electrode assembly prepared by a pulse electrodeposition technique. The deposition was carried out on uncatalyzed carbon substrate. The substrate consists of a hydrophobic carbon cloth and a carbon paste layer placed on the top of the carbon cloth. This whole layer acts as a gas diffusion layer (GDL) in a conventional electrode. In the modified electrode a hydrophilic carbon layer is added to the substrate for reasons explained below.

During electrodeposition, the platinum penetration in the bulk of the material is controlled by the electrolyte penetration into the uncatalyzed carbon electrode. Since this phenomenon depends on the hydrophilic nature of the carbon electrode in case of an excessive hydrophilic nature of the layer, the electrolyte penetrates deeply into the carbon support and the resulting catalyst layer is thicker than desired. On the other hand a strong hydrophobic layer results in a deposition within a very narrow layer thereby leading to a formation of dendrites. Thus, the optimized surface properties of the carbon support would lead to a desired particle size while reducing the catalyst layer thickness. In order to examine the exact structure of MEA, EPMA and EDX spot analysis were performed.

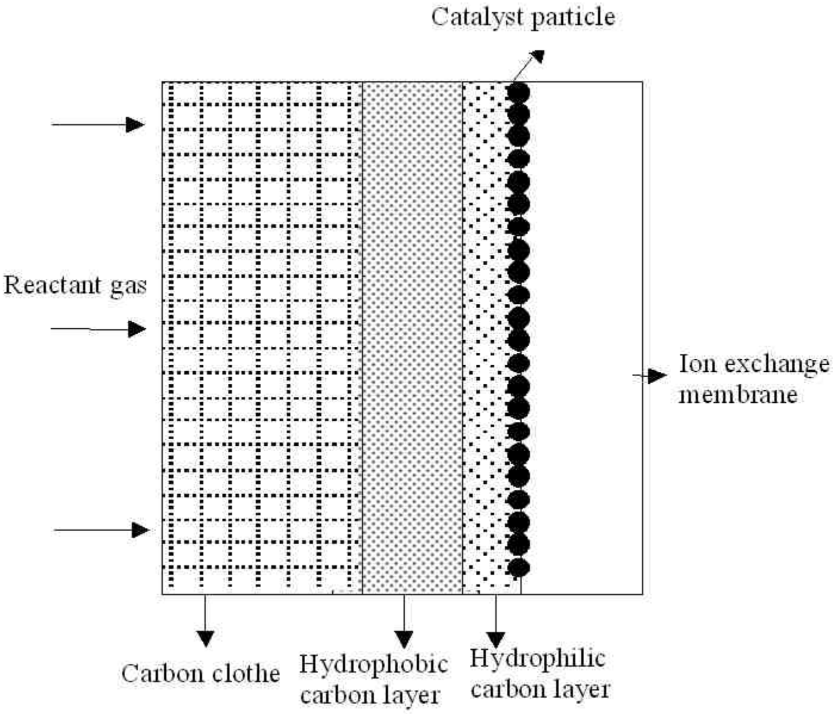

Figure 3: Schematic diagram of the electrode prepared by pulse electrodeposition.

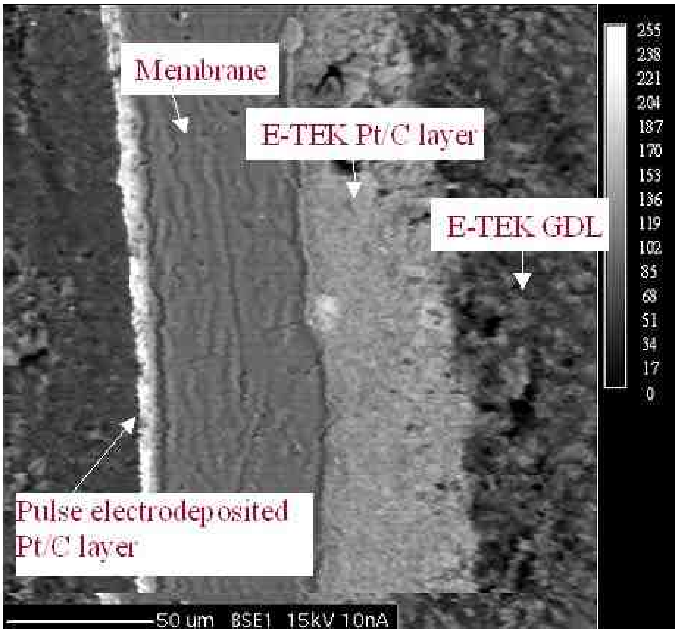

Figure 4: Back-scattered electron image of the cross section of the membrane and electrode assembly.

Figure 4 displays the back-scattered electron image of the cross-section of MEA consisting of an E-TEK anode and pulse deposited cathode. This image shows the five layers clearly and is useful for identifying the thickness of the membrane, catalyst layer and gas diffusion electrode regions. The thickness of Nafion 112 membrane is confirmed to be 50 µm according to the scaling bar given in the bottom of the picture. The bright portion between the membrane and gas diffusion layer is associated with the presence of the heavier element such as Pt. Thus, these two light colored bands on either side of the membrane show the thickness of the electrocatalyst layer on the anode and cathode side. The most striking aspect of this image is that the thickness of the pulse electrodeposited Pt electrocatalyst layer is only 5µm, which is ten times thinner than that of the E-TEK electrode. This is also confirmed from the concentration profile of Pt measured across a typical portion of the cross section of MEA by line scan using EPMA as shown in Figure 5. It is useful here to distinguish between the two different approaches used to prepare the anode and cathode. The E-TEK anode was prepared using the conventional powder type approach where Pt/C mixture is dispersed and then loaded on the gas diffusion layer by spraying or coating. The cathode has been prepared by the pulse electrodeposition approach by plating Pt on the blank carbon electrode and subsequently attaching it to the Nafion membrane. In Figure 5, the pulse electrodeposited cathode exhibits much higher intensity of Pt peak in the limited area near the membrane while Pt line scan across the E-TEK anode electrode shows a relatively uniform intensity with a thickness of 50 µm of thickness. Since the EPMA line profile has a broad resolution, in order to quantify the Pt ratio in the catalyst layer, the EDX spot analysis coupled with ESEM was also carried out for this cross section of the MEA. The results are shown in Figure 6. According to this analysis, the Pt content in the cathode catalyst layer prepared by

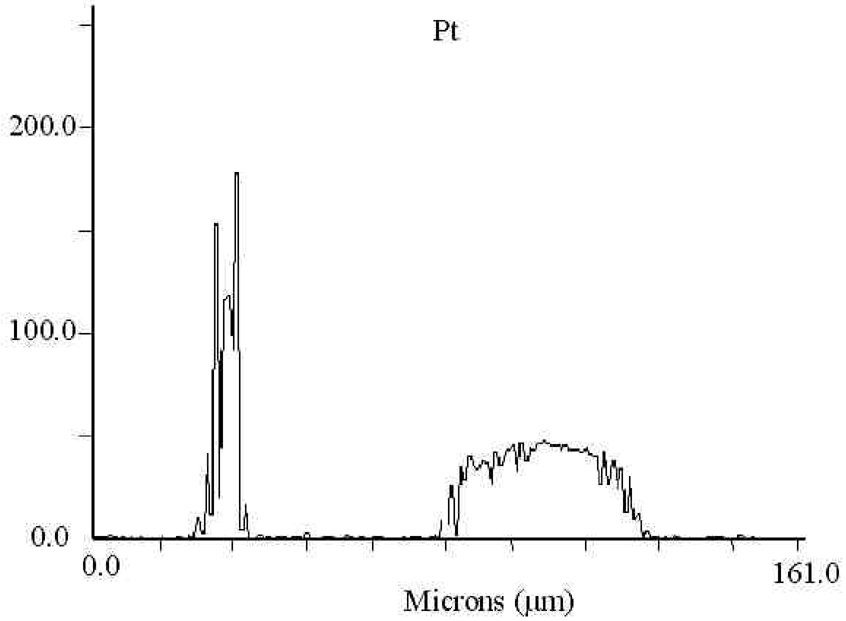

Figure 5: Platinum profile of the cross-section of the membrane and electrode assembly in Figure 4.

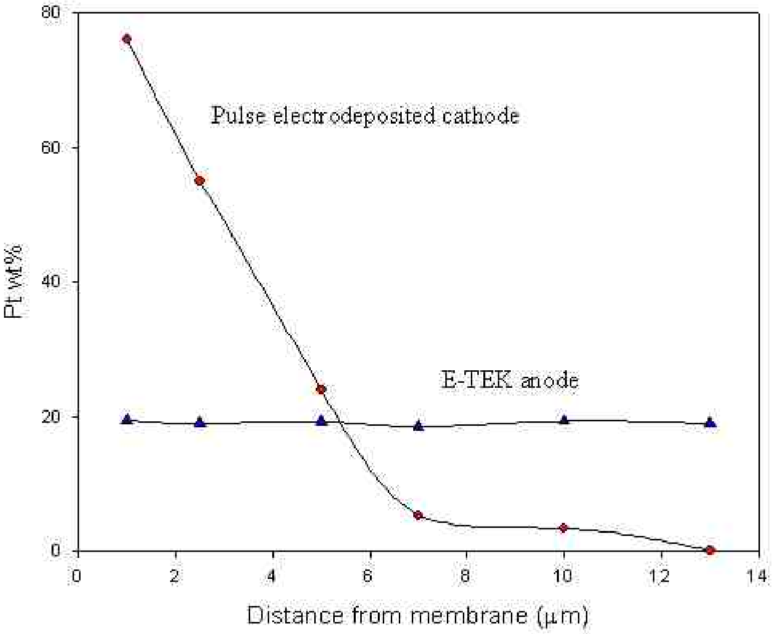

Figure 6: The concentration distribution of Pt in the electrocatalyst layer of E-TEK anode and pulse electrodeposited cathode with a distance from the membrane.

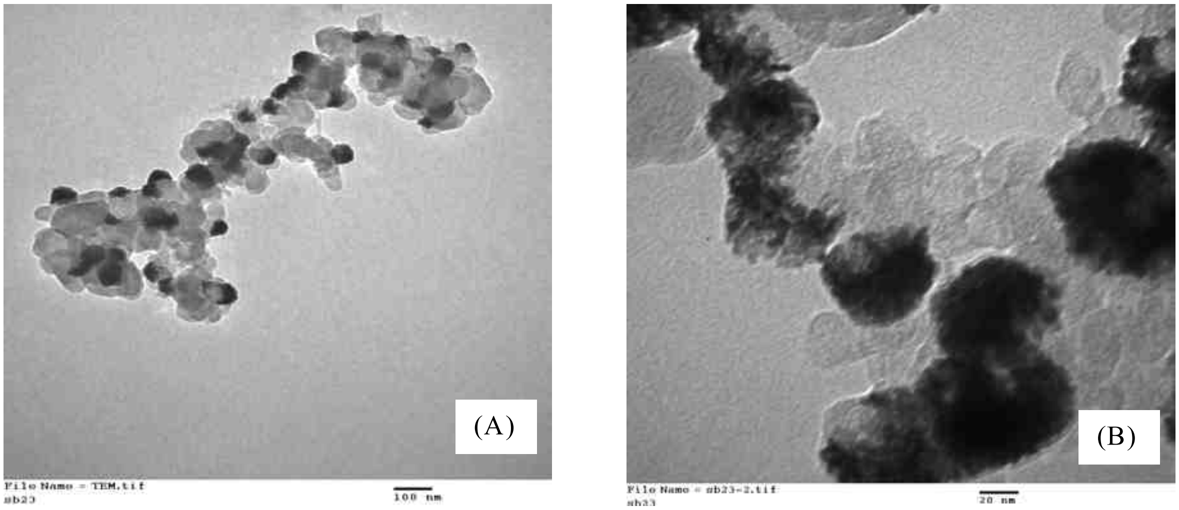

Fig. 7. TEM image of Pt supported on carbon prepared by pulse electrodeposition, (A) 100000 magnitude (B) 400000 magnitude.

pulse electrodeposition decays with increasing distance from the membrane to the GDL. The Pt to carbon ratio at 1 μm distance from the membrane is about 75wt% and this value reduces to almost zero at a distance of 7 μm from the membrane. In contrast, E-TEK electrode shows about 20wt% of Pt/C ratio distributed uniformly over the entire range of catalyst layer. Both experimental and modeling studies of membrane electrodes indicate that active layers thicker than 10 μm result in low catalyst utilization due to transport limitations of dissolved oxygen and protons in the ionomer [16].

Figure 7 shows a typical TEM image of catalyst prepared by pulse electrodeposition. From the low magnitude TEM image noted as A, the dark spot indicates the presence of platinum. Scaling bar of 100 nm is given in the bottom of the image. According to this data, the particle size of carbon is 60 to 70nm and the particle size of platinum seems to be a little smaller. So it would be a reasonable guess that much smaller particle of platinum deposits on the surface of carbon and for this reason, both particle sizes look similar. Next, the magnitude of TEM was increased to 400000. This TEM image, (Fig. 7B) shows that the previously observed large dark particles (Fig. 7A) consist of smaller particles in rage of 3~4nm. Also as shown in this figure, platinum exists in isolated places. Due to the fact that only one side of carbon is exposed to the electrolyte, the platinum is deposited only on the exposed side of the particle. Therefore, Pt metal particles exist very close to the surface of the electrode and a thinner catalyst layer was obtained by using the pulse electrodeposition approach.

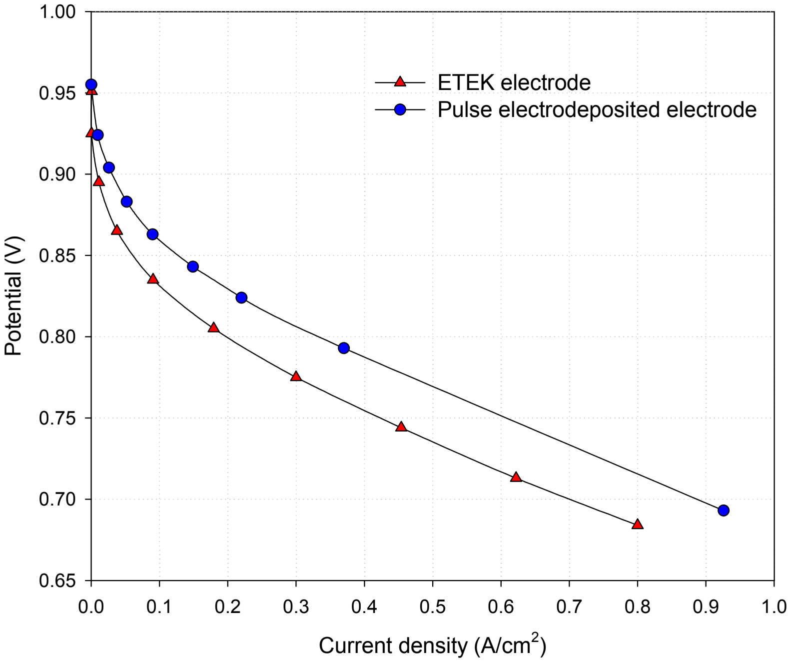

Fig. 8. Comparison of MEA performance between pulse electrodeposited electrode and E-TEKelectrode, H_2/O_2, 75°C, 1atm.

Figure 8 shows the performance of PEM fuel cell using two different types of cathode – one was prepared using our selective deposition method and the other prepared using conventional Pt/C power type method. The peak current density was optimized to be 200 mA/cm^2, on time is 5 ms, off time is 102.8 ms and total charge density is 11C/cm^2. The results indicated that this method enables a selective deposition of Pt which leads to higher current densities at a given potential. For example our electrode generates 0.33A/cm^2 current density at 0.8 V, whereas the commercial E-TEK electrode gives only 0.2 A/cm^2 under same conditions. Further, the pulse electrodeposited electrode uses only 62% of the Pt used in the conventional electrode. The enhanced performance results from the improved electrode structure prepared by the pulse electrodeposition.

Conclusion

A new approach based on pulse electrodeposition was developed to prepare MEAs. Pulse plating has traditionally been shown to produce deposits with lower grain sizes and particle sizes as compared to DC plating. For MEAs, this method showed that has the potential to create Pt particles smaller than 5 nm while generating a high Pt/C ratio at the membrane-electrode interface. Further, this technique ensures that most of the platinum is in close contact with the membrane. The MEA prepared by this method showed higher performance with smaller amount of Pt than conventional electrodes.

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