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Preparation and characterisation of Pt deposition on ion conducting membrane for direct methanol fuel cell electrodes

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Abstract

Membrane-electrode assemblies (MEAs) for direct methanol fuel cells (DMFC) have been prepared by depositing platinum on the surface of solid polymer electrolytes (SPE). Chemical and electrochemical depositions were used to achieve good adhesion between platinum particles and the SPE and for reducing the contact resistance. Platinum particle structure and composition were investigated by means of SEM and EDX. Cyclic voltammetry (CV) and methanol oxidation tests were used to determine the electrochemical characteristics of the Pt-SPE electrodes which can be applied in DMFC. Overall the electrodes produced by chemical and electrochemical deposition of Pt onto the membranes are not as active as those produced by hot pressing carbon supported Pt catalyst layers onto the membrane.

1. Introduction

Direct methanol fuel cells (DMFC) based on solid polymer electrolytes (SPE) are attractive for transport and portable applications. The most important component part of a DMFC is the membrane-electrode assembly (MEA). A typical method of making the MEA is hot pressing catalyst layers onto polymer electrolyte membranes (PEMs) [1–3]. The catalyst layers are prepared separately by painting, spraying or printing catalyst inks containing catalyst particles and polymer electrolyte suspension on the surface of gas diffusion layers (GDL).

Despite substantial amounts of research and development of DMFCs, several problems still limit their practical use. One problem is methanol crossover [4–7] and another is low catalytic activity or catalyst utilization for methanol oxidation [8, 9]. To increase the catalytic activity and decrease the internal resistance of fuel cells, research has been carried out to increase the specific area of catalyst particles and to enhance the contact between catalyst particles and PEM. When catalyst material is directly contacted with the three-phase boundary which consists of proton conducting electrolyte, methanol solution and electrode, the catalyst utilization will increase effectively.

A practical way of improving electrocatalyst adhesion to the membrane and catalyst dispersion is to deposit catalyst directly on to the surface of a PEM. This has been achieved by chemical [10, 11] and electrochemical deposition [12, 13] to make metal-SPE electrodes for electrolysis cells [14] and wide ranging sensor devices [15].

There are in general two kinds of chemical deposition methods; one is the impregnation–reduction (IR) method [10, 16–18]; and another is the reduction permeation method developed by Takenaka and Torikai (T–T method) [11, 19, 20]. In the IR method, the cation-exchange membrane with pre-exchanged cationic metal species, e.g. $[Pt(NH_3)_4]^{2+}$, is immersed in a reducing solution (e.g. $NaBH_4$, NH_2NH_2), which reduces and displaces the metal towards the outer surface of the membrane. The electrodes prepared by this method have been found to be a few microns in thickness and porous. They exhibit good adhesion and durability, due the fact that the metal particles are not only deposited on the membrane surface but also embedded in the membrane as well.

In the T–T method, a solution of metal anions, such as $[Pt(NH_3)_4]^{2+}$, and a reducing agent, typically sodium tetrahydroborate ($NaBH_4$), are exposed to opposite sides of a stationary SPE membrane. $[Pt(NH_3)_4]^{2+}$ ions continuously penetrate the membrane and come into contact with BH_4^- ions on the opposite membrane face, where the platinum ions are reduced to platinum metal at the membrane surface according to the redox reactions:

$$[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3 \quad (1)$$

$$BH_4^- + 3H_2O - 4e^- \rightarrow BO_3^{3-} + 2H_2 + 6H^+ \quad (2)$$

To give the over all process:

$$\begin{aligned} &2[Pt(NH_3)_4]^{2+} + BH_4^- + 3H_2O \\ &\quad \rightarrow 2Pt + 8NH_3 + BO_3^{3-} + 2H_2 + 6H^+ \end{aligned} \quad (3)$$

Overall, both the T–T [20, 21] and IR [10] methods produce porous platinum structures on the membrane surface with high particle dispersion on the surface as well as inside the membrane. The particle size is typically less than 1 μm. Although the IR method is convenient in practice, the T–T method gives better control of the amount of deposition and particle size. These factors are important for good electronic contact between catalyst particles on the surface of SPE membrane.

As an alternative, electrochemical deposition [12, 13, 22] has also been used to deposit catalyst on the surface of electrode. One advantage of electrochemical deposition is that typically, every catalyst particle has good contact with the electrode. The catalyst efficiency has also been reported to be increased by using pulsed current deposition of platinum [12].

In DC electrodeposition, the current has a strong influence on the catalyst particle structure [12]. As the current increases, metal ions near the cathode are depleted. In this situation, the limiting current is approached and dendritic crystals are formed. Pulse electrodeposition, on the other hand, lowers mass transfer limitation, since metal ions are supplied from bulk solution during the off-time of the pulse current. Choi et al. [12] investigated electrodeposition of Pt on carbon. They achieved good deposits at 25 mA cm^{-2} for DC plating and 320 mA cm^{-2} for pulse electrodeposition with 100 ms on-time and 300 ms off-time.

Another method of making a MEA is to put the catalyst material on the three-phase boundary [13, 22]. This method used impregnation of the carbon layer with platinum salt solution and Nafion solution, followed by *in situ* electrochemical reduction of Pt nanoparticles onto carbon particles inside Nafion. The electrode structure achieved with this method is quite similar to a conventional MEA. However the deposited material still had to be hot pressed with the PEM before electrochemical deposition. The advantage of the method is that it connects Pt particles with carbon particles, raising catalyst efficiency and lowering electrical resistance.

In this work, chemical and electrochemical deposition have been used to deposit Pt on the surface of Nafion membranes to make Pt-SPE electrodes. The purpose of this work is to investigate Pt-SPE electrodes in DMFC and to compare their performance against that of a standard electrode made from commercial carbon supported Pt catalyst (Pt/C). The aim was to establish whether or not the Pt-SPE electrodes were potentially viable as cathodes or anodes for producing MEAs for DFMC. Although it is known that Pt alone is not the most active methanol oxidation catalyst, it was used as a useful "model" catalyst to assess the different methods of preparing catalyst. The longer term goal of the work was to assess alternative methods (to using Pt/C catalyst) of electrocatalyst layer preparation that were applicable to membranes which incorporated, or were coated with, conducting (electronic and ionic) polymers.

2. Experimental

Three types of electrodes are examined in this work, made by chemical deposition, electrochemical deposition and from commercial carbon supported Pt catalyst. The structure and composition of the electrodes were determined by SEM and EDX. The electrocatalytic activity of electrodes were investigated using cyclic voltammetry (CV) and methanol oxidation.

2.1. *Chemical deposition*

The T–T method was used to deposit Pt on the surface of the Nafion membrane to make the Pt-SPE electrode. Figure 1 is a schematic of the chemical deposition cell . Deposition area of the cell was 30×40 mm. $NaBH_4$ solution and Pt $(NH_3)_4Cl_2$ solution were pumped over opposite sides of the membrane. In this method $[Pt(NH_3)_4]^{2+}$ cations diffused through the membrane and reacted with the $NaBH_4$ solution. Platinum was deposited on the membrane surface which faced the $NaBH_4$ solution.

Prior to dposition the Nafion® 117 membrane (Du Pont, thickness 178 μm) was boiled in de-ionized water for 1 h. The concentration of $[Pt(NH_3)_4]Cl_2$ (Aldrich) solution was 1 mM (mol m^{-3}) and the concentration of $NaBH_4$ (Aldrich) was 5.4 mM adjusted to

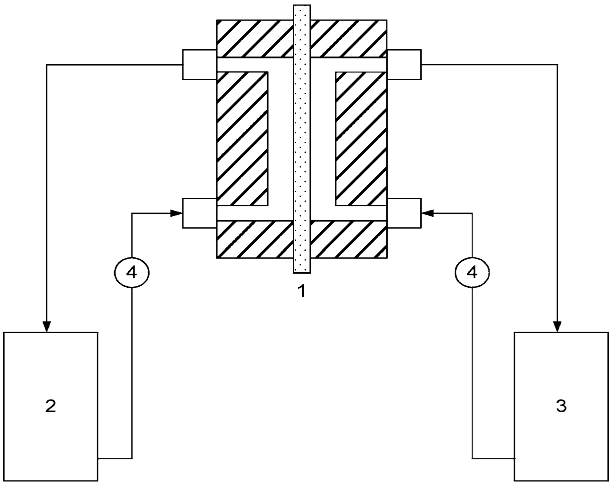

Fig. 1. Schematic of the chemical deposition cell. (1) Membrane (2) $NaBH_4$ solution (3) Pt $(NH_3)_4Cl_2$ Solution (4) Circulating pump.

pH = 13 with 0.1 M NaOH (from Aldrich) solution. The cell temperature was controlled at 50 °C with a water bath. A peristaltic pump (Mode 505S from Watson Marlow) was used to circulate the solution at 160 cm^3 min^{-1} on both sides of the membrane. Different deposition times were used to obtain different amounts of platinum. The platinum loading on the Pt-Nafion electrode was determined by gravimetry. The membranes were boiled in de-ionized water for 1 h and dried at 353 K and 0.48 bars for 20–24 h prior to weighing.

2.2. *Electrochemical deposition*

Electrochemical deposition using direct current was applied to deposit Pt particles at the interface of the electrode and SPE membrane surface. Figure 2 shows schematic of the electrochemical deposition cell. The deposition area was 30×30 mm. Carbon paper (E-Tek, TGPH-090) was used as the cathode current collector, which was tightly pressed against the Nafion® 117 membrane, which was boiled in de-ionized water for 2 h before deposition. Platinum mesh was used as the anode. The concentration of $[Pt(NH_3)_4]Cl_2$ (from Aldrich) solution was 7.5 mM and the cell temperature was 23 °C. A peristaltic pump was used to circulate the solution, at a flow rate of 160 cm^3 min^{-1}, through the electrochemical deposition cell. In this method $[Pt(NH_3)_4]^{2+}$ ions diffused through the ion conducting membrane and platinum was deposited at the interface of the membrane and carbon paper.

The electrochemical reactions are:

$$\text{Cathode}: [Pt(NH_3)_4]^{2+} + 2e \rightarrow Pt + 4NH_3 \tag{4}$$

$$\text{Anode}: 2Cl^- - 2e \rightarrow Cl_2 \tag{5}$$

$$\begin{aligned}\text{Total process}: &[Pt(NH_3)_4]Cl_2 + 4H_2O \\ \rightarrow\quad &Pt + Cl_2 + 4NH_3H_2O\end{aligned} \tag{6}$$

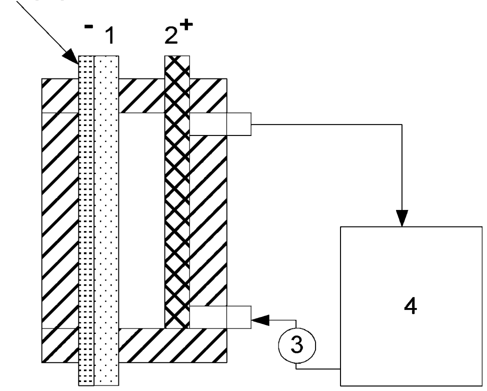

Fig. 2. Schematic of the electrochemical deposition cell. (1) Membrane (2) Platinum mesh (3) Circulating pump (4) $Pt(NH_3)_4Cl_2$ Solution.

Since the diffusion rate of $[Pt(NH_3)_4]^{2+}$ ions through the ion conducting membrane is smaller than in water, the "limiting current density" for Pt electrodeposition was lower than 25 mA cm^{-2}, which was used in Choi's work [12]. When the deposition voltage was 3.6 V, the initial deposition current density was 5.5 mA cm^{-2}. Platinum deposition was determined from the deposition time and deposition current using Faraday law.

2.3. *Commercial Pt/C electrodes*

Electrodes using commercial catalysts were made using a hot pressing method [6]. The electrode consisted of a Teflonised (20%) carbon paper (E-Tek, TGPH-090), upon which a thin layer of uncatalysed (ketjenblack EC-300J) 10 wt. % teflonised carbon black was spread. The catalysed layer consisted of 60 % Pt/C (2 mg cm^{-2} metal loading, E-Tek) dispersed on carbon and bound with 10 wt. % Nafion®, from a solution of 5 wt. % Nafion® dissolved in a mixture of water and lower aliphatic alcohols (Aldrich), and was spread on the diffusion backing layer.

2.4. *Cyclic voltammetry (CV) and methanol oxidation tests*

Figure 3 shows a schematic of the CV cell. All experiments were performed under a nitrogen atmosphere and the temperature was controlled at 23 °C. The electrolyte solution in CV was 1 M H_2SO_4 (from Aldrich) and the solution used in the methanol oxidation tests was 2 M CH_3OH (from Aldrich) in 1 M H_2SO_4. The scan rate was 25 mV s^{-1} and the scan ranged from −680 to 630 mV (vs. mercury/mercurous sulphate, reference electrode). The geometric surface of the electrode was 0.785 cm^2. A piece of carbon paper, which contacted the Pt-SPE was used as a current collector. A reversible mercury/mercurous sulphate (MMS) electrode was used as the reference electrode and a platinum mesh was used as the auxiliary electrode. The CV measurements were carried out with a model PGP 201 scanning potentiostat, from Radiometer Copenhagen.

2.5. *Morphology and composition analysis*

Scanning electron microscope (SEM) analysis (Mode JEOL JSM 5300 LV electron microscope), was used to examine the surface morphology of deposition film, and EDX was used to examine the composition. Transmission Electron Microscopy (TEM) analysis (Mode CM 100 Philips) was used to detect the platinum particles on the carbon surface of commercial Pt/C catalyst.

3. Results and discussion

For the T–T chemical deposition method, deposition temperature, concentrations of $[Pt(NH_3)_4]Cl_2$ and

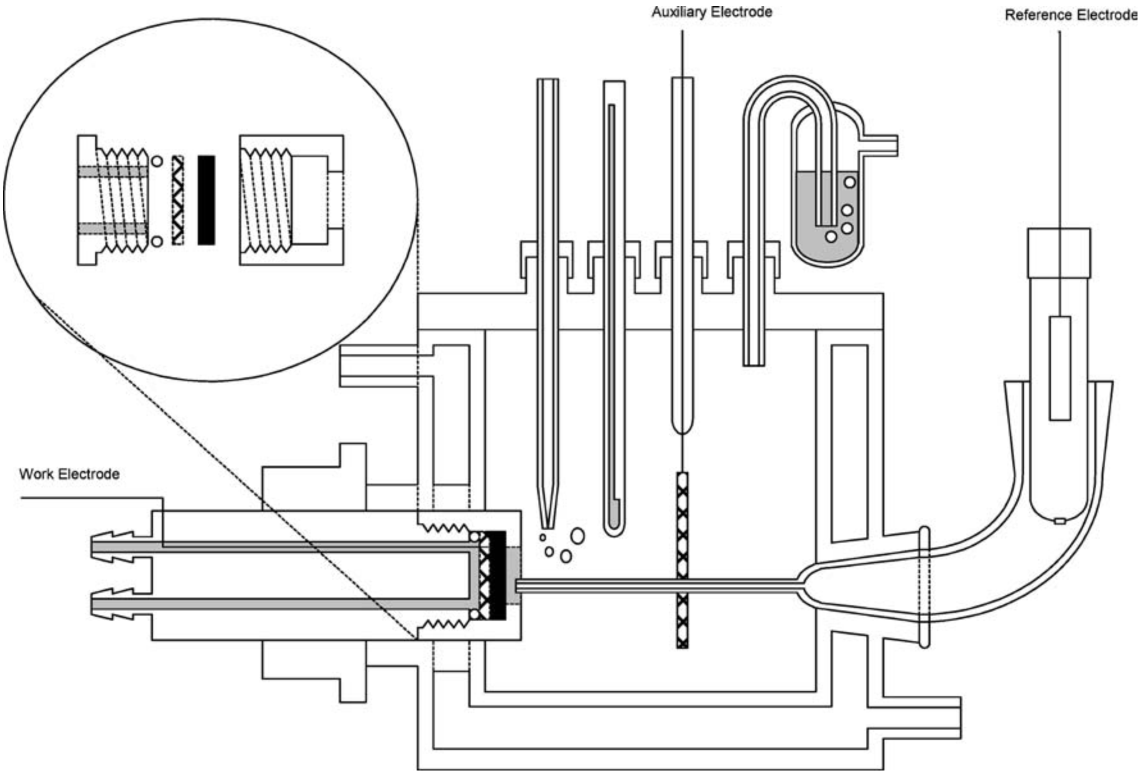

Fig. 3. Schematic diagram of the cyclic voltammetry cell.

$NaBH_4$ and deposition time are expected to influence the deposition amount and morphology. When the concentrations of $[Pt(NH_3)_4]Cl_2$ and $NaBH_4$ were 1.0 mM and 5.4 mM respectively and the solution pH 13 and the cell temperature 50 °C, the amount of deposition varied from 0.2 to 4.2 mg cm^{-2} with deposition times from 10 to 60 min.

Figure 4 shows the variation in amount of deposit with deposition time with the T–T method. Pt deposition was very slow before 10 minutes. Between 10 and 30 min, Pt deposition increased quickly. At this stage, enough $[Pt(NH_3)_4]^{2+}$ ions arrived at the interface between the Nafion membrane and the reducing solution. For deposition times above 35 min, the Pt deposition rate dropped, mainly due to the accumulation of Pt particles on the membrane surface, which slowed down the diffusion of $[Pt(NH_3)_4]^{2+}$ ions.

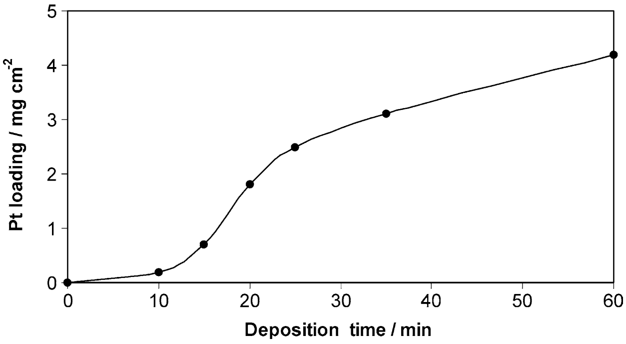

Fig. 4. Deposition time and Pt loading amount in T–T method.

EDX analysis showed that the deposited material was Pt. Figure 5 shows the morphology of the deposition layer after deposition times of 10 and 35 min, i.e. loading of 0.2 and 3.1 mg cm^{-2} respectively. The images show that the platinum films are porous with platinum particle clusters of size around 0.2 μm. The deposition time can be used to control the deposition amount, the size and the density of particle clusters.

The electrocatalytic activity of Pt-Nafion electrode was measured by CV. With the electrolyte solution of 1 M H_2SO_4 and the scan rate of 25 mV s^{-1}, Figure 6 shows that the current–potential response of the Pt-Nafion electrodes made with chemical deposition time of 10, 20 and 35 min, corresponding to Pt loadings of 0.2, 1.8 and 3.1 mg cm^{-2} respectively. Figure 7 compares the cyclic voltammograms of electrodes formed by, chemical deposition (T–T), for 60 min, electrochemical deposition and the conventional MEA.

The active area of the Pt catalyst was calculated from the area of hydrogen absorption region in Figure 6, by multiplying the value of current density with the scan time and comparing the area of hydrogen adsorption region of platinum foil which is about 210 μC cm^{-2}. Values of the Pt active area of the three Pt-Nafion electrodes were: 12, 112 and 334 cm^2 cm^{-2} of geometric area, respectively. With an increase in the deposition time to 60 min, the Pt loading of 4.2 mg cm^{-2}, the catalytic active area was found to be 384 $cm^2 cm^{-2}$; similar to that for the 35 min deposition time. The surface area obtained in this work are lower than those

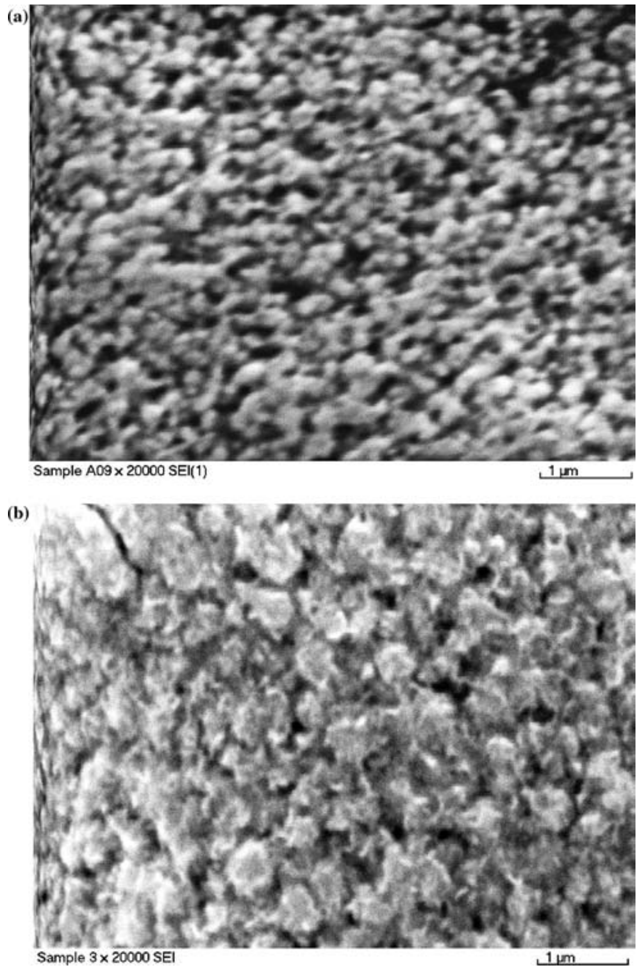

Fig. 5. SEM picture of platinum film deposited on Nafion 117 for 10 min (a) and 35 min (b).

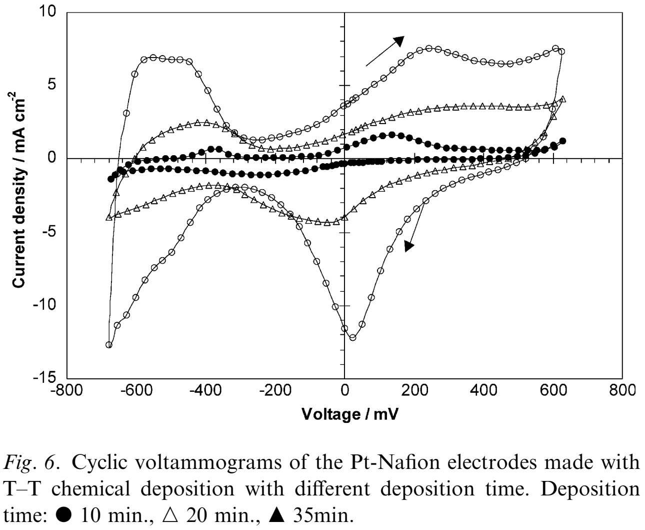

Fig. 6. Cyclic voltammograms of the Pt-Nafion electrodes made with T–T chemical deposition with different deposition time. Deposition time: ● 10 min., △ 20 min., ▲ 35min.

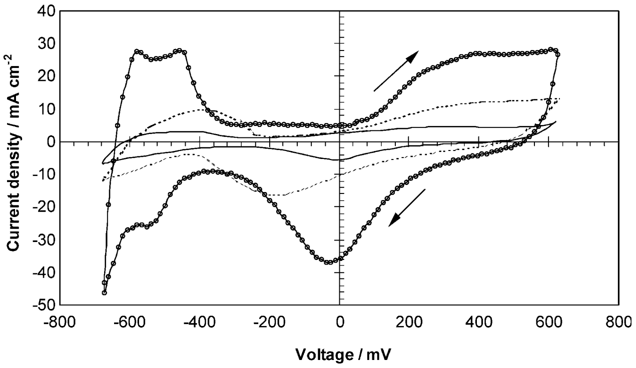

Fig. 7. Cyclic voltammograms of the electrodes made with the T–T method, by DC deposition and the conventional MEA. ○ conventional MEA. ········· T–T method; — DC deposition.

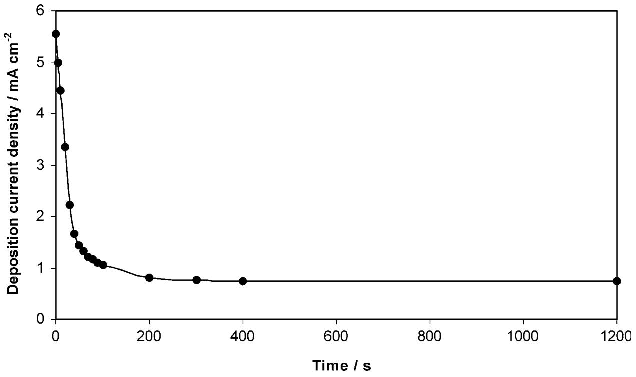

Fig. 8. Current and time plot of electrochemical deposition with dc method.

reported by other researchers [10, 21] using similar deposition methods. One factor for this could be the influence of the different counter anion (OH^- as opposed to Cl^- in this work) in the Pt amine complex.

Figure 8 shows the variation of the deposition current with time when a voltage of 3.6 V was applied to deposit Pt. The amount of platinum deposited was calculated as 1.5 mg cm^{-2} using Faraday's law. After peeling apart the carbon paper and the membrane after deposition, the deposit was found on interface of the carbon paper and the membrane. EDX analysis showed that the material was platinum.

Figure 9 shows the SEM of the platinum particles on the carbon paper and the Nafion membrane. The particle deposit had a porous structure and was approximately 0.2 μm in size. The catalytic active area was about 177 cm^2 cm^{-2} as estimated from the cyclic voltammograms in Figure 7.

The conventional MEA made with commercial Pt/C catalyst (from E-Tek) had a Pt loading of 2 mg cm^{-2}. The catalytic active area was about 1150 cm^2 cm^{-2} as estimated from the cyclic voltammograms in Figure 7. Figure 10 shows the TEM analysis for commercial Pt/C catalyst. The Pt particle size on carbon surface was around 5 nm.

The cyclic voltammograms of the Pt-SPE electrodes, made with both deposition methods and the commercial Pt/C catalyst, (Figure 6 and 7) have similar shapes. Figure 11 and Figure 12 show the methanol oxidation voltammograms for these three electrodes. Methanol oxidation is initiated at a potential of approximately 0.4 V (vs. SHE) and clearly exhibits a substantial degree of overpotential, which is characteristic of Pt

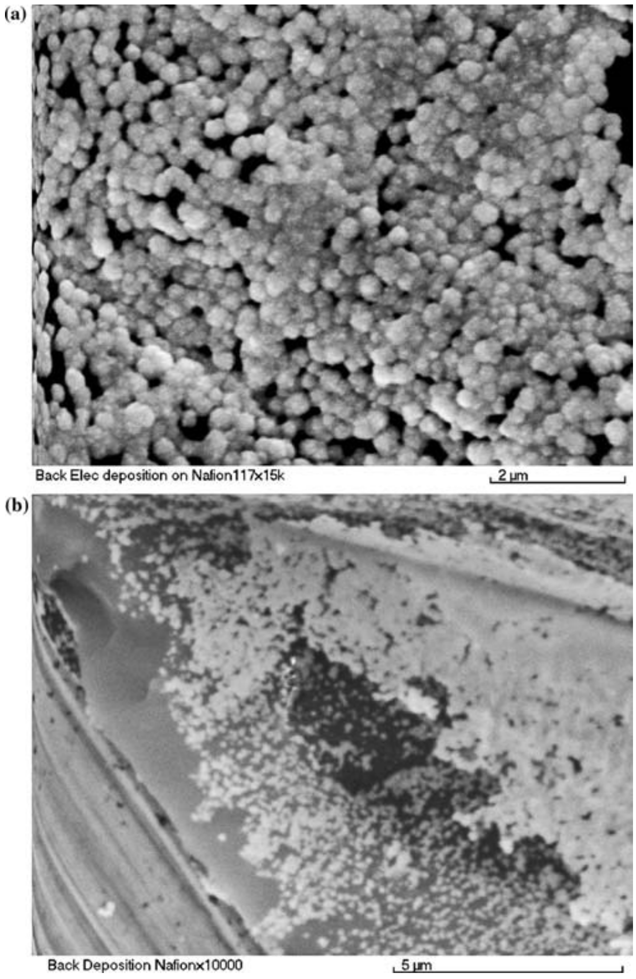

Fig. 9. SEM picture of platinum particles with DC method on carbon paper side (a) and on Nafion membrane side (b).

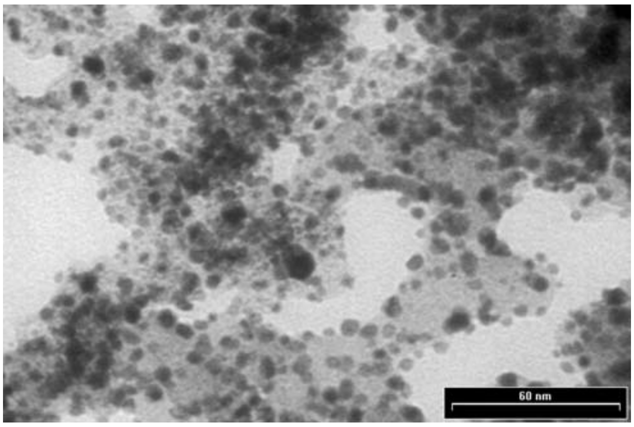

Fig. 10. TEM analysis for commercial Pt/C catalyst.

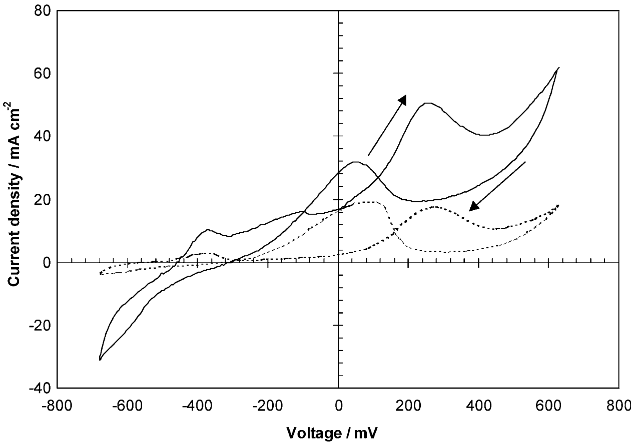

Fig. 11. Methanol oxidation test for of the electrodes made with chemical deposition method and DC deposition method. — DC deposition electrode; ········· Chemicals deposition electrode.

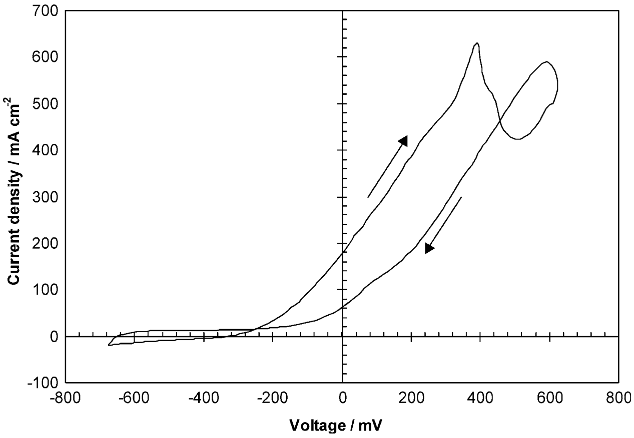

Fig. 12. Methanol oxidation test for of the electrodes made with commercial catalyst.

catalysts for methanol electro-oxidation, where poisoning by methanolic residues occurs. All three electrodes possess typical platinum catalytic characteristics for hydrogen reduction and methanol oxidation, which means that the Pt-SPE electrodes have the same electrochemical characteristics as platinum and thus could be used as electro-catalysts in the DMFC as a new application. Figures 5 and 9 show that the platinum particles have good particle adhesion with the membrane, which can decrease the contact resistance, decrease the methanol crossover, increase the three-phase boundary and enhance the mass transport. All these advantages would theoretically enhance the DMFC performance.

However, as shown in the data of Figures 11 and 12, the catalytic active areas of Pt-SPE electrodes were smaller than the conventional MEA electrode. The electrode made with Pt/C catalyst had the highest hydrogen reduction and methanol oxidation current density. The reason is that the Pt-SPE electrodes had smaller specific area than the conventional Pt/C electrode, as shown in Table 1. The smaller specific area is attributed to a larger platinum particle size. Comparing the platinum particle sizes; for the Pt/C catalyst it was 5 nm (see Figure 10), while it was approximately 200 nm for the Pt-SPE electrode (see

Table 1. The specific area of electrodes

Electrodes	Pt loading/ mg cm^2	Specific area/ cm^2 cm^{-2}	Specific area/ cm^2 mg^{-1}
Pt-Nafion (T–T) method	4.2	384	91
Pt-Nafion Electrodeposition	1.5	177	118
Pt–C Commercial catalyst	2	1150	575

Figures 5 and 9). Typically the ideal platinum particle sizes for the DMFC electrodes are of the order of 2–6 nm [23]. To improve the electrocatalyst activity of Pt-SPE electrodes, further work is required to deposit platinum particle in the nanometer size range. However it would appear that from this work and previous work [10, 21] that chemical and electrochemical deposition of Pt catalysts directly onto ion-exchange membranes will not result in electrodes which achieve activity that approaches that of conventional Pt/C electrodes. In addition, for the DMFC anode, it would also be necessary to deposit a mixed Pt and Ru metal or alloy catalyst for high activity in methanol oxidation.

4. Conclusions

With the T–T chemical deposition method, Pt particles have been deposited on the surface of the Nafion membrane and the Pt particle cluster sizes were around 0.2 μm. The deposited layer possesses catalytic activity for methanol oxidation. The deposition time can be used to control the Pt loading and the catalyst activity.

When Pt was deposited by DC electrochemical deposition, particles were deposited on the interface of electrode and Nafion membrane. The particle cluster size of Pt was again around 0.2 μm. The deposited layer possesses catalyst activity for methanol oxidation, and was higher than that of the Pt-Nafion electrode made using the T–T chemical deposition method.

Chemical deposition and electrochemical deposition can both deposit platinum on Nafion membrane as well bonded layer, with a porous structure, which decreases the contact resistance of Pt-Nafion electrode and enhances the effect of mass transport. The catalyst layers made with both methods had similar electrochemical characterisation as commercial Pt–C catalyst which can be used in the DMFC. However, the active areas of Pt-Nafion are only around one fifth of the active area of the conventional MEA.

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