# Suppressing Methanol Crossover with Nanometer-Sized Pt<sub>3</sub>Sn Particles Self-Assembled on a Nafion Membrane Surface

Chien-Heng Lin<sup>1</sup>, Chieh-Hao Wan<sup>2\*</sup>, Weite Wu<sup>1\*\*</sup>

<sup>1</sup>Department of Materials Science and Engineering, National Chung Hsing University, Taiwan. 250 Kuo Kuang Rd., Taichung 402, Taiwan.
<sup>2</sup>Department of Electro-Optical and Energy Engineering, MingDao University, Taiwan. 369, Wen-Hua road, Peetow, 52345, Changhua, Taiwan.
\*E-mail: <u>Chiehhao@mdu.edu.tw; chiehhaowan1206@gmail.com</u>
\*\*E-mail: <u>weite@dragon.nchu.edu.tw</u>

Received: 6 April 2013 / Accepted: 16 May 2013 / Published: 1 June 2013

In this paper, 5 and 10 poly(allylamine hydrochloride) (PAH)/poly(styrene sulfonic acid sodium salt) (PSS) bi-layers with dispersed Pt<sub>3</sub>Sn alloy nano-particles are self-assembled onto both sides of the Nafion-117 membrane to suppress methanol crossover. The Pt<sub>3</sub>Sn alloy in PAH/PSS bi-layers are synthesized by the reduction of Pt and Sn ions in PSS with NaBH<sub>4</sub>. The UV-visible spectroscopy was used to monitor the PAH/PSS self-assembly bi-layers. The methanol crossover in membrane electrode assembly (MEA) was determined by measuring the CO<sub>2</sub> concentration at cathode exhaust using a CO<sub>2</sub> sensor. The results confirm that the Pt and Sn deposited in PAH/PSS bi-layers exist in a Pt-Sn alloy phase with atomic ratio of 3:1 (Pt:Sn). The layer thicknesses of 5 and 10 PAH/PSS bi-layers containing Pt-Sn alloy are 150nm and 300nm, respectively. The MEA, with 5 PAH/PSS bi-layers containing Pt-Sn alloy nano-particles (average particle size is 17 nm) catalyst, suppress methanol crossover by 50% and slightly improve the output current by 6% (@0.40V). This is because the presence of Pt-Sn alloy and PAH/PSS bi-layers itself functions like a catalytic active layer and methanol barrier that react and block the crossed-over methanol. These dual roles contribute to the suppression of methanol crossover and performance improvement. However, the thickness effect is evident for the 10 PAH/PSS bi-layers sample and results in the decrease of cell performance by 19%, while suppressing methanol crossover by 50%.

**Keywords:** methanol crossover, self-assembly layer, proton conductivity, Platinum-Tin alloy, nanoparticles

# **1. INTRODUCTION**

The direct methanol fuel cell (DMFC) is attractive for application in a variety of mobile or portable power sources due to its simple system design and easy fuel storage. However, the efficiency

of the DMFC is relatively low as compared to the proton exchange membrane fuel cell (PEMFC), mainly due to the weak reaction kinetic of anode catalyst and methanol crossover. A possible strategy to meet the first challenge is to develop a new catalyst with high catalytic activity toward methanol oxidation. The quaternary Pt-based catalyst, such as Pt-Ru-Ir-Os, could achieve several times higher power density than the  $Pt_{50}Ru_{50}$  catalyst. However, the difficulties of the synthesis of this catalyst limit the wide use of this catalyst for commercialization. A possible strategy for the second challenge is to prevent methanol crossover. Methanol crossover is a process in which the un-reacted methanol diffuses from anode to cathode. It thus reduces the cell performance and stability of DMFC due to the poisoning of the Pt catalyst and mixed potential effect at cathode as well as the decreasing of fuel utilization [1-5]. Therefore, it is essential to improve the stability and cell performance of the DMFC before this technology can be commercially viable.

Many approaches have been proposed to mitigate the methanol crossover during the last decades. The first approach concerned the adding of second species such as  $Ce^{4+}$  [6], SiO<sub>2</sub> [7-8] and Zr(HPO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O [9] into the Nafion membrane to form a composite Nafion membrane with low methanol permeability. This approach can drastically reduce the methanol permeability and slightly decrease the proton conductivity. The second approach focused on the development of a new membrane with low methanol permeability and high proton conductivity [10-14], i.e. acid-doped polybenzimidazole (PBI), sulfonated-poly(arylene ether ketone)s (SPAEKs), etc. This approach can drastically reduce the methanol permeability and retain or increase the proton conductivity of the membrane. However, the problems remain with the chemical, mechanical, and thermal stability of this new membrane. The third approach concerns the deposition of the Pd layer onto the Nafion membrane to form a sandwich structure to block the crossed-over methanol [15]. This approach reduces the methanol crossover and cell performance at the same time. The fourth approach addresses the deposition of the double Pt-Ru layer, a Pt-Sn layer or a Pt layer [16-18] onto the Nafion membrane surface to react with and block the crossed-over methanol. This approach can drastically suppress methanol crossover and improve cell performance due to the deposited layer, which functions like a catalytically active layer, an electrode, and a methanol barrier.

Recently, the layer-by-layer (LbL) technique has been applied to self-assembly polyelectrolyte bi-layers on the Nafion membrane surface to block the crossed-over methanol [19-27]. LbL technique is a simple and efficient way to produce multi-layers of thin film through the electrostatic adsorption force between positive and negative polyelectrolytes. Hammond et al. [19] showed that the self-assembly of 3~5 poly(diallyl dimethyl ammonium chloride) (PDAC) and sulfonated poly(2,6-dimethyl 1,4-phenylene oxide) (sPPO) bi-layers onto the Nafion-1135 membrane surface significantly reduces the methanol permeability by 99% and improve power density by 50%. They concluded that the reduction of methanol permeability and the improvement of power density depend on the kinds and layer numbers of the positive and negative polyelectrolytes. Similar results have been reported in [20-21]. Jiang and coworkers studied the self-assembly of the PDAC and poly(sodium 4-styrenesulfonnate) (PSS) or poly(1-(4-(3- carboxy -4-hydroxy -phenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt) (PAZO) onto the Nafion-1135 membrane surface. They found that the composite Nafion-1135 membrane with PDAC/PSS bi-layers has better power density improvement and greater reduction of methanol crossover current as compared with PDAC/PAZO bi-layers. They also investigated the self-

assembly of PDAC with phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) (PWA) onto the Nafion-212 membrane to mitigate methanol crossover. The results showed that the composite Nafion-212 membrane with 4 PDAC/PWA bi-layers drastically reduces the methanol permeability by 87% and enhances the power density by 103%, although the proton conductivity of this composite Nafion-212 membrane had been reduced by 41%. They indicated that the reduction of performance from the adding of PDAC/PWA self-assembly bi-layers itself on to the Nafion membrane surface is lower than the performance improvement attributed to the reduced mixture's potential effect at cathode by the effective suppression of methanol crossover. Deligöz's team [22-24] studied the self-assembly of poly(allylamine hydrochloride) (PAH) and PSS onto the Nafion-117 membrane surface to mitigate methanol crossover. The results demonstrated that the composite Nafion membrane with 10 PAH/PSS bi-layers reduced the methanol permeability by 26% and the proton conductivity by 82% at the same time. When decreasing the bi-layers number to 5, the reduction of methanol permeability and proton conductivity are down to 19% and 56%, respectively. They recently changed the PSS to poly(vinyl sulfate potassium salt) (PVS) [25] to produce the self-assembly PAH/PVS bi-layers onto the Nafion-117 membranes surface. The proton conductivity has been improved by 107% while the methanol permeability has been reduced by 43% as compared to the un-treated Nafion membrane. However, there is no further cell performance result with those composite Nafion membranes to confirm the actual output performance and suppression of methanol crossover.

Another approach reported by Pan's team [26] concerned the self-assembly of the PDAC containing Pd metal on the Nafion-112 membrane to suppress methanol crossover. They demonstrated that 3 bi-layers of PDAC containing Pd metal suppress methanol crossover by 99% and retain 84% proton conductivity as compared with pristine Nafion membrane. The methanol blocking effect of the self-assembly of the PDAC containing Pd metal on the Nafion membrane surface that reduces the mixed potential effect at cathode contributes to the suppression of methanol crossover. A similar approach had been reported by Jiang's team, too [27]. The only different is in the metal deposited in PDAC, i.e. Pt in Jiang's study vs. Pd in [26]. The Pt has the catalytic ability toward methanol oxidation. This means that the Pt reacts with the crossed-over methanol and thus reduces the amount of methanol crossover. This composite Nafion-1135 membrane with a PDAC layer containing Pt catalyst suppresses methanol crossover by 20% and improves power density by 34%.

According to the Deligöz's results [22], the composite Nafion membrane with self-assembly PAH/PSS bi-layers suppresses methanol crossover while drastically reducing the proton conductivity at the same time. Therefore, the adding of Pt-Sn alloy catalyst in PAH/PSS bi-layers is expected to improve the cell performance while retaining the suppression of methanol crossover. The selection of Pt-Sn alloy is two-fold [28-29]: 1) the catalyst activity of Pt<sub>3</sub>Sn alloy toward methanol oxidation comes after the Pt-Ru alloy catalyst; 2) the Sn is a cheaper raw metal as compared with the Ru metal. In this study, the Pt-Sn alloy nano-particles are introduced to the self-assembly PAH/PSS bi-layers by reducing the Pt and Sn ions in PSS to mitigate methanol crossover and improve cell performance. The designed membrane electrode assembly (MEA) structure is shown in figure 1. The effects of the 5, 10 PAH/PSS bi-layers with Pt<sub>3</sub>-Sn alloy nano-particles on the suppression of methanol crossover and improved performance is investigated. The possible suppression mechanism of methanol crossover is also studied.



Figure 1. Diagram of the proposed MEA.

# 2. EXPERIMENTAL

2.1 Preparation of self-assembly layers composed of Pt-Sn nano-particles



**Figure 2.** An idealized scheme of layer-by-layer deposition of the anionic and cationic polyelectrolytes on the Nafion-117 membrane.

We prepared the aqueous solution of poly(allylamine hydrochloride) (PAH) (Mw 15,000) and poly(sodium 4-styrenesulfonnate) (PSS) (Mw 70,000) in a concentration of 10<sup>-2</sup>M separately. The

[Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and SnCl<sub>2</sub>·2H<sub>2</sub>O were added into the PSS solution to form the PSS solution with Pt and Sn ions. The pH of PSS and PAH was adjusted to 1.80 by adding the HCl into these two solutions. After drying the Nafion-117 membrane in an oven at 60 °C, the membrane was alternately dipped into PAH and PSS solutions at an appropriate time. The excess PSS and PAH solution was rinsed with ultra-pure water after each dipping process. These procedures were repeated until the desired number of layers on the Nafion membrane surface was obtained. This sample is denoted as PAH/PSS-Pt<sup>+</sup>-Sn<sup>+</sup>. To obtain the Pt-Sn alloy in PAH/PSS, the samples were put into NaBH<sub>4</sub> solutions to carry out the reduction reaction at 60 °C for 1 hour. After the treatment of 0.50M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 1 hour, the sample was rinsed with ultrapure water. Finally, the sample with Pt-Sn metal on the Nafion membrane surface was obtained, which is denoted as the PAH/PSS-Pt-Sn sample. Figure 2 shows the diagram of PAH/PSS self-assembly layer containing Pt and Sn alloy on Nafion membrane surface.

#### 2.2 Characterization of self-assembly layers with Pt-Sn

The UV-visible spectroscopy was used to monitor the coating of PAH/PSS self-assembly layers on Nafion membrane with a scan rate of 400 nm min<sup>-1</sup>. The pristine Nafion-117 membrane is used as the reference. A field emission-scanning electron microscope (FESEM) (JEOL, JSM-6700F) was adopted to characterize the morphology, composition and cross-sectional view of PAH/PSS bilayers with Pt-Sn catalyst. The morphology and composition of resulting Pt-Sn particles was examined by a field emission-transmission electron microscope (FE-TEM) (JEM-2100F) with an energy dispersive X-ray spectrometer (EDS) (an Oxford INCA Energy TEM 200 system). The crystalline phase analysis was performed by comparison of the selected area diffraction (SAD) patterns of the catalyst particles to those of standard compounds reported in the JCPDF file. The X-ray diffraction (XRD) pattern of Pt-Sn was obtained by an X-ray diffractometer (BRUKER, D8 Discover) using a CuK $\alpha$  radiation source operating at 40kV and 30 mA. The proton conductivity of composite Nafion membrane was measured by a two-probe AC method using an AC impedance analyzer (EG&G, model 5210 lock in amplifier). The sample was cut in 3.50 cm x 3.50 cm dimensions and impedance measurements were performed in 95% RH at 60 °C.

## 2.3 Preparation of anode $(Pt_{50}Ru_{50})$ , cathode (Pt/C) and MEA

Anode or cathode catalyst ink was prepared by mixing  $Pt_{50}Ru_{50}$  or 40% Pt/C, 5% Nafion solution, n-butyl acetate and isopropanol (IPA) by homogenizer for 10 minutes. The catalyst ink was sprayed onto the carbon cloth, which served as a gas diffusion layer (GDL), and Nafion membrane surface to form the  $Pt_{50}Ru_{50}$  anode and Pt/C cathode. The anode and cathode loadings were 4 mg  $Pt_{50}Ru_{50}$  cm<sup>-2</sup> and 4 mg Pt cm<sup>-2</sup>, respectively. The MEA was formed by hot-pressing the sandwich structure of the PAH/ PSS-Pt-Sn sample, anode and cathode under the pressure of 5 ~ 6 MPa at 138 °C for 2 minutes. The structure of proposed MEA in this study is shown in figure 2. This MEA is referred to as MEA-Pt-Sn-5 or MEA-Pt-Sn-10. The 5 at the end of the sample code represents the 5 PAH/PSS

bi-layers sample, while the 10 represents the 10 self-assembly bi-layers sample. The MEA without any self-assembly layer on the Nafion membrane is denoted as MEA-N-117.

# 2.4 Measurement of performance and methanol crossover

The MEAs (5 cm<sup>2</sup>) were tested with 1M methanol as anode fuel (1cc/min) and pure oxygen as cathode fuel (400 sccm) at cell temperature of 80 °C by a fuel cell test station, manufactured by Fuel Cell Technology, USA. Since the amount of methanol crossover is proportional to the  $CO_2$  concentration of cathode exhaust, we used the  $CO_2$  sensor (Testo 535) to monitor the amount of methanol crossover. This was because most of the crossed-over methanol entering the cathode reacts with  $O_2$  to produce the  $CO_2$ . Due to the  $CO_2$  concentration, output current remains steady 45 minutes into the test for one corresponding voltage. The current and  $CO_2$  concentration were measured after 45 minutes. The polarization curve was obtained after collecting the output current and voltage from open circuit voltage (OCV) to 0.30V with a total measuring time of 360 minutes.

#### **3. RESULTS AND DISCUSSION**



3.1 Characterization of PAH/PSS self-assembly layer with Pt-Sn

Figure 3. UV-vis absorption spectra of PAH/PSS polyelectrolytes with 5 and 10 bi-layers.



**Figure 4.** UV-vis absorption spectra of PAH/PSS-Pt<sup>+</sup>-Sn<sup>+</sup> samples with 5 and 10 bi-layers.



**Figure 5.** XRD patterns of PAH/PSS-Pt-Sn sample with 5, 10 bi-layers and PAH/PSS-Pt sample with 10 bi-layers.

Figures 3 and 4 show the UV-visible spectra of Nafion membrane self-assembled with PAH/PSS and PAH/PSS containing Pt and Sn ions, respectively. The peak at 228 nm is the wavelength of the Na ion in PSS [21]. The PAH is transparent in the range of UV-visible spectra we measured. Therefore, the strong absorbance at 228 nm in figure 3, particularly for the 10 PAH/PSS bi-layers sample, indicates the PAH/PSS is adsorbed onto the Nafion membrane surface.



Figure 6. TEM micrographs of prepared Pt<sub>3</sub>Sn nanoparticles with (a) 5 bi-layers in bright field images;
(b) 10 bi-layers in bright field images and (c) 5 bi-layers in SAD patterns (the SAD patterns for 5 and 10 bi-layers are same to each other).

On contrast, the peak at 228 nm almost disappears when Na ion ion-exchanged by Pt and Sn ions (as shown in figure 4). However, it still has a small absorbance at 228nm for the sample containing Pt and Sn ions. This implies that a small portion of Na ions still exists in PSS. Due to the fact that the peaks of Pt and Sn ions cannot be observed in the range of UV-visible spectra we measured, the existence of Pt and Sn alloy were verified by XRD and TEM analysis.

Figure 5 shows the XRD patterns of the PAH/PSS-Pt-Sn and PAH/PSS-Pt samples. In order to verify the Pt element and alloy phase in the PAH/PSS-Pt-Sn sample, we also prepared the PAH/PSS-Pt sample with only the Pt element that was fabricated by the same conditions as in the PAH/PSS-Pt-Sn sample. The XRD pattern of the PAH/PSS-Pt sample is shown in figure 5(a). That the characteristic peaks at 39.84°, 46.56° and 67.88° indicates the existed phase is Pt element. Similar peak positions are obtained for the PAH/PSS-Pt-Sn sample. Consequently, the PAH/PSS-Pt-Sn sample has the Pt element. The peak of Pt(111) face is selected as the reference peak to verify the alloy phase by comparing the lattice constant of Pt and Pt-Sn. Bragg's equation yields lattice constants of 3.928 Å for 5 bi-layers and 3.930 Å for 10 bi-layers, respectively, which are slightly longer than that of pure Pt, i.e. 3.920 Å. Since the lattice constant of pure Sn in FCC structure is greater than that of the pure Pt [30-31], the lattice constant is expected to become longer when the Sn atom is incorporated into the Pt FCC structure. However, the lattice constant of the PAH/PSS-Pt-Sn sample is slightly longer than that of Pt, indicating that Pt-Sn may exist in alloy phase. To confirm this, the TEM diffraction analysis is used to verify the alloy phase in the PAH/PSS-Pt-Sn sample. Figures 6(a) and 6(b) show the bright field morphology of PAH/PSS-Pt-Sn samples with 5 and 10 bi-layers, respectively. The nano-particles and lattice spacing can be clearly observed. The EDS results confirm the nano-particles containing the Pt and Sn elements, and the atomic ratio of Pt to Sn is 3:1. The average particle sizes are 17 nm for 5 bilayers and 23 nm for 10 bi-layers of the PAH/PSS-Pt-Sn samples, respectively. The d spacing obtained from the SAD pattern (Figure 6c) is 2.345 Å, which corresponds to the (111) reflection of the Pt<sub>3</sub>Sn alloy phase (based on the data in JCPDF file No.: # 351360). Accordingly, the Pt-Sn in the PAH/PSS-Pt-Sn sample exists in alloy phase with atomic ratio of 3:1 (Pt:Sn).



Figure 7. Cross-sectional SEM picture of 10 bi-layers of PAH/PSS containing Pt-Sn.

Figure 7 shows the cross-sectional SEM view of the PAH/PSS-Pt-Sn sample with 10 bi-layers. Two morphologies are observed. The upper layer is the PAH/PSS self-assembly layer with Pt-Sn nanoparticles, implying that the self-assembly layer is concentrated on the Nafion-117 membrane surface. The corresponding thickness is 300 nm. Accordingly, the thickness of a PAH/PSS bi-layer containing Pt<sub>3</sub>Sn alloy is 30 nm. Therefore, the thickness of a PAH/PSS-Pt-Sn sample with 5 bi-layers is 150 nm.



**Figure 8.** CV profile for PAH/PSS-Pt-Sn sample with 5 bi-layers. (Testing in 0.50 M CH<sub>3</sub>OH and 0.50 M H<sub>2</sub>SO<sub>4</sub> solution at 25 °C).

Figure 8 presents the cyclic voltammograms (CV) profile for 5 bi-layers of PAH/PSS-Pt-Sn samples measured in a solution of 0.50 M methanol and 0.50 M H<sub>2</sub>SO<sub>4</sub> at a scanning rate of 50 mV s<sup>-1</sup>. A small peak of methanol oxidation is found at the potential range of 0.54-0.78 V when carefully examined (as shown in an enlarged picture on the right hand side in figure 8). The peak current density at 0.66 V is 2.7 x  $10^{-3}$  mA cm<sup>-2</sup>. This result indicates that the Pt<sub>3</sub>Sn alloy deposited in the PAH/PSS bi-layers can oxidize methanol and functions like a catalyst and an electrode with even a low Pt-Sn loading of 23µg cm<sup>-2</sup> for 5 bi-layers and 38 µg cm<sup>-2</sup> for 10 bi-layers, respectively.

Figure 9 shows the Nyquist plots of PAH/PSS-Pt-Sn samples with 5 and 10 bi-layers and Nafion-117 membrane. The proton conductivity of Nafion-117 is 14.23 mS cm<sup>-1</sup>, while the proton conductivity of 5 and 10 bi-layers of PAH/PSS-Pt-Sn samples are 5.55 and 3.62 mS cm<sup>-1</sup>, respectively.



**Figure 9.** Nyquist plots of the PAH/PSS-Pt-Sn samples with 5,10 bi-layers and the pristine Nafion-117 membrane.

These results imply that the self-assembly of PAH/PSS with Pt<sub>3</sub>Sn alloy on Nafion membrane surface increases the resistance of Nafion membrane and will reduce the cell performance.

#### 3.2 Methanol crossover and cell performance

Figure 10 shows the CO<sub>2</sub> concentrations at cathode exhaust varied with current density at 80 °C. The square, triangle and diamond symbols represent the curves for MEA-N-117, MEA-Pt-Sn-10 and MEA-Pt-Sn-5, respectively. According to the result of H. T. Liu and coworkers [32], the amount of methanol crossover is proportional to CO<sub>2</sub> concentrations at cathode exhaust. Therefore, the CO<sub>2</sub> concentrations at cathode exit are used to monitor the rate of methanol crossover. The CO<sub>2</sub> concentrations of MEA-Pt-Sn samples with 5 and 10 bi-layers are lower than those of MEA-N-117 by 50%. Figure 11 indicates the OCVs of MEA-Pt-Sn with 5 and 10 bi-layers are 0.82V and 0.83V, respectively, which are higher than the OCV of MEA-N-117 (i.e. 0.72V) by about 0.10V and 0.11V, respectively. It is known that the OCV increases as methanol crossover decreases [32]. Therefore, the increments of OCV of 0.10V and 0.11V are attributed to the suppression of methanol crossover due to the existence of the PAH/PSS bi-layers with Pt<sub>3</sub>Sn alloy deposited on Nafion membrane surface. This result is consistent with the results in figure 10.



Figure 10. Steady-state  $CO_2$  concentrations at the cathode exhaust vs. current density at cell temperature of 80°C.

Figure 11 shows the polarization curves of MEA-Pt-Sn with 5 and 10 bi-layers and MEA-N-117. The current density of MEA-Pt-Sn with 5 bi-layers is slightly higher than that of MEA-N-117 by 6% (@0.40V), while the current density of MEA-Pt-Sn with 10 bi-layers is 19% (@0.40V) lower than that of MEA-N-117. There is a contrary result between 5 and 10 bi-layers. This is because the layer thickness and proton conductivity for 10 bi-layers of PAH/PSS with Pt-Sn catalyst are thicker and lower than those of the 5 bi-layers sample (i.e. 300nm vs. 150nm, 3.62 mS cm<sup>-1</sup> vs. 5.55 mS cm<sup>-1</sup>).

In order to clarify the suppression mechanism of methanol crossover for MEA with selfassembly PAH/PSS bi-layers containing Pt-Sn alloy nano-particles, we applied the mechanism reported in [33] for this study due to the fact that the two MEAs have a similar structure and composition. The only difference lies on the deposited layer in PAH/PSS self-assembly bi-layers, i.e. Pt<sub>3</sub>Sn in this study vs. Pt<sub>35</sub>Ru<sub>65</sub> in [33]. We propose that the crossed-over methanol reaches the Pt<sub>3</sub>Sn deposited layer and reacts to form the CO<sub>2</sub>, electros and proton. The reaction over Pt<sub>3</sub>Sn nano-particles reduces the amount of methanol crossover and mixed potential effects at cathode. Furthermore, the produced electrons conduct to cathode through the  $Pt_{50}Ru_{50}$  anode catalyst layer via external circuit, while the protons transfer from anode to cathode through the Nafion membrane. The combination of electrons and protons at cathode generate an extra current that improves the cell performance. Moreover, the solid Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers provide a barrier to block the crossedover methanol and thus reduce the methanol crossover. In addition, the PAH/PSS self-assembly layer itself could suppress methanol crossover as well [22]. Due to these four reasons, the MEA with deposited  $Pt_3Sn$  alloy particles in PAH/PSS bi-layers suppresses methanol crossover by 50%. In fact, the current density of this MEA has been increased by only 6% for 5 bi-layers and dropped by 19% for 10 bi-layers.



Figure 11. Polarization curves of MEA-Pt-Sn-5, MEA-Pt-Sn-10 and MEA-N-117 at 80°C.

This is due to two reasons. Firstly, both of the depositions of Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers and the PAH/PSS self-assembly layer itself reduce the proton conductivity of Nafion membrane about one-seventh times and thus reduce the cell performance. Secondly, due to the good dispersion of Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers, the generated electrons are difficult to transfer to cathode due to the high resistance between Pt<sub>3</sub>Sn alloy particles and the anode catalyst Pt<sub>50</sub>Ru<sub>50</sub> layer. The generated extra current is thus limited. This means that the performance improvement offered by the Pt<sub>3</sub>Sn alloy particles is limited. Therefore, for 5 bi-layers, the performance improvement attributed to 1) the oxidation reaction of crossed-over methanol over the Pt<sub>3</sub>Sn alloy particles, and 2) the reduction of mixed potential effect at cathode is slightly higher than the increasing resistance of PEM from producing solid Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers and the PAH/PSS self-assembly layer itself. Accordingly, MEA with deposited Pt<sub>3</sub>Sn alloy particles in 5 PAH/PSS bi-layers, the increasing thickness increases the resistance of PEM. The performance improvement due to the

reaction over the Pt-Sn alloy particles and reduced mixed potential effect at cathode is thus lower than the increasing resistance of PEM resulting from solid Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers and the PAH/PSS self-assembly layer itself. Consequently, MEA with 10 PAH/PSS bi-layers containing Pt<sub>3</sub>Sn alloy particles suppresses methanol crossover and reduces the cell performance.

To clarify the effect of deposited Pt-Sn in PAH/PSS, we compare the reduction of proton conductivity and methanol permeation rate for 5 and 10 bi-layers between our samples and the sample in reference [22] (as shown in table 1).

**Table 1.** Comparison of reduction of proton conductivity and methanol permeation rate for 5 and 10 bi-layers between ours samples and reference [18] (concentration of polyelectrolytes are 10<sup>-2</sup> monomole).

Polyelectrolytes	Number of deposited bi-layers	Reduction of proton conductivity <sup>1</sup> (%)	Reduction of methanol permeation rate <sup>2</sup> (%)
PAH/PSS [18]	5	56%	19%
	10	82%	26%
PAH/PSS-Pt <sub>3</sub> Sn	5	60%	50%
	10	74%	50%
1			

<sup>1</sup> Reduction of proton conductivity = [(proton conductivity of Nafion-117 - proton conductivity of sample) / proton conductivity of Nafion-117] x 100%

<sup>2</sup> Reduction of methanol permeation rate = [(methanol permeation rate of Nafion-117 - methanol permeation rate of sample) / methanol permeation rate of Nafion-117] x 100%

The only different between these two samples is in the deposited Pt-Sn layer in this study. For 5 bi-layers, the reduction percentages of methanol permeation rate and proton conductivity for our sample are higher than those of the sample reported in [22], i.e. 50% vs. 19% and 60% vs. 56%, respectively. This indicates that our sample has a lower amount of methanol crossover and cell performance as compared with Deligöz's sample. In fact, the actual output current density of our sample has been improved. This is because the deposited Pt-Sn nanoparticle oxides the crossed-over methanol to produce an extra current and thus improve output current density, although the proton conductivity is low. In contrast, the thickness of the 10 bi-layers sample is 2 times thicker than that of the 5 bi-layer sample and the 10 bi-layers sample shows an increasing resistance of composite Nafion membrane. The resistance increment of this composite membrane from increasing thickness is higher than the performance improvement due to the oxidation reaction of crossed-over methanol over the deposited Pt-Sn. Therefore, the output cell performance decreases while suppressing methanol crossover for our 10 bi-layers sample. This analysis supports the above inference.

Jiang's team [27] studied the self-assembly of PDAC containing the Pt on the Nafion-1135 membrane surface to mitigate methanol crossover. They showed that this composite Nafion-1135 membrane with a PDAC layer containing Pt nano-particles has improved the power density by 34% and reduced methanol crossover by 19%. Comparing our sample with Jiang's sample, our sample with 5 bi-layers of PAH/PSS containing Pt<sub>3</sub>Sn alloy nano-particles has a low power density increment than the Jiang's sample, i.e. 16% vs. 34%. Howerver, our sample has a greater reduction of methanol

crossover than Jiang's sample, i.e. 50% vs. 19%. This is because the thickness effect of 5 bi-layers of PAH/PSS with Pt-Sn in our sample is more significant than that of a layer of PDAC with Pt in Jiang's sample. This increases the resistance of composited Nafion membrane and reduces methanol crossover in our sample. Furthermore, the presence of Pt<sub>3</sub>Sn nano-particles in PAH/PSS self-assembly layer oxides the crossed-over methanol and reduce methanol crossover. Therefore, our sample greatly mitigate methanol crossover while slightly improve power density as compared with the Jiang's sample. Indeed, the presence of Pt<sub>3</sub>Sn nano-particles in the PAH/PSS self-assembly layer has better

CO tolerance than the Pt nano-particles.

# **4. CONCLUSION**

5 and 10 PAH/PSS bi-layers containing Pt<sub>3</sub>Sn alloy nano-particles are self-assembled on both sides of Nafion-117 membrane under the designed conditions. The layer thicknesses of 5 and 10 PAH/PSS bi-layers with Pt-Sn alloy are 150nm and 300nm, respectively. This self-assembly layer with Pt<sub>3</sub>Sn alloy nano-particles functions like a catalytic active layer and a methanol barrier that react and block the crossed-over methanol. These two roles contribute to the suppression of methanol crossover and improved performance. Therefore, the composite Nafion membrane with 5 PAH/PSS bi-layers containing the Pt<sub>3</sub>Sn alloy suppresses methanol crossover by 50% and improved current density by 6% (@0.40V). In contrast, the composite Nafion membrane with 10 PAH/PSS bi-layers containing the Pt<sub>3</sub>Sn alloy mitigates methanol crossover by 50% while decreasing performance by 19% (@0.40V). This is because, for 5 PAH/PSS bi-layers, the performance improvement is attributed to 1) oxidation reaction of crossed-over methanol over the Pt<sub>3</sub>Sn alloy particles, and 2) reduction of mixed potential effect at cathode, which is slightly higher than the increasing resistance of PEM from producing solid Pt<sub>3</sub>Sn alloy particles in PAH/PSS bi-layers and the PAH/PSS self-assembly layer itself. For 10 bilayers, the thickness effect significantly decreases the cell performance. Hence, the MEA with 10 PAH/PSS bi-layers with Pt<sub>3</sub>Sn alloy particles decreases current density by 19% while suppressing methanol crossover. In short, the suppression of methanol crossover and the performance improvement of MEA with the existence of deposited catalyst layer in self-assembly layer are affected by the kinds, morphology and loading of the deposited catalyst layer and the self-assembly layer itself.

### ACKNOWLEDGMENTS

We greatly thank the National Science Council of Taiwan (R.O.C) for the financial support under the NSC Project No. NSC 99-2221-E-451-014-MY2 and NSC 101-2221-E-451 -003 -MY2.

# References

- 1. A. Heinzel, V. M. Barragán, J. Power Sources, 84 (1999) 70
- 2. G. T. Burstein, C. J. Barnett, A. R. Kucernak, K. R. Williams, Catal. Today, 38 (1997) 425
- 3. T. Frelink, W. Visscher, J. A. R. van. Veen, Surf. Sci., 335 (1995) 353
- 4. B. R. Rauhe, Jr., F. R. Mclarnon, E. J. Cairns, J. Electrochem. Soc., 142 (1995) 1073

- 5. T. Frelink, W. Visscher, A. P. Cox, J. A. R. van. Veen, Electrochim. Acta, 40 (1995) 1537
- 6. V. Tricoly, J. Electrochem. Soc., 145 (1998) 3798
- 7. N. Miyake, J.S. Wainright, R.F. Savinell, J. Electrochem. Soc., 148 (2001) A905
- P. Staiti, A.S. Aricò, V. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, Solid State Ionics, 145 (2001) 101
- 9. C. Yang, S. Srinivasan, A.S. Arico`, P. Creti, V. Baglio, V. Antonucci, *Electrochem. Solid-State Lett.*, 4 (2001) A31
- 10. J. S.Wainright, D.Wang, R. F.Weng, M. Savinell, J. Electrochem. Soc., 142 (1995) 121
- 11. M.Weng, J. S.Wainright, U. Landau, R. F. Savinell, J. Electrochem. Soc., 143 (1996) 1260
- 12. J. T.Wang, S.Wasmus, R. F. Savinell, J. Electrochem. Soc., 143 (1996) 1233
- 13. S.Wasmus, J. T.Wang, R. F. Savinell, J. Electrochem. Soc., 142 (1995) 3825
- 14. P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, Polymer, 46 (2005) 3257
- 15. C. Pu,W. Huang, K. L. Ley, E. S. Smoktin, J. Electrochem. Soc., 142 (1995) L119
- 16. C. H. Wan, J. M. Wei, M. T. Lin, C. H. Lin, Int. J. Electrochem. Sci., 6 (2011) 889
- 17. C. H. Wan, C. L. Chen, Int. J. Hydrogen Energy, 34 (2009) 9515
- 18. H. Uchida, Y. Mizuno, M. Watanabe, J. Electrochem. Soc., 149 (2002) A682
- 19. A. A. Argun, J. N. Ashcraft, P. T. Hammond, Adv. Mater., 20 (2008) 1539
- 20. S. P. Jiang, Z. Liu, and Z. Q. Tian, Adv. Mater., 18 (2006) 1068
- 21. M. Yang, S. Lu, J. Lu, S. P. Jiang and Y. Xiang, Chem. Commun., 46 (2010) 1434
- 22. H. Deligöz, S. Yılmaztürk, T. Karaca, H. Özdemir, S. Naci Koc, F. Öksüzömer, A. Durmus, M. Ali Gürkaynak, J. Membr. Sci., 326 (2009) 643
- 23. S. Yılmaztürk, H. Deligöz, M. Yılmazoğlu, H. Damyan, F. Öksüzömer, S. N. Koç, A. Durmuş, M. A. Gürkaynak. *J. Membr. Sci.*, 343 (2009) 137
- 24. H. Deligöz, S. Yılmaztürk, M. Yılmazoğlu, H. Damyan, J. Membr. Sci., 351 (2010) 131
- 25. S. Yılmaztürk, H. Deligöz, M. Yılmazoğlu, H. Damyan, F. Öksüzömer, S. N. Koç, A. Durmuş, M. A. Gürkaynak, *J. Power Sources*, 195 (2010) 703
- 26. H. L. Tang, M. Pan, S. P. Jiang, Z. H. Wan, R. Z. Yuan, Colloids Surf., A : Physicochem. Eng. Aspects, 262 (2005) 65
- 27. S. P. Jiang, Z. Liu, H. L. Tang, M. Pan, Electrochim. Acta, 51 (2006) 5721
- 28. W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, Appl. Catal., B: Environmental, 46 (2003) 273
- S. C. Zignani, V. Baglio, J. J. Linares, G. Monforte, E. R.Gonzalez, A. S. Aricò, *Electrochim. Acta*, 70 (2012) 255
- 30. H. Li, G. Sun, L. Cao, L. Jiang, Q. Xin, Electrochim. Acta, 52 (2007) 6622
- 31. J. M. Leger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, Electrochim. Acta, 50 (2005) 5118
- 32. J. H. Han, H. T. Liu, J. Power Sources, 164 (2007) 166
- 33. C. H. Wan, M. T. Lin, J. Power Sources, 222 (2013) 470

© 2013 by ESG (www.electrochemsci.org)