

# Cobalt coated electrodes for high efficiency PEM fuel cells by plasma sputtering deposition

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**Abstract** Proton exchange membrane (PEM) fuel cell electrodes coated with ultra-thin Co layer have been successfully fabricated via plasma sputter-deposition. In order to investigate the influence of Co layers on the oxygen reduction reaction, a series of Co layers with different nominal thickness have been deposited into the cathode–membrane interface. The polarization curves confirmed visible enhancement in cell performance when a 5 nm Co layer on cathode gave rise to a high current density of  $750 \text{ mA cm}^{-2}$  at 0.6 V. Scanning electron microscopy showed that the sputter deposited 5 nm Co layer formed nanosized island structures on the porous electrode, while electrochemical impedance spectra confirmed that a reduction in the total impedance of the electrode led to the improvement of the membrane electrode assembly (MEA) performance.

**Keywords** Proton exchange membrane fuel cell · Membrane electrode assembly · Sputtering · Cobalt

## 1 Introduction

Fuel cell technology is gaining increasing attention in recent years and is viewed as an advanced energy device for the future. This is due to the consequence of limited resources available as well as the serious environmental problems caused by using fossil fuels [1, 2]. Proton exchange membrane (PEM) fuel cells have been well known for their high energy conversion efficiency and low greenhouse gas emission as compared to combustion engines. Therefore, PEM fuel cells provide promising mass market applications in the automotive, stationary and portable power industries. A PEM fuel cell is an electrochemical energy conversion device, converting chemical energy, typically from hydrogen, directly into electrical energy. In a PEM fuel cell, the membrane electrode assembly (MEA), consist of the proton exchange membrane and the catalyst/electrode layer, which forms the key configuration element and basic reaction unit. Hence, the design and fabrication method of MEA is highly critical as it affects performance of the PEM fuel cell. Conventional catalyst/electrode structure is usually chemically prepared by ink processes and consists of a gas diffusion layer and a catalyst layer spread on a carbon backing layer. As the oxygen reduction reaction (ORR) is the rate determining step of the fuel cell process, most research performed on PEM fuel cells are currently dedicated to applying advanced catalyst materials and optimized fabrication methods for cell electrodes.

The catalyst currently used today for the PEM fuel cells is platinum (Pt) [2–9]. One of the key objectives of PEM fuel cell research is to reduce the Pt loading and improve the Pt performance as an electrocatalyst for both the hydrogen evolution/oxidization reaction (HER/HOR) and oxygen reduction reaction (ORR). Generally, the catalytic performance can be fine tuned either by the catalyst

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composition or by structure. Recently, composite catalytic materials such as Pt–M (M = Co, Ni, Fe, etc.) alloys have been extensively investigated and their electrocatalysis on ORR reported [10–12]. On the other hand, physical vapor deposition technique such as radio frequency magnetron sputtering has been recently employed in PEM fuel cells for its high potential in reducing the Pt loading for PEM fuel cell electrodes, owing to its capability to form ultrathin metal layers in vacuum with excellent control of film thickness and uniformity [13–23]. In 1987, Weber et al. [13] reported that the electrode fabrication could be greatly streamlined by sputter-deposition of Pt catalyst onto wet-proofed, porous substrates. They also found that the performance of their sputtered electrodes depended more on the substrate structure and substrate property, than on the sputtering process. In 2002, O'Hayre et al. [14] reported that an ultralow Pt loading of about  $0.04 \text{ mg cm}^{-2}$  sputter-deposited on their electrodes which enabled the MEA to give rise to a maximum power output up to three-fifths that of a commercial E-TEK MEA. The commercial E-TEK MEA has a Pt loading of  $0.4 \text{ mg cm}^{-2}$  [14]. In addition, Brault et al. [15] found that the maximum size of the Pt nano-clusters formed on electrodes by sputtering was about 4 nm and the optimum Pt loading was about  $0.1 \text{ mg cm}^{-2}$ , which gives comparable performance as commercial MEAs with a Pt loading of  $0.4 \text{ mg cm}^{-2}$ . Their results also showed that the sputter-deposited electrode had greater influence on cell performance at the cathode rather than the anode. Furthermore, utilization of the sputtered Pt catalyst was greatly enhanced due to the highly localized Pt particles at the electrode–membrane interface where the reaction takes place [15].

In our study, Co coated fuel cell electrodes were prepared by sputtering an ultrathin Co layer on a  $0.2 \text{ mg cm}^{-2}$  Pt catalyzed electrode and their performance investigated. Cobalt was chosen as a coating material for cathode as previous studies have demonstrated that Co showed high catalytic activity for ORR at the cathode of direct methanol fuel cells [24]. Similar reactions also occurs at the cathode of a PEM fuel cell [24]. In order to evaluate the effectiveness of sputter-deposited Co layers for ORR, a number of Co layers with varying thickness of up to 10 nm were investigated by polarization measurement. Their corresponding polarization curves showed that cell performance was improved by sputtering a ultrathin Co layer at the cathode–membrane interface. Microstructural and electrochemical studies indicated that the additional Co layer sputter-deposited on cathode might change the microstructure of the electrode–membrane interface as well as vary the charge transfer and mass transport properties of MEAs. Our results suggest an effective route to enhance the electrocatalyst efficiency for PEMFC via a reliable industrial sputtering technique.

## 2 Experimental method

### 2.1 Preparation of MEA with sputter-deposited Co layer

In our study, fuel cell performance tests were evaluated based on a  $5 \text{ cm}^2$  MEA with Nafion<sup>®</sup> 117 (Dupont) as solid electrolyte. Prior to Co sputter-deposition, porous electrodes with carbon supported platinum nanoparticles were first fabricated by conventional thin-film method [25]. Carbon paper TGPH090 (Toray Corp.) was first coated with a porous gas diffusion layer consisting of a mixture of VCX72R and PTFE. Catalyst layer was then applied with VCX72R supported platinum (E-TEK) and Nafion<sup>®</sup> (Dupont) mixture. Vacuum-deposited Co catalysts were prepared by sputtering an ultrathin Co layer on a  $0.2 \text{ mg cm}^{-2}$  Pt catalyzed electrode. A radio frequency magnetron sputtering system Denton Discovery-18 was used to deposit metal layers on the cathode to investigate their influence on ORR. The sputtering deposition was carried out at the input power of 100 W and sputtering gas pressure of 10mTorr. The sputtering rate of Co layer was calibrated by a surface profiler (Alpha-Step 500) to control the metal loading in the specimens. A series of MEAs coated with different Co layers on cathode with nominal thickness of 3, 5, 7 and 10 nm were fabricated and their performance was investigated by a single cell test system 890B (Electrochem Corp.). To determine the catalytic performance of the Co coated electrodes, two standard MEAs with Pt loading of 0.2 and  $0.4 \text{ mg cm}^{-2}$  were used as references.

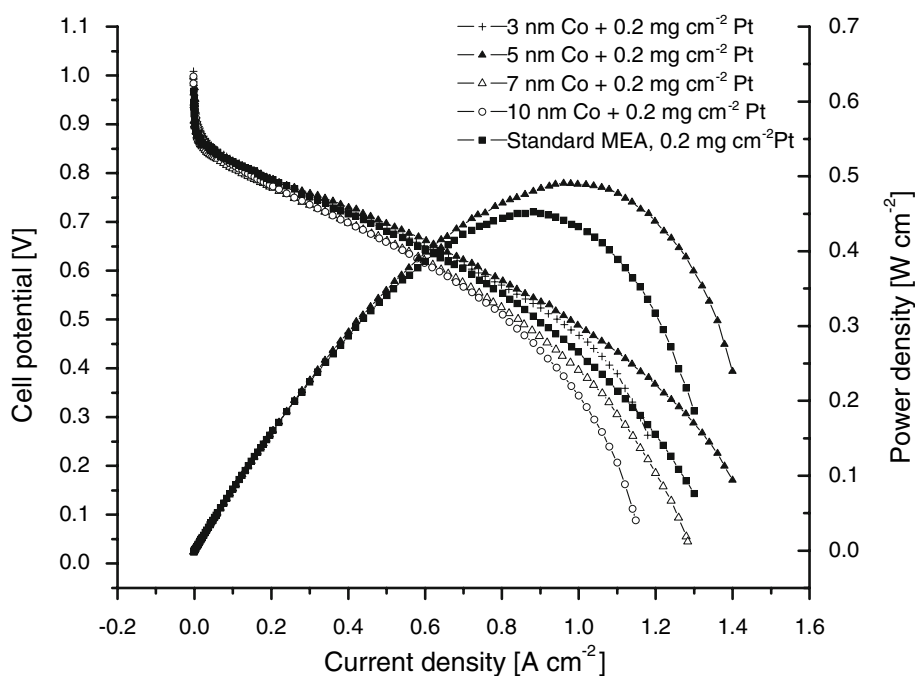
### 2.2 Characterization of Co coated electrode

A field emission scanning electronic microscopy (JOEL 200) was used to characterize the microstructure of the sputtered Co layers on the porous electrodes. In addition, in situ electrochemical impedance spectra (EIS) measurement was carried out to evaluate the transport properties of the Co coated electrodes. The EIS data was measured by a Solartron SI1280B electrochemical measurement unit. Impedance measurement was performed at 0.9 and 0.7 V for following MEAs: 5 nm Co coated MEA, 10 nm Co coated MEA, standard MEA with  $0.2 \text{ mg cm}^{-2}$  Pt, and standard MEA with  $0.4 \text{ mg cm}^{-2}$  Pt. The amplitude of the ac signal was 10 mV rms and the frequency typically varied from 8 kHz to 10 mHz. Nyquist impedance spectra was employed in our results.

## 3 Results and discussion

Figure 1 shows the polarization curves of a series of MEAs with sputtered Co layers of different thickness, as well as a

**Fig. 1** Polarization curves of MEAs with 3–10 nm Co layer coated on  $0.2 \text{ mg cm}^{-2}$  Pt catalyzed cathode, in comparison with a standard MEA with  $0.2 \text{ mg cm}^{-2}$  without Co layer



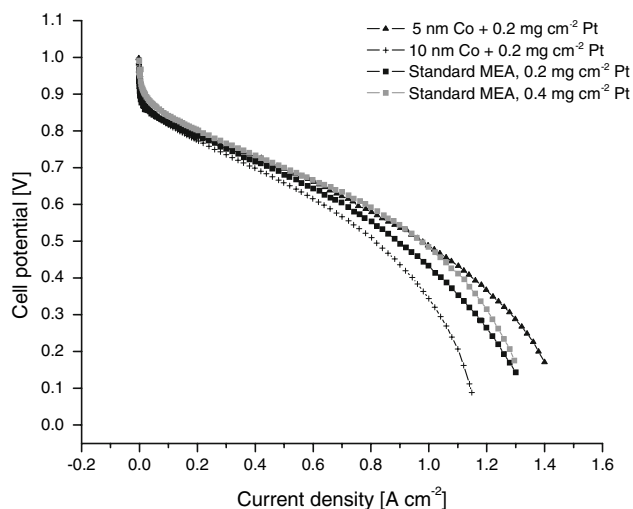
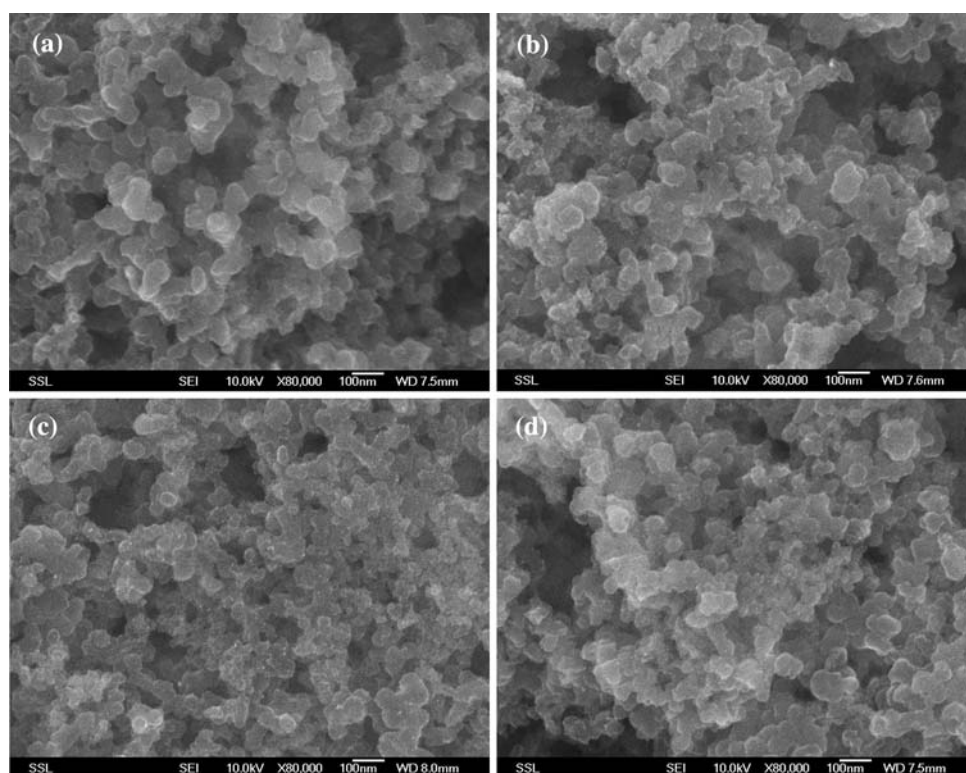
standard MEA with  $0.2 \text{ mg cm}^{-2}$  Pt loading. As shown in Fig. 1, among the four specimens coated with 3, 5, 7 and 10 nm Co layers obtained by sputter-deposition, the 5 nm Co layer coated MEA demonstrates the best cell performance. The polarization curve shows a high current density of  $750 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  with a maximum output power of  $0.49 \text{ W cm}^{-2}$  in comparison to  $0.45 \text{ W cm}^{-2}$  for the reference MEA with the same Pt loading without Co layer deposition. In addition, Co layer as thin as 3 nm has also shown to be able to improve cell performance at low current densities when compared to non Co-containing MEA; however, a potential drop becomes evident when the current densities reach over  $1 \text{ A cm}^{-2}$ . In contrast, cell performance was slightly deteriorated when the Co layer thickness extended to 7 nm or thicker. These results suggest that the sputter-deposited Co layer may have changed the structure of the electrode surface and there exists an optimum Co loading of around 5 nm in nominal thickness.

Figure 2 shows the SEM images of the electrode surface with and without Co layers. Firstly, a highly porous structure was observed in the standard electrode when no Co layer was sputtered on it. Small Pt particles can be seen on carbon support with a diameter less than 10 nm. When a 3 nm Co layer was sputtered on the electrode, the layer was too thin to form a film and instead, the Co particles aggregated into clusters, whose size was comparable to that of the Pt particles. As the layer increased to 5 nm the Co clusters grew bigger and some began to coalesce to form a Co–Pt network, with many nano-sized clusters and pores. This island structure may help us understand better the improvement in cell performance by adding such a Co

layer on cathode. The nano-sized Co–Pt network formed at this thickness by sputtering could promote the catalytic effect for cathode reaction and increase the three-phase zone, and the abundant cracks and pores guarantee the gas diffusion from reaction site to the electrolyte. Nevertheless, 3 nm Co layer may not be adequate to contribute to such enhancement when only small Co clusters was formed on the surface of the electrode. On the contrary, a potential drop in large current densities was observed, probably due to the excess water trapped on the rough surface. When a 10 nm Co layer is sputtered on the electrode, it can be seen that the electrode surface is covered by a dense Co film where fewer metal nano-particles are present. A notable decrease in porosity of the electrode is also observed, suggesting that the performance of the 10 nm Co coated MEA can deteriorate by the increased mass transport limitations.

Polarization curves of the 5 nm and 10 nm Co coated MEAs were further compared with two standard MEAs with Pt loading of  $0.4 \text{ mg cm}^{-2}$  as well as  $0.2 \text{ mg cm}^{-2}$  in Fig. 3. As shown in Fig. 3, the 5 nm Co coated MEA can give rise to comparable performance when compared to standard MEA with doubled Pt loading. In addition, this exceeded over the reference cells at large current densities. Figure 4 shows the EIS data of above four specimens at 0.9 V and 0.7 V, respectively. At 0.9 V, the major impedance of all the MEAs arose from the charge transfer resistance  $R_{ct}$  and double-layer capacitance  $C_{dl}$ , in the catalyst layer observed as the higher frequency semicircular arcs in Fig. 4a. In this low overpotential region, the rate determining step was controlled by the kinetics of

**Fig. 2** SEM images of the sputter-deposited Co layer on  $0.2 \text{ mg cm}^{-2}$  Pt catalyzed electrodes: **a** Top surface of electrode before Co sputtering; **b** 3 nm Co sputtered; **c** 5 nm Co sputtered and **d** 10 nm Co sputtered

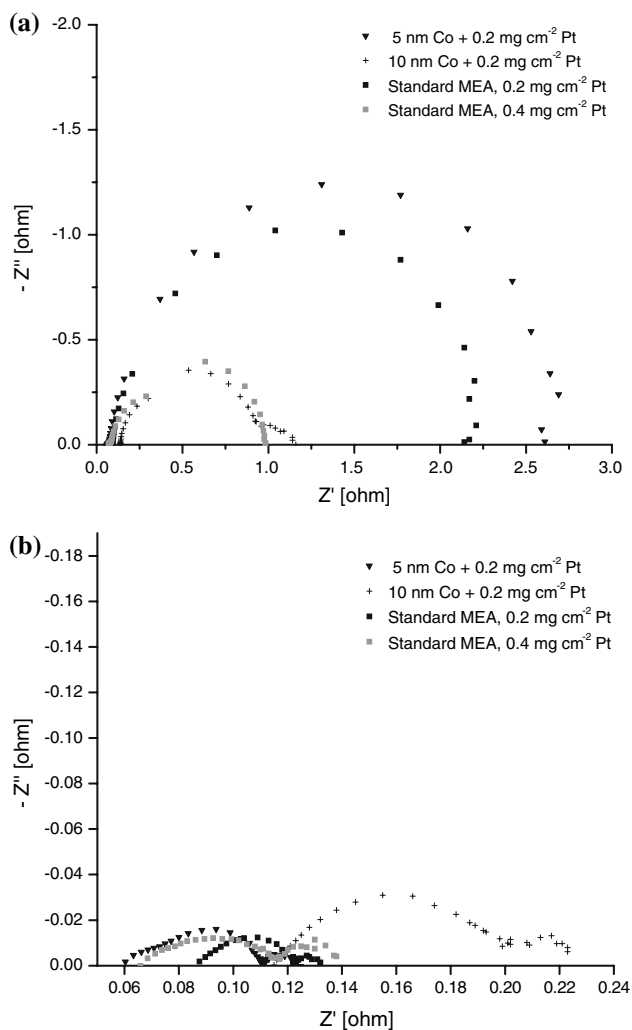


**Fig. 3** Polarization curves of MEAs with 5 nm and 10 nm Co coated on cathode in comparison with standard MEAs with 0.2 and  $0.4 \text{ mg cm}^{-2}$  Pt

ORR and thus the radius of the impedance arc was defined by the charge transfer resistance. The 5 nm Co layer coated MEA gave the highest  $R_{ct}$  while the one with 10 nm Co layer showed the lowest impedance similar to the  $0.4 \text{ mg cm}^{-2}$  Pt-contained MEA. In addition, it is noticed in the Nyquist plot that a lower frequency arc was visible for the MEA with a 10 nm Co layer at 0.9 V, indicating a more humid environment in the catalyst layer due to the

thicker Co layer, hence leading to increased mass transport resistance. On the other hand, the moist catalyst layer in this MEA might probably be in favor of reducing  $R_{ct}$  by offering sufficient water for the cathode reaction. This phenomenon aligns well with the results by Uribe et al. [26], whom highlighted the importance of adequate water for the reaction kinetics at the electrode–membrane interface.

When cell potential decreased to 0.7 V, the charge transfer resistance  $R_{ct}$  of the MEAs showed a dramatic decrease as cathode overpotential increases, suggesting the increasing driving force for the ORR (see Fig. 4b). Moreover, the lower frequency arc was prominent in all the MEAs, especially for the 10 nm Co coated and  $0.4 \text{ mg cm}^{-2}$  Pt-contained MEAs. These results indicated that the mass transport process occurring in the electrodes was contributing to additional overpotential. At this potential, it can be seen from the impedance spectra that the MEA with a 5 nm Co layer displays the minimum overall impedance while the 10 nm Co layer coated sample bears the maximum. As shown previously in Fig. 2d, it was likely that the dense Co film was blocking the charge transfer pathways for protons and mass transport pathways for oxygen, since the 5 nm Co layer did not exhibit such impediment. On the contrary, the ORR limitations were reduced by adding a sputter-deposited 5 nm Co layer onto the surface of MEA cathode. In addition, the interception at the high frequency end of the higher frequency arc reveals



**Fig. 4** Nyquist impedance spectra of Co coated MEAs and standard MEAs at **a** 0.9 V and **b** 0.7 V

the electrical resistance  $R_{EI}$  in the MEA, which stems mostly from the ionic resistance of electrolyte. As shown in Fig. 4b,  $R_{EI}$  could be reduced by adding a 5 nm Co layer. On the other hand, a 10 nm Co layer sputter-deposited on the cathode can increase its  $R_{EI}$ . The decrease of  $R_{EI}$  by the 5 nm Co layer can be attributed to the reduction of contact resistance at the interface by the Co–Pt network. Yet, as Co layer increased to 10 nm, water in the humidified fuel accumulated in the catalyst layer due to the thick Co layer, thus drying out the electrolyte membrane during the process, leading to a boost-up in  $R_{EI}$ .

#### 4 Conclusion

In summary, Co coated PEM fuel cell electrodes have been successfully fabricated via plasma sputter-deposition

technique. Prominent improvement in cell performance has been achieved by sputtering a 5 nm Co layer on the cathode surface of a standard MEA. The 5 nm Co layer formed an island structure of considerable Co nano-clusters on the carbon support while higher loading of Co created a dense film which decreases the cell performance. The electrochemical properties of the Co coated electrodes have been successfully investigated by in situ EIS measurement, which demonstrated that the overall impedance was reduced by sputtering a 5 nm Co layer into the cathode–membrane interface. Although current studies show that the catalytic activity of the Co coated electrode is stable and reproducible, more detailed optimization studies will be carried out in the future. Our study suggests that PVD techniques such as sputtering may provide a promising approach in MEA fabrication to modify the catalyst layer for PEM fuel cell applications.

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