A Novel Cathode Architecture Using Ordered Pt Nanostructure Thin Film for AAEMFC Application

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\textbf{ABSTRACT}

A novel cathode architecture using vertically aligned Co-OH–CO\textsubscript{3} nanoneedle arrays as ordered catalyst support for AAEMFC application is developed. Co-OH–CO\textsubscript{3} nanoneedle arrays are directly grown on a stainless steel sheet via hydrothermal reaction. A Pt nanostructure thin film is prepared on the surface of Co-OH–CO\textsubscript{3} by sputter deposition to form Pt/Co-OH–CO\textsubscript{3} nanoneedle arrays and the thickness of the Pt nanostructure thin film is only several nanometers. After transferring the Pt/Co-OH–CO\textsubscript{3} nanoneedle arrays on an alkaline anion exchange membrane by hot pressing and acid washing, the novel cathode catalyst layer is formed, with the thickness of several hundred nanometers. Without alkaline ionomer in the cathode catalyst layer and the AAEMFC with the prepared MEA shows a peak power density of 113 mW cm\textsuperscript{-2} with ultra-low Pt loading down to 20 µg cm\textsuperscript{-2}. This is the first time that order-structured electrode architecture is applied in the AAEMFC, which can deliver higher power density without alkaline ionomer than the conventional MEA with the same Pt loading.

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1. Introduction

In recent years, the rise of a new class of fuel cells, alkaline anion-exchange membrane fuel cells (AAEMFCs), has attracted increasing attention [1,2]. Compared with proton exchange membrane fuel cells (PEMFCs), AAEMFCs have some outstanding advantages to overcome the technical and cost issues of PEMFCs, including the faster electrochemical reaction kinetics of oxygen reduction reaction (ORR), minimized corrosion issues, decreased fuel crossover rates and potentially improved water management. In particular, the enhanced kinetics in alkaline media can reduce the demand for platinum-based catalysts and realize the application of non-precious metal catalysts.

However, until now the power densities of AAEMFCs reported in the literature are still lower than that of PEMFCs in similar operating conditions. Even with pressurized H\textsubscript{2}/O\textsubscript{2} fed in, the power densities are still lower than that of the acid counterpart. In order to improve AAEMFCs performance, much effort has been made to develop alkaline anion-exchange membranes (AEMs) with high hydroxide ion conductivity that are thought to be the most critical material for AAEMFCs [3–7], anion-exchange ionomers (AEI) [8–10] and electro-catalysts for both oxygen reduction reaction (ORR) [11–14] and hydrogen oxide reaction (HOR) [15–18]. However, the catalyst layers (CLs) architecture, which is crucial to the performance of the AAEMFCs [19–22], has been paid little attention to. Currently, the state-of-the-art method for CLs preparation concludes the catalyst coated membrane (CCM) where CLs are formed by directly coating catalyst slurry on both sides of the AEM [21,22] and the gas diffusion electrode (GDE) where CLs are brushed on the micro-porous layer side of the gas diffusion layer [19,20]. Yet these electrode designs come from electrode architecture of the PEMFCs and may not be suitable for AAEMFCs, as the ionic conductivity of state-of-the-art anion ionomers is insufficiently high and the stability is also not good enough. In addition, the electro-catalysts embedded in ionomer or non-contacted with ionomer will lose electronic and hydroxide ion conducting paths, leading to low catalyst utilization efficiency. Therefore, AAEMFCs fabricated by aforementioned structure are not able to achieve high performance and high utilization of catalyst.

It has been recognized that the efficient utilization of electro-catalysts in PEMFCs not only relies on the intrinsic catalytic activity
of these electro-catalysts, but also strongly depends on the structure of the catalyst layer. Ordered nanostructure CLs have been proposed in PEMFCs [23–26], and 3M company has developed electrodes using nanostructured thin film (NSTF) Pt catalyst coated organic whiskers [23]. The NSTF electrodes have shown a significant activity improvement over the conventional Pt/C-based one due to the thin film structure of the catalyst, the ordered and the ultrathin structure of the CLs that can facilitate the mass transfer at high current density. An ordered electrode structure with high Pt dispersion and low loading is developed by growing arrays of vertically aligned carbon nanotubes (VACNT) as cathode [26]. The VACNT electrodes also show high performance due to ordered VACNTs providing more efficient and uniform reaction environments for Pt catalysts. Besides, ordered electrode structure with the hydrogenated TiO2 nanotube arrays is investigated for PEMFCs [25]. The hydrogenated TiO2 nanotube arrays electrode show good long-term electrochemical durability as compared to the Johnson Matthey 20% Pt/C. However, such advanced CLs structure has not been tested in AAEMFCs.

In the present study, a new ordered porous cathode architecture is constructed based on Co-OH-Co3 nanoneedle arrays as the catalyst support instead of conventional carbon powder for AAEMFCs. The Pt/Co-OH-Co3 nanoneedle arrays are fabricated by directly depositing platinum (Pt) nanoparticles onto the surface of Co-OH-Co3 nanoneedle arrays. After transferring on an alkaline anion exchange membrane by hot pressing and acid washing, the Pt nanostructure thin film arrays is formed and the novel cathode catalyst layer is prepared. The influences of Co-OH-Co3 nanoneedle area density and water management are also investigated. The novel cathode structure not only extends the electrochemical active surface area, but also facilitates the oxygen transport and thus improves the cell performance.

2. Experimental

2.1. Materials preparation

Firstly, Co-OH-Co3 nanoneedle arrays are directly grown on stainless steel sheet via a hydrothermal method. In a typical synthesis process, Co(NO3)2·6H2O (0.233 g), NH4F (0.148 g) and urea (0.48 g) are dissolved into 40 mL distilled water by magnetic stirring for 30 min. Then the homogenous solution is transferred into a 120 mL Teflon lined stainless steel autoclave. A piece of clean stainless steel sheet (2.5 cm × 7 cm) is cleaned with ethanol and distilled water in turn, and then immersed into the above solution.

The autoclave is sealed and kept at 120 °C for 5 h. After cooling down to room temperature, the stainless steel sheet with Co-OH-Co3 nanoneedle arrays is collected and washed for several times with distilled water, and then dried under ambient conditions for 12 h.

Secondly, Pt/Co-OH-Co3 nanoneedle arrays electrode is prepared via a vacuum sputter-deposition method. In a typical synthesis process, Pt is sputtered onto the surface of the Co-OH-Co3 nanoneedle arrays by vacuum sputter-deposition with a platinum target at 120 W and 1.0 bar Ar so as to encapsulate them.

2.2. Material characterization

The morphology and the microstructure of the products are characterized using a field emission scanning electron microscope (FESEM, JSM-7800F) with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM) (TEM, JEM2010-HR, 120 kV). The area density of the sample is calculated by measuring the average distances between two nanoneedles. The phase and the composition of the samples are investigated via X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu Kα radiation (λ=1.5418 Å). The metal loadings of the electrodes are measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on Leeman Plasma-Spec-4 equipment.

2.3. MEA fabrication and single cell test

The Pt/Co-OH-Co3 core–shell nanoneedle arrays electrode is hot-pressed onto one side of a home-made alkaline membrane [7], and the other side of the membrane is a home-made catalyst coated membrane (CCM, PtRu loading: 0.1 mg cm⁻²). The prepared electrode is immersed into 1.0 M HCl for more than 1 hour to wash off the Co-OH-Co3 nanoneedle arrays. Then the electrode is washed with distilled water for several times and immersed into 1.0 M KOH for more than 12 hours to exchange Cl⁻ into OH⁻. Two pieces of carbon papers (Toray, TGP-H-060) coated with MPL are utilized as the anode and the cathode gas diffusion layer, respectively, which sandwich the electrode above to form a MEA by hot-pressing at 60 °C and 1 Mpa for 2 min. The prepared MEAs are assembled into fuel cells with the effective area of 4 cm². A conventional MEA is prepared for comparison. PtRu/C is used as anode catalyst (PtRu loading: 0.1 mg cm⁻²) and Pt/C is used as cathode catalyst (Pt loading: 0.02 mg cm⁻²). The same home-made alkaline membrane is used.

Fig. 1. Schematic illustration of synthesis of Pt catalyst on Co-OH-Co3 nanoneedle arrays and fabrication of AAMEFC.
Fuel cell tests are conducted at 50 °C by feeding H2/O2 (100% relative humidity, RH) with the flow rate of 100/200 mL min⁻¹ at 0.2 MPa, respectively. The i-V curves and high-frequency resistance (RHF) of single cells are measured and recorded by an electric load system (KMF2030, Kikusui Electronics Corp.). The electrochemical impedance of an AAEMFC is tested using the Solartron cell tester. Impedance spectra is recorded by superimposing a 10 mA AC signal on the different current density in the galvanostatic mode with frequencies ranging from 100 KHz to 0.1 Hz.

3. Results and discussion

The fabrication process of Pt electro-catalyst on Co-OH-CO3 nanoneedle arrays is schematically illustrated in Fig. 1. In this method, a cheap stainless steel sheet is used as substrate for growing Co-OH-CO3 nanoneedle arrays. The solution of Co(NO3)2, urea and NH4F are used as precursors to prepare Co-OH-CO3 nanoneedle arrays on cleaned stainless steel sheet under the hydrothermal condition. Pt nanoparticles are then deposited onto the Co–OH–CO3 nanoneedle arrays/stainless steel sheet by physical vapor sputtering system. Finally, the Pt electro-catalyst on Co-OH-CO3 nanoneedle arrays is transferred from the stainless steel sheet onto an AAEM by hot press to fabricate the cathode catalyst layer. Typical SEM and TEM images of the Co–OH–CO3 nanoneedle arrays and Pt/Co-OH-CO3 nanoneedle arrays are shown in Fig. 2, respectively. It can be seen that the Co-OH-CO3 arrays are homogeneously aligned and grow evenly on the stainless steel sheet (Fig. 2a). The Co–OH–CO3 arrays are mainly dominated by needle-like nanostructure arrays with the length of several micrometres and the diameter of less than 50 nm (Fig. 2c). After the Pt nanoparticles are sputtered onto the surface of the Co–OH–CO3 nanoneedle arrays, the needle-like nanostructure maintains (Fig. 2b). However, Pt nanoparticles are not obvious on the surface of the Co–OH–CO3 nanoneedle arrays in SEM image, since the diameter of Pt nanoparticles is only about 2–5 nm and the distribution of Pt nanoparticles is uniform by DC sputtering technique (Fig. 2d). While Pt nanoparticles and nanostructure thin film can be observed on the surface of Co–OH–CO3 nanoneedle in TEM image (Fig. 2d).

Fig. 3a shows the EDS spectrum of the prepared Pt/Co–OH–CO3 nanoneedle arrays and from the figure it can be seen that the Pt/Co–OH–CO3 nanoneedle arrays consist of four elements: Pt, Co, C and O. Fig. 3b shows the XRD patterns of the Co–OH–CO3 nanoneedle arrays and the Pt/Co–OH–CO3 nanoneedle arrays, respectively. There are characteristic diffraction peaks of Co–OH–CO3 at 11.5°, 23.1°, 33.5°, which are assigned to the (100), (111) and (221) faces. The XRD patterns are consistent with the value in the standard card (JCPDS Card no. 048–0083). There are faint peaks at 39.8°, 46.7°, 68.1° and 81.9° after sputtering Pt nanoparticles, corresponding to the Pt (111), (200), (220), (311) crystal faces in the Pt/Co–OH–CO3 nanoneedle arrays. Further, the sample contains strong diffraction peak of the stainless steel.

The Pt/Co–OH–CO3 nanoneedle array film coated AAEM is prepared by hot press. The transfer process do not need any chemical removal of the substrate and the stainless steel sheet can be easily peeled off from the AAEM without any destroy to the membrane. The Pt/Co–OH–CO3 nanoneedle array is uniformly attached to one side of the AAEM and used as cathode catalyst layer, while the other side of the AAEM is coated with PtRu/C as anode catalyst layer before the transfer process. Due to the low electronic conductivity of Pt/Co–OH–CO3 nanoneedle array in the cathode catalyst layer, the electrode is immersed into 1.0 M HCl for more than 1 hour to wash off the Co–OH–CO3 and keep the Pt nanostructure thin film, as can be seen in the inset graph of Fig. 3a. After acid washing, the electrode is immersed into 1.0 M KOH for more than 12 hours for ion exchange. Fig. 4a shows the
conformation of Pt/Co-OH-CO$_3$ nanoneedle array coated on AAEM after transferred by hot press, which is dominated by needle-like nanostructure with the length less than 1 μm and the diameter less than 50 nm. After acid washing, as can be seen in Fig. 4b and Fig. 4c, the morphology of the nanostructure arrays changes significantly that the Pt/Co-OH-CO$_3$ nanoneedle arrays convert into Pt nanostructure thin film arrays. From the TEM image after acid washing in Fig. 4d and Fig. 4e, the nanostructure thin film of the Pt is kept and the thickness of the film is only about 10 nm. The Pt nanostructure thin film shows a nanofiber morphology rather than a tube morphology and the reason is that the thickness of the Pt nanostructure is too thin and the generated CO$_2$ during acid washing can easily break the tube. As shown in Fig. 4d and Fig. 4e, the thickness of Pt nanostructure thin film arrays is only about 350 nm, which is 10 times thinner than the conventional CCM electrode.

The catalytic activity of Pt nanostructure thin film arrays in a single AAEMFC as the cathode is evaluated using H$_2$ and O$_2$ at 50 °C, and the i-V curves and power density are shown in Fig. 6a. Through adjusting the proportion of Co(NO$_3$)$_2$$_n$ in precursor solutions, Co-OH-CO$_3$ nanoneedle arrays with different area densities are prepared and its effect on the cell performance is studied under the same Pt loading (20 μg cm$^{-2}$). The four samples of 0.01 M, 0.02 M, 0.03 M and 0.05 M refer to Co-OH-CO$_3$ nanoneedle arrays prepared using precursor solutions with different proportions of Co(NO$_3$)$_2$$_n$ in them, while keeping area and Ni$_4$F the same. The area densities of Co-OH-CO$_3$ nanoneedle arrays calculated based on the SEM images shown in Fig. 5 are 1.6 × 10$^4$ cm$^{-2}$, 1.2 × 10$^4$ cm$^{-2}$, 6.3 × 10$^3$ cm$^{-2}$, 4.0 × 10$^3$ cm$^{-2}$ for the samples of 0.01 M, 0.02 M, 0.03 M and 0.05 M, respectively. Fig. 6a shows the cell performance of the MEAs fabricated from Co-OH-CO$_3$ nanoneedle arrays with different area densities, in which the activation, cell resistance and mass transport-control regions are distinct. At the activation region, from open circuit voltage to 0.8 V, all cells show almost the same performance, indicating that the area density of Co-OH-CO$_3$ nanoneedle arrays hardly affects the activation polarization of the cell. However, as the cell voltage decreases to less than 0.8 V (ohmic resistance and mass transport-control regions), the cell performance shows difference significantly. In the ohmic resistance-control region, the current density of the cell-0.05 M at around 0.5 V is 70.25 mA cm$^{-2}$ and increases to 90 mA cm$^{-2}$, 100 mA cm$^{-2}$ and 110 mA cm$^{-2}$ for the cell-0.03 M, cell-0.02 M and cell-0.01 M, respectively. In the mass transport-control region, the current density of the cell-0.05 M at around 0.2 V is 130 mA cm$^{-2}$, which increases to 155 mA cm$^{-2}$, 165 mA cm$^{-2}$ and 195 mA cm$^{-2}$ for the cell-0.03 M, cell-0.02 M and cell-0.01 M, respectively. The maximum power density of cell-0.05 M is 58 mW cm$^{-2}$ of cell-0.01 M. Since there is no alkaline ionomer in the cathode catalyst layer, OH$^-$ may conduct via water in the cathode catalyst layer. The significant performance difference at the ohmic resistance control region of the cells fabricated from Co-OH-CO$_3$ nanoneedle arrays with different area densities suggests that the area density of Co-OH-CO$_3$ nanoneedle arrays may influence the mass transport of water in ordered electrode. Similar to the ohmic resistance-control region, performance difference at the mass transfer control region suggests that the area density of Co-OH-CO$_3$ nanoneedle arrays significantly influence O$_2$ mass transport in ordered electrode. The proper area density of Co-OH-CO$_3$ nanoneedle arrays is a very important factor to obtain a higher performance of AAEMFC. In this experiment, the best performance is obtained by the cell-0.01 M, so the Co-OH-CO$_3$ nanoneedle arrays are prepared using 0.01 M Co(NO$_3$)$_2$$_n$ in the following samples.

The thickness of cathode catalyst layer with Pt nanostructure thin film arrays is only several hundred nanometers and there is no alkaline ionomer in the cathode catalyst layer. Based on the fact above, it is believed that water plays an important role in conducting OH$^-$ in the cathode catalyst layer [22]. However, unlike the PEMFC which produces water in the cathode, the oxygen reduction reaction (ORR) in the cathode of AAEMFC consumes water which leads to the cathode dry out easily, so there is not enough water to conduct OH$^-$ in the cathode catalyst layer as the current densities increases over 100 mA cm$^{-2}$ and the cell performance is limited. Meanwhile, the hydrogen oxidation reaction (HOR) in the anode of AAEMFC generates water that makes the anode of the cell susceptible to flooding. To solve the problem of low OH$^-$ conductivity in the cathode catalyst layer due to drying out and increase the performance of the cell by increasing the water content in the cathode side of the cell, the gas diffusion layer (GDL) of the cathode side is optimized. Due to the similarity between PEMFC and AAEMFC, some mature electrode structure of PEMFC can be directly applied on AAEMFC. For example, the GDL used in the PEMFC with micro-porous layer (MPL) to mitigate flooding can be introduced into AAEMFC. Whereas, using GDL with MPL at the cathode side will accelerate the cathode to dry out and decrease the cell performance due to the fact that water is the only OH$^-$ conducting medium in the cathode catalyst layer with Pt nanostructure thin film arrays. As a result, decreasing the hydrophobicity of the GDL is a feasible choice to retain the water in the cathode catalyst layer.
Fig. 6d and e show that the Toray carbon papers (TGP-H-060) with macro-pores used as the cathode GDL without any further treatment exhibit less hydrophobicity compared to the Toray carbon papers coated with MPL (Sunrise Power). The i-V curves and power densities of the cells with different cathode GDLs are compared in Fig. 6b. The cells using Toray carbon papers (TGP-H-060) as the cathode GDL are denoted as cell-mac and the cells using Toray carbon papers coated with MPL as the cathode GDL are denoted as cell-mic. The cell-mac displays significantly higher performance as compared with the cell-mic. At the activation-control region, from open circuit voltage to 0.8 V, the two cells show almost the same performance. Nevertheless, as the cell voltage decreases to less than 0.8 V (ohmic resistance and mass transport-control region), the cell performance is obviously different. At the ohmic resistance control region, the current density of the cell-mic at around 0.6 V is 90 mA cm⁻² and increases to 130 mA cm⁻² for the cell-mac. With the increase of the current density, mass transport resistance presents obviously for the
Fig. 6. i-V curves and power density of single AAEMFCs using Pt nanostructure thin film arrays as cathode: (a) effect of area density of Co-OH-CO₃ nanoneedle arrays, (b) effect of different GDL hydrophobicity, (c) comparison of Pt nanostructure thin film arrays, which has Pt loading of 20 μg/cm², with commercial Johnson Matthey 20% Pt/C catalyst (Pt loading of 20 μg/cm²); (d) EIS comparison of Pt nanostructure thin film arrays with commercial Johnson Matthey 20% Pt/C catalyst; The CA images of of different GDL: (e) Toray carbon papers (TGP-H-060), (f) Toray carbon papers coated with MPL.
cell-mic while little mass transport resistance presents for the cell-mac. Cell-mac shows the maximum current density of 600 mA cm$^{-2}$, which is 173% higher than that of cell-mic (220 mA cm$^{-2}$). The maximum power density also increases significantly from 65 mW cm$^{-2}$ of cell-mic to 113 mW cm$^{-2}$ of cell-mac. The significant difference in the performance of the cells with different cathode GDL suggests that water plays an important role in conducting OH$^-$ in cathode catalyst layer with Pt nanostructure thin film arrays. By increasing the water content in the cathode, the ohmic resistance of the cell is reduced significantly, which means that water not only acts as reactant reacting with O$_2$ to form OH$^-$, but also acts as ion conductor to replace alkaline ionomer in conducting OH$^-$ in the cathode catalyst layer. The electrochemical impedance spectra at 100 mA cm$^{-2}$ is shown in Fig. 6c, as can be seen Toray carbon papers coating with MPL show smaller electric resistance but larger charge transfer resistance and mass transfer resistance compared with Toray carbon papers. This result also indicates that water plays a key role in increasing the cell performance.

To further confirm the performance improvement of the novel catalyst layer structure, a conventional cathode electrode is fabricated with Johnson Matthey 20% Pt/C electrocatalyst with the Pt loading at 20 $\mu$g cm$^{-2}$, and the cell performance is compared in Fig. 6f. Besides, the anode electrode and AEM are the same for the two electrodes. The cell with Pt nanostructure thin film arrays displays a higher performance compared with the cell using commercial Pt/C catalyst as cathode catalyst. Though the two i-V curves are almost the same from open circuit voltage to 0.6 V, obvious difference appear when the voltage decreases to less than 0.6 V (ohmic resistance and mass transport-control region). The conventional cathode catalyst layer, usually prepared by wetting process, is randomly constructed by Pt/C catalysts and ionomer, while the Pt nanostructure thin film arrays electrode has a thin-film catalyst layer, as shown in Fig. 4c. The thinner catalyst layer and the regular hole structure of the ordered catalyst layer can reduce the transport resistance of oxygen and water, resulting in a higher maximum current density. The result is confirmed by the electrochemical impedance spectra shown in Fig. 6g. In the same current density, the Pt nanostructure thin film arrays electrode shows only one arc while the conventional cathode catalyst layer has two. The second arc in the EIS means that the conventional cathode catalyst layer has larger mass transfer resistance. Therefore, the Pt nanostructure thin film arrays cathode can yield a relatively better performance than the conventional cathode.

4. Conclusions

In conclusion, a new cathode architecture for AAMEFC is developed by forming Pt nanostructure thin film on the surface of vertically aligned Co-OH-CO$_3$ nanoneedle arrays. The thickness of cathode catalyst layer composed of Pt nanostructure thin film arrays is about 350 nm. The AAMFCs with the novel ordered structure catalyst layer shows a better performance compared to the one with conventional cathode catalyst layer with the same Pt loading. The underlying reason is that the catalyst layer of the conventional design is thicker than the ordered nanostructure thin film catalyst layer, resulting in a higher oxygen and water transfer resistance. Besides, the present work lies in the fact that without the existence of alkaline ionomer in the cathode catalyst layer, AAMEFC can output preferable performance.

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