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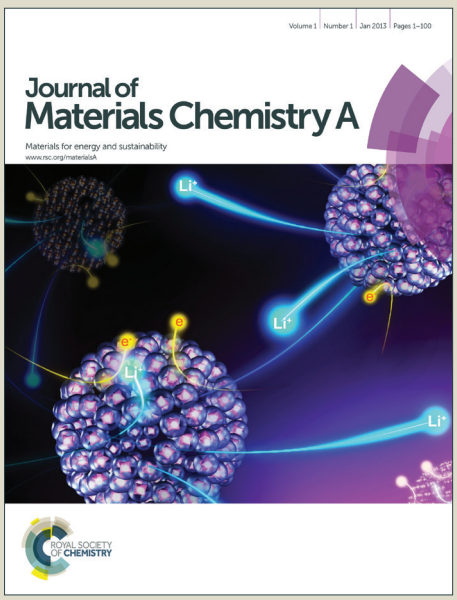

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Shape-controlled porous heterogeneous PtRu/C/Nafion microspheres enabling high performance direct methanol fuel cells

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Anode catalytic layer for direct methanol fuel cells (DMFCs) with decreased PtRu loading as low as 1.0 mg cm^{-2} has been prepared by an electrospray method. The morphology of electrosprayed composite of PtRu/C/Nafion/polyethylene oxide (PEO) is altered from irregular particle to porous microsphere and to nanofiber by adjusting the PEO content. A hybrid structure is assembled by the porous microspheres as the anode catalytic layer for DMFC, leading to a remarkable enhancement in the maximum power density of 35.4 mW cm^{-2}, which is ~50% higher than that of conventional one at the same PtRu loading of 1.0 mg cm^{-2} and is even comparable to that (31.5 mW cm^{-2}) of conventional one at higher PtRu loading of 2.0 mg cm^{-2}. Further investigation reveals that the improved performance is mainly attributed to its hierarchical factual structure. In the primary structure, the single microsphere is with well-distributed PtRu/C and fully rich in nano-pores and nano-channels, contributing to an increase in the electrochemical active surface area and higher catalyst utilization. In the secondary structure, the micro-sized pathways are formed by the stereoscopic microspheres, contributing to the enhanced mass transport, higher current density and power density.

Introduction

Over the last decade, direct methanol fuel cell (DMFC) has attracted significant interests as portable power sources due to its unique properties, including high energy density, easy fuel storage, simplicity and convenience[1–3]. Although great progress has been made in the DMFC technology, there are several challenges that have limited its practical applications, such as high cost, low power density, methanol crossover and poor durability[4–6].

The membrane electrode assembly (MEA) is the most important part in DMFC with the highest impact on power density, durability and cost[7–10]. Generally, the noble metal loading on each side of an MEA is ca. 3–4 mg cm^{-2}, which represents 30%~40% of the total cost. To reduce noble metal loading within the MEA, extensive efforts are devoted to enhance the electrocatalytic activities toward decreasing the Pt content in catalyst materials. Recently, there are some meaningful approaches in developing nanostructured catalytic layers, by improving the densities of so-called triple-phase reaction boundary (TPRB) and optimizing the pathways for electron, proton and mass transport[11–18]. Higher MOR catalytic activities have been achieved by using one-dimensional (1D) nanomaterials (Pt nanowires, carbon nanotubes, etc.) to displace the conventional 0D nanomaterials[19–21]. Similarly, pore-forming templates (magnesium oxide nanoparticles, silica nanoparticles, etc) have been used to control the morphology of the catalytic layer, leading to an increase in the performance at the PtRu loading of 2.0 mg cm^{-2} [22]. Particularly, soft-lithography[23–25] and other nanotechnology are more and more involved in the construction of new electrodes. A nanofiber network catalytic layer is designed and constructed by electrospinning, and thereby significantly improved the catalyst utilization and mass transport[26–33].

According to Fick's law, the mass transport on porous media is simultaneously affected by its pore size, porosity and tortuosity. Fig. 1A schematically shows a conventional electrode assembled by PtRu/C/Nafion agglomerates with small pore size and long tortuosity, resulting in the slow mass transport. In order to address these problems, two structural approaches have been explored successfully, that the one is to increase the pore size and porosity by using pore forming agent or sacrificial template (Fig. 1B[22]) and the other is to reduce the tortuosity by using ordered nanowire array (Fig. 1C[34]). However, it is impossible to get the balance of the pore size, porosity and tortuosity by using a simple structure. A hybrid structure is expected which is formed by two types of pores, including the nanopores toward increasing the TPRB densities and the micropores toward enhancing the mass transport(Fig.1D).

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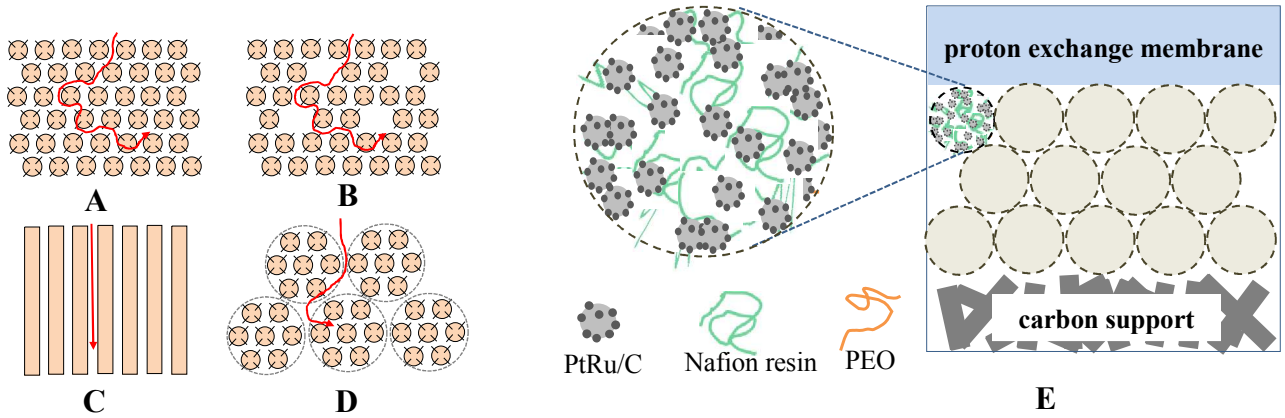

Fig.1 The schematic diagram of four different catalytic layers and their corresponding mass transport pathways: a conventional electrode (A), an electrode with pore forming agent (B), an electrode in ordered nanowire array (C), an electrode in hybrid structure with porous microspheres (D) and the corresponding anode catalytic layer by using porous PtRu/C/Nafion/PEO microspheres (E)

Electrospray as a very useful technique is used to fabricate different types of particles with diameter ranging from micrometer to nanometer. Herein, the electrospray technique was used to fabricate platinum ruthenium/carbon/Nafion/polyethylene oxide (PtRu/C/Nafion/PEO) microspheres as the porous anode catalytic layer for DMFC (Fig.1E). The microspheres with different morphologies were obtained by adjusting the PEO content, and further evaluated as the anode catalytic layer for DMFC. The morphology, electrochemical performance and relationship between the performance and porous microspheres were investigated. The fabricated porous microspheres were rich in nanopores and nanochannels, which were beneficial for improving the electrochemical surface active area (ESA) and PtRu utilization. The microspheres stacked and formed microchannels, which were favorable for methanol and carbon dioxide transport. The PtRu loading in anode is significantly reduced to as low as half, while the performance is maintained in comparison with the conventional one.

Experimental Section

Apparatus and materials

PEO(molecular weight, Mw = 300,000)was purchased from Aldrich. Nafion@ solution (5 wt.%) was from DuPont Co., USA. PtRu/C (40 wt.% Pt and 20 wt.% Ru) and PtRu (1:1) black were obtained from Johnson Matthey Company. Carbon paper (TGPH060, 20wt.% polytetrafluoroethylene, PTFE) was from Toray Company. The microporous layer was composed of XC-72R and PTFE with the mass ratio of 4:1. All chemicals were of analytical grade. The homemade electrospinning/electrospraying setup included a high voltage (0–30 kV) power source, a syringe pump, a steel needle and an aluminum plate as the ground collector.

Electrospray fabrication of PtRu/C/ Nafion/PEO microsphere catalytic layer

Synthesis of PtRu/C/Nafion/PEO particles, porous microspheres and nanofibers: An electrostray ink was prepared by mixing PEO (0–20 mg) into 5 wt.% Nafion solution (1.330 g) by stirring for 2 h, then adding a mixture of PtRu black (166.67 mg) and PtRu/C (55.55 mg, 60 wt.%) by stirring for another 2 h. The ink was electrosprayed at a rate of 0.2 ml h^{-1} by a syringe pump (KDS 200) with 12 cm grounded collector to the needle at a high voltage of 16 kV at room temperature and at the humidity of 45±5%.

The conventional MEA was prepared as before with a Nafion® 115 membrane, a cathode by air brush with a Pt loading of 4 $mgcm^{-2}$ and an anode by air brush with a PtRu loading of 1~2 mg cm^{-2}. The electrosprayed MEA was prepared with the same membrane and cathode, while the anode was displaced with the microsphere catalyst layer with a PtRu loading of 1 mg cm^{-2}.

Morphology and electrochemical characterization of the microspheres

Characterization: FESEM images were collected on Field Emission Scanning Electron Microscopy (FESEM, Hitachi S-4800) and TEM image was conducted with Field Emission Transmission Electron Microscopy (FETEM, JEOL 2100F) .

Cyclic voltammetric (CV) measurements were carried out with a Solatron SI1287 Potentiostat/Galvanostat system to characterize the ESA of the MEAs, by feeding the water to the anode as the working electrode, humidified H_2 to the cathode at a flow rate of 5

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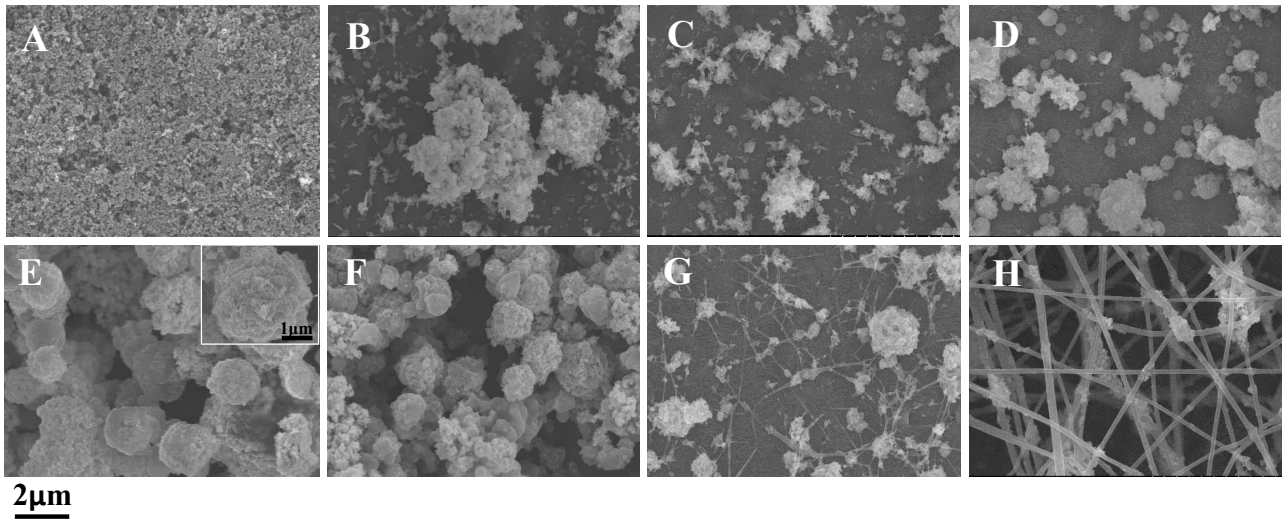

Fig. 2. The SEM images of electrodes fabricated by air brush without PEO (A), and by electrospray with PEO of different contents: 0mg (B), 4mg (C), 8mg (D), 10mg (E,insert, it is SEM image of a single microsphere), 12mg (F),16mg (G) and 20mg, (H).

mL min^{-1} as the counter electrode and the reference electrode (dynamic hydrogen electrode, DHE). The working potential was cycled from 0 to 0.7 V and at a scan rate of 20 mV s^{-1}.

The ESA of the anode was further checked by CO-stripping method with a Solartron SI1287 Potentiotat/Galvanostat system, since it directly denotes the electrocatalytic active sites for methanol oxidation reaction (MOR). Firstly, the anode catalyst layer was completely pre-absorbed with CO for 30 min at the hold potential of 0.2 V. Then, the residual free CO was removed by N_2 for 20 min. Finally, the CO-stripping voltammogram was carried out in the potential range of 0–1.0 V and at a scan rate of 20 mV s^{-1} where the anode was fed with N_2 as the working electrode and the cathode was fed with humidified H_2 as the counter and reference electrode.

Electrochemical impedance spectra (EIS) measurements of the anodes were carried out with a Solatron SI1260 and Solatron SI1287 Potentiostat /Galvanostat system. The anode was fed with 4M methanol solution as the working electrode and cathode was passively fed with oxygen from air as the counter electrode. The EIS measurements were performed at a voltage of 0.4 V with a frequency range from 100 kHz to 0.01 Hz, and at the amplitude of the sinusoidal voltage signal of 10 mV.

The performance evaluation of the MEAs

The performance of the MEAs was evaluated by polarization tests with an Arbin Fuel Cell Testing System (Arbin Instrument Inc., USA). The as-prepared MEAs with an active surface area of 4 cm^2 were activated in 2 mol L^{-1} methanol solution and measured in a DMFC testing setup. Methanol solution (4 mol L^{-1}) was passively fed to the anode by self-transport and the cathode was exposed to the atmosphere (air-breathing mode). All electrochemical tests were performed at a temperature of ca. 25 °C and the humidity of 30-40%. The durability test of the MEA was measured at a constant current discharging of 40 mA cm^{-2} with discontinuous feed with 4 mol L^{-1} of methanol solution.

Results and discussion

Effect of PEO content on the morphology of the electrosprayed catalytic layer

The natural properties of the electrospray ink, including viscosity, polymer concentration, ion concentration and solvent evaporability, are significantly important for the formation of particles and morphology controlling of the catalytic layer. Herein, the PEO is used as the carrier polymer to control the ink viscosity and further to control the morphology of the electrosprayed catalytic layers. Different shapes of particles and fibers are fabricated by varying the PEO content from 0, 4, 8, 10, 12, 16 to 20 mg as shown in Figs. 2B–H. As a comparison, a conventional anode catalytic layer was prepared by airbrush as shown in Fig. 2A. From Figs. 2B, 2C and 2D, small irregular particles are formed at the PEO contents of 0, 4 and 8 mg, because the ink viscosity is too low to form a stable Taylor cone. With an increase in the PEO content to 10 and 12 mg, the irregular particles disappear and porous microspheres with an average diameter of 1–3 μm are formed as

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shown in Figs. 2E and 2F. From the inset of Fig. 2E, the surface of a typical microsphere is very rough and there are many deep nano sized folds within the microsphere, which can remarkable increase the surface area and help more catalyst nanoparticles to be exposed. Furthermore, it is a hybrid structure of microsphere and fiber when the PEO content is increased to 16 mg (Fig. 2G). Continuous nanofibers are fabricated by so called electrospinning, when the PEO content is 20 mg (Fig. 2H). Therefore, the morphology of the anode catalytic layers, including irregular particles, microspheres and nanofibers is facilely controlled by just varying the PEO content in the range of 0–20 mg.

TEM images show the inner structures of the microsphere. A typical microsphere is almost of spherical and its surface is very rough in Fig.3A. It is clearly shown the surface of the microsphere in Fig. 3B, suggesting that the PtRu nanoparticles are almost individually distributed and there are several nanochannels on the surface, which would result in higher ESAs and higher PtRu utilization. The high-resolution TEM image in Fig. 3C further proves that PtRu nanoparticles are well distributed in the electrospray composites and the average diameter is about 2.5 nm.

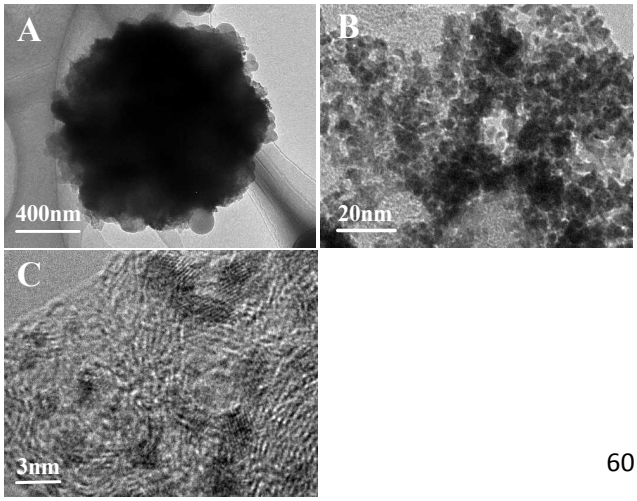

Fig.3. The TEM images of electrosprayed microsphere (A, a single microsphere; B, the edge of the microsphere; C, the HRTEM image of the electrosprayed microsphere).

The Raman and FT-TR spectra are to reveal the chemical structure changes as shown in Fig.4. The Raman spectra with two bands of 1345cm^{-1} and 1595cm^{-1} can be attributed to the D-band and G-band of carbon, respectively. From Fig. 4A, the Raman spectra for the two catalytic layers are almost same, implying that the carbon structure stays the same after the electrospraying. Fig. 4B shows the FT-IR spectra of the two catalytic layers, where the similar vibrating peaks corresponding to the –C–O–C, –S-O and –C–F bonds are attributed to Nafion resin, suggesting that the Nafion resin structure maintains unchanged. It should be noticed that there is no special peaks for PEO, suggesting that the PEO ratio is too low to be measured. In brief, there are only physical morphology changes and no chemical structure changes after electrospraying process.

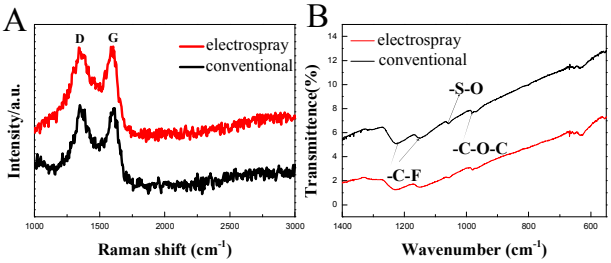

Fig.4. A comparisons of the Raman spectra(A) and FT-IR spectra (B) between the electrosprayed catalytic layer and conventional one.

Performance comparison of the DMFCs with different anode catalytic layers

The porous microspheres were used as the anode catalytic layer and further evaluated by the polarization measurement in DMFCs. The effects of PEO contents on the polarization curves are shown in Fig. 5A. The maximum power densities vary dramatically (22.86, 29.62, 35.44, 32.23, 28.04 and 21.01 mW cm^{-2}) when the PEO content is increased from 4 to 20 mg cm^{-2} (The MEA can not be prepared by electrospraying without PEO). Corresponding to the PEO content of ~10 mg, the DMFC exhibits the best power density of 35.44 mW cm^{-2}, which confirms that the microspheres are more promising as the structure for anode catalytic layer than the others (irregular particle and nanofiber).

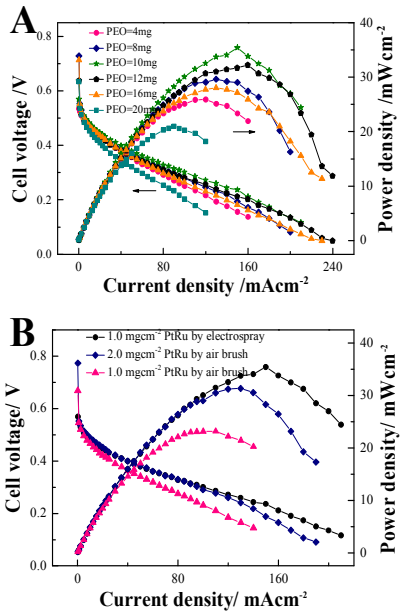

Fig.5. The steady-state polarization curves of the DMFCs with electrosprayed anode with different PEO content at PtRu loading of 1.0mg cm^{-2} (A), and the comparison of the polarization steady-state polarization curves of the DMFCs with electrosprayed anode and the airbrushed anode at different PtRu loadings (B).

The DMFC performance was also compared by the polarization curves as shown in Fig. 5B, where the DMFC with electrosprayed anode was at a PtRu loading of 1.0 mg cm^{-2} (curve a) and that with

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conventional anode was at a PtRu loading of 1.0 mg cm^{-2} (curve b) and 2.0 mg cm^{-2} (curve c). The maximum power density of DMFC by electrospray can reach to about 35.4 mW cm^{-2}, which was 50% higher than that (23.5 mW cm^{-2}) by airbrush at the same PtRu loading and was even comparable to that (31.5 mW cm^{-2}) by airbrush at double PtRu loading. Importantly, the PtRu loading could be dramatically reduced to half of the conventional one by using this porous microsphere structure. From the SEM images as shown in Figs. 2E and 2A, the surface of electrosprayed anode is extremely rough and the average diameter of the channels formed by the microspheres is 1~3 μm, thus leading to almost free mass transport. However, the surface of the conventional anode was smooth and the average diameter of the channels between the nanoparticles was only about tens of nanometers, thus leading to sluggish mass transport. Therefore, the performance improvement by using the electrosprayed anode can be attributed to its fine pathways for mass transport.

Electrochemical measurement

Analysis of the ESA by CVs and CO-stripping voltammogram

To explore the possible reasons for the improved performance of the DMFCs, the CVs and CO-stripping voltammograms measurements were carried out to compare the ESAs of the anode catalytic layers with different morphology as shown in Figs. 6A and 6B, respectively. The redox peaks in the potential range 0.05–0.4 V can be ascribed to the absorption and desorption of hydrogen on the surface of PtRu particles. ESA is calculated quantitatively by the equation: ESA = $Q_H/m \times C$, where Q_H is the charge for hydrogen desorption (mC cm^{-2}); m is the amount of Pt loading (mg cm^{-2}); C is the charge required to oxidize a monolayer of hydrogen on Pt (0.21 mC cm^{-2}) after subtracting the charge caused by the electric double layer. The calculated ESA by hydrogen adsorption of the anodes by electrospray and by airbrush at PtRu loading of 1.0 mg cm^{-2} were 27.27 and 18.03 m^2 g^{-1}, respectively. The ESA in electrosprayed anode increases by ~50%, indicating a significant improvement in catalyst utilization of the anode catalytic layer fabricated by electrospray.

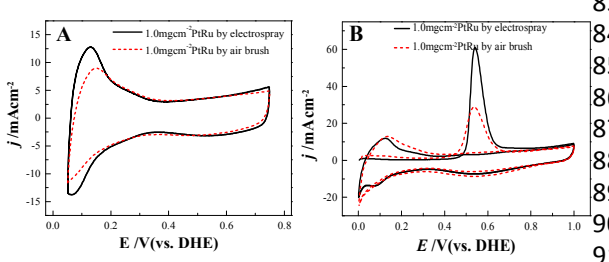

Fig. 6. CVs (A) and CO-stripping voltammograms (B) of electrosprayed anode and air brushed anode with the PtRu loading of 1.0 mg cm^{-2}.

For PtRu (1:1, atom ratio) alloy catalyst, the ESA by H adsorption is only for Pt in the PtRu catalysts and that by CO-stripping are for both Pt and Ru in the PtRu catalysts. Hence, the calculation of CO-stripping can more accurately display the MOR sites of the PtRu nanoparticles. Fig. 6B clarified that the calculated ESA by CO-stripping of electrosprayed anode was 53.37 m^2 g^{-1}, which was almost twice that of the conventional one (27.91 m^2 g^{-1}). The notable increase in the ESA is mainly attributed to its highly porous structure of the microspheres, which is in good agreement with the morphology results. Moreover, high ESA is also attributed to the well-distribution of the PtRu nanoparticles and the enhanced interactions among the catalysts and ionomer.

Analysis of the anodes by the EIS

EIS can help to understand the mechanisms of the oxidation of the DMFC under actual operating conditions, by comparing the effects of reaction resistance, charge transfer resistance and mass transport resistance. Fig. 7 shows the comparison of the results of the EIS of the DMFCs with electrosprayed anode and conventional anode, respectively, at the PtRu loading of 1.0 mg cm^{-2}. Corresponding equivalent circuit model is shown in Fig. 7. The constant phase element (CPE) is considered as the current capacities including the Faraday current and charging current as a non-uniform structure of porous electrodes. Therefore, the physical meanings of each element used in the equivalent circuit model are as follows:

Where Rm denotes the resistance of membrane;

CPEi and Ri display the properties of the anode membrane interface including the capacitive behavior and interface resistance between the catalytic layer and the Nafion membrane, respectively.

Rct is the charge-transfer resistance of the electrode reaction;

CPEdl is the capacitive behavior of the catalytic layer with roughness of the catalytic layer and non-uniform catalyst distribution.

Rc and Lco are the current signal following the voltage perturbation with a phase-delay due to coverage change of the intermediate CO_{ad} in the anode catalytic layer because the oxidation of the CO_{ad} is the rate-limiting step for DMFC.

The fitted parameters are listed in Table 1. Comparison of the DMFCs with the conventional anode and electrosprayed anode, respectively, indicated the occurrence of an obvious smaller arc for DMFC with the electrosprayed anode at the middle-frequency region, resulting in a significant decrease in the values of Rc, Lco, and Rct. The reduced values of Rc and Lco indicate that the oxidation reaction rate of the intermediate (Pt active site)-CO is more rapid and efficient, attributed to its high ESA and rapid transport of the product CO_2 by the new structure. The decreased value of Rct is due to its high ESA, uniform distribution and efficient pathways for electron and proton transport. As a consequence, there is corresponding relationship between the parameter changes in the EIS analysis with the structural changes in the physical and electrochemical evaluations.

The energy conversion efficiency and durability measurements

To explore the energy conversion efficiency and durability, Fig. 8 shows the corresponding discharging curves at constant voltage (0.35 V) and constant current (160 mA) of the DMFCs with different anodes by feed with 4 mL of 4 mol L^{-1} methanol solution. The

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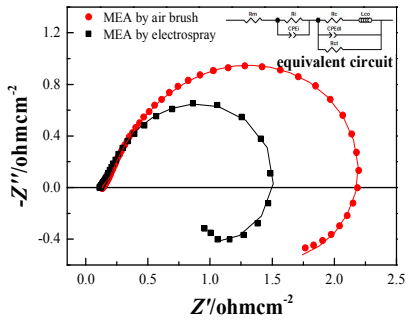

Fig. 7. Electrochemical impedance spectra (Insert, the equivalent circuit) of the anodes of the two MEAs with the anodic catalytic layers fabricated by air brush and electrospray with a PtRu (1:1) loading of 1.0 mg cm^{-2} at a given DC potential of 0.4 V.

Table 1 Fitting parameters for the CPE-based equivalent circuit models for the anodes at 0.4 V and at 25°C.

Parameter	GDE anode (1mgcm^{-2})	Electrospray anode (1mgcm^{-2})
Rm	0.53	0.46
Ri	0.19	0.23
CPEi-T	0.21	0.22
CPEi-P	0.83	0.80
Rc	4.31	2.33
Lco	89.90	32.22
CPEdl-T	0.29	0.27
CPEdl-P	0.82	0.87
Rct	11.35	6.86

energy conversion efficiency of the DMFCs with conventional anode and electrosprayed anode were 13.24 and 18.42%, respectively, indicating that the energy conversion efficiency was improved significantly when using the microsphere structure. Fig.8 also demonstrated that the discharging current of the DMFC with electrosprayed anode is much higher than that of the conventional one during the first 20 h, indicating that the formation of porous microspheres can obviously improve the electrocatalytic activities. From a 120 h durability testing of the DMFC as shown in the insert of Fig. 8, the discharging voltage keeps at ca. 0.35 V with some fluctuation at a given current density of 40 mA cm^{-2}, confirming that the durability of such a DMFC is good for the practical application with an improved cell performance. The voltage fluctuation may be due to the water flooding at cathode side and to the possible change in methanol concentration during the test.

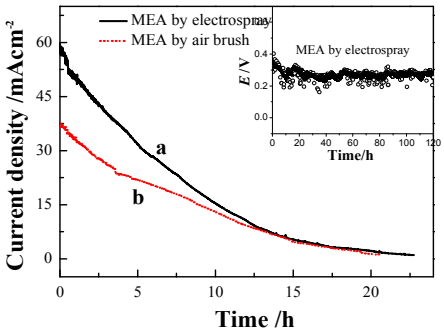

Fig. 8. The energy conversion efficiency measurements of DMFCs with electrosprayed anode (a) and air brush anode (b) at the PtRu loading of 1.0mgcm^{-2}. Insert: the stability of a DMFC with electrosprayed catalytic layer of 1.0 mg cm^{-2} PtRu and at a constant current of 160 mA.

Conclusions

A structure of porous microspheres was successfully designed, fabricated and applied as the anode catalytic layer for DMFC, which can result in a significant decrease in the PtRu loading and enhancement in the DMFC's performance. This hierarchical factual structure with micropores for enhancing the mass transport and nanopores for increasing the PtRu utilization could be responsible for the improved performance. The usage and the content change of PEO is the key factor in forming the shape-controlled microspheres. This technology could provide a simple and promising way to fabricate shape-controlled porous hybrid catalytic layers, thus significantly improving the catalyst utilization and decreasing the noble metal loading in fuel cell.

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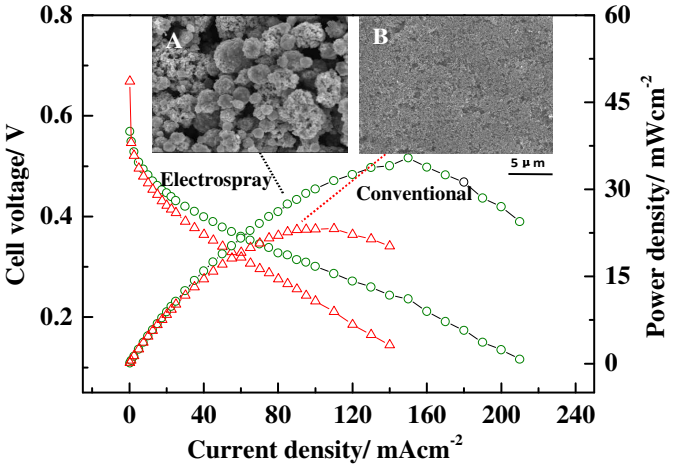

Electrospray porous heterogeneous PtRu-C/Nafion/PEO microsphere as the anode catalytic layer for direct methanol fuel cells with enhanced performance.

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