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Synthesis of platinum nanoparticles and then self-assembly on Nafion membrane to give a catalyst coated membrane

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A catalyst-coated membrane (CCM) for a proton exchange membrane fuel cell (PEMFC) with Pt loading of 2.8 μg/cm^2 have been prepared by self-assembling charged Pt particles on a sulfonic acid function group, SO_3^-, on the membrane surface. Proton conductivity of the as-obtained CCM is 0.0932 S/cm. Half-cell polarisation showed that the self-assembled membrane is electrochemical active. Electrochemical characterisation of the self-assembled electrode showed that the Pt-PDDA nanoparticles were electrocatalytic active. The performance of self-assembled MEA with a Pt loading of 2.8 μg/cm^2 achieved 2.3 mW/cm^2. This corresponds to Pt utilisation of 821 W per 1 g Pt. The results demonstrated the feasibility of the formation of monolayered Pt nanoparticle structure on the membrane interface. Such a monolayered structure could offer a powerful tool in fundamental studies of polymer electrolyte systems.

Keywords: platinum nanoparticles, Nafion membrane, catalysis

Much attention has been paid to proton exchange membrane (PEM) fuel cells because they offer a highly efficient and environmentally friendly technology for energy conversion. An important research and development goal is to produce efficient, low-cost electrodes and catalyst layers. The ideal catalyst layer would be gas and water permeable, and conduct both protons and electrons.[1,2] Catalyst layers are conventionally fabricated by mixing Pt/C agglomerates with a soluble polymer electrolyte (such as Nafion® ionomer) and applying this paste to a carbon paper. However, platinum particles deposited within the pores of carbon black may be inaccessible to the polymer electrolyte; accessibility is necessary to the three-phase reaction zone, up to 90% of the platinum atoms in such electrodes may be inactive.[3,4] In this communication, fabrication of a catalyst-coated membrane (CCM) for PEM fuel cell via electrostatic self-assembly technology was proposed. As shown in Fig. 1, charged platinum nano-particles were modified with positive ionomers, and then anchored on SO_3^- function groups by means of the electrostatic force between as-modified positive ions and SO_3^- negative ions. Compared with conventional catalyst layers, the platinum particles in the self-assembled membrane (CCM) have an intimate connection to sulfonic acid function group, SO_3^-, on the membrane surface. Furthermore, there are not mechanical actions during the assembling procedure, which could destroy the PEM, especially when the membrane is very thin.

Experimental

Synthesis of charged platinum particles

Charged platinum nanoparticles were prepared by reducing the metallic ions with an alcohol in the presence of poly (diallymethyl-ammonium chloride) ionic polymers, PDDA. Starting materials were as follows: H_2PtCl_6 (Aldrich, purity; 99.9%), PDDA (Aldrich, M*w*~5,000) and EtOH (Shenhua chemical, purity; 99.9%).

PDDA solution (0.002 mol l, 80ml) was put in a three-neck flask under intensive stirring for 10 min and then mixed with the appropriate amount of H_2PtCl_6 solution (0.02 mol/l, 8ml) for another 10 min. EtOH (60 ml) was then added to the solution under continuous stirring. The pH of the solution was adjusted to 8.5 by adding NaOH. The solution was then refluxed at –84°C in temperature-controlled water bath. *In situ* UV–vis spectrometer (UV-2550, Shimadzu, Japan) was used to supervise the reduction and formation reaction.

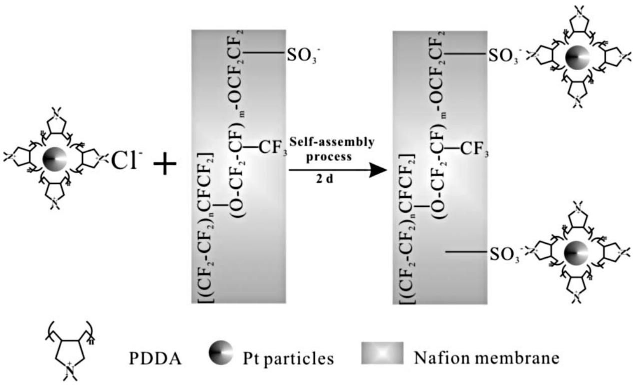

Fig. 1 Model of PDDA decorated Pt particles self-assembly on Nafion membrane.

Preparation of self-assembled MEA

The self-assembled MEA was prepared by charged platinum nanoparticles dispersed in solution and Nafion 112 membrane. The Nafion membrane was treated according to the standard procedure of 30 min in 30wt% H_2O_2 solution at 80°C, 30 min in minipore water at 80°C, 30 min in 8wt% H_2SO_4 solution at 80°C and finally 30 min in minipore water at 80°C again. The self-assembly of Pt–PDDA onto the Nafion membrane was carried out by immersing the pre-treated membrane in Pt–PDDA colloid solution at room temperature. Then the membrane was treated in 8wt% H_2SO_4 solution at 80°C for 30 min, followed by rinsing in Milli-Q water at 80°C for 30 min. After the self-assembly process in Pt–PDDA solution, the colour of the Nafion membrane became dark, indicating the assembly and immobilisation of Pt–PDDA nanoparticles on the membrane surface. The Pt loading of the self-assembled membrane was analysed by atomic adsorption analysis and the loading was 2.8 μg/cm^2. To our knowledge this is probably the lowest Pt loading for MEA ever reported. The cleaned self-assembled membrane was sandwiched between two E-TEK carbon papers as gas diffusion layer and hot-pressed at 0.2 MPa and 120°C for 0.5 min.

Results and discussion

Fig. 2 shows UV–vis absorbance spectra of platinum solutions during the refluxing procedure. The spectrum reveals strong absorption bands at 220 nm 260 nm before refluxing (0 min). These bands were previously assigned as absorption of $PtCl_6^{2-}$ and $PtCl_4^{2-}$.[5] The absorption peak of $PtCl_6^{2-}$ at 260 nm declined rapidly during the first 5 minutes, and disappeared ultimately. Lowing of the absorption peak at 220 nm cannot obviously be distinguished in the Fig. 2. The peak gradually blue shifts when the refluxing time increases and finally reached 215 nm after 9 min. That indicated that the reducing

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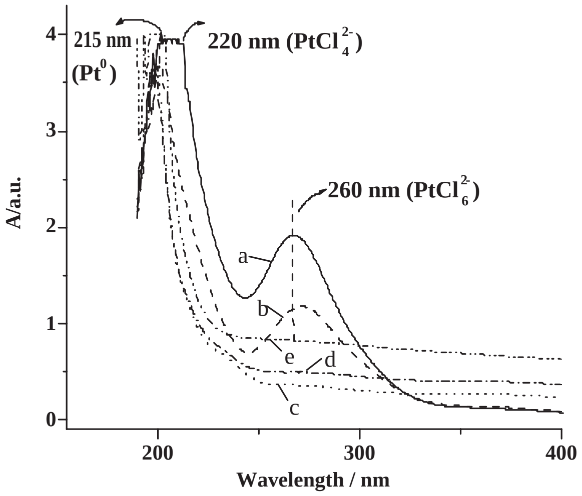

Fig. 2 UV–vis spectra of platinum reaction solution time/min: a:0; b:1; c:5; d:7; e:9.

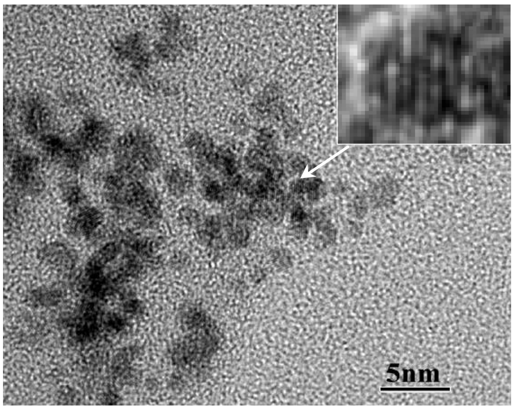

Fig. 3 HRTEM images of charged Pt nanoparticles.

reaction was complete. Pt nanoparticles were examined by high-resolution transmission electron microscopy (JEM-2010FEF) and X-ray diffraction (Phillips PW 1830). Figure 3 shows TEM images of charged platinum nano-particles. The images reveal widely separated platinum nano-particles and little aggregation. This may be a consequence of the high charge density on the surface of the PDDA polyions (zeta potential analysis has shown the potential of charged platinum particles was 28 mV). Charged platinum particles are –1.8 nm and have a narrow size distribution. XRD patterns show that the particles have been crystallised and have broad peaks of (111) and (200). The particles size calculated from the (111) peak of the XRD pattern by the Scherrer formula is 1.6 nm, which is very close to the value of 1.8 nm discerned from TEM.

Self-assembled CCM was obtained by immersing H^+ -form Nafion®112 membrane into charged platinum nanoparticles dispersed in solution. As shown in Fig. 4, the assembled platinum content on Nafion membrane increased rapidly during the first 8 h, followed by a slow increase in the next 16 h. After 24 h, the balance of assembled platinum was reached. During the assembly procedure, the conductivity of the Nafion® membrane decreased rapidly and a conductivity balance was reached (~12 h) before the Pt assembled balance was reached (~24 h). It is revealed that the assembly procedure can be divided into two segments: the small cations (such as Na^+) will interact with the $–SO_3^-$ anion groups due to their rapid thermal velocity on the first step, then the small cations will be replaced by charged platinum particles during the prolonged assembly-desorption dynamic balance. Energy diffraction of the assembled membrane (Fig. 5) shown that there are many Na and Pt atoms on the surface of the Nafion membrane besides of C, F, O, S, which are element of pure Nafion polymer. Fortunately, diffraction of the N element did not lount in the ED parttern, which shows there are little PDDA poly-ions on the Pt surface which probably has little effect on Pt activity. In order to remove Na ions and recover the self-assembled CCM, the assembled membrane was re-protonated in the following procedure: (1) 30 min in 0.5 mol/l H_2SO_4 solution at 80°C, (2) 30 min in ultrapure water at 80°C.

The Pt loading in this CCM is very low. If the particles are close packing, the loading can be approximately calculated with the following formulae:

$$n_{particle} = 2(\frac{1}{d+l})^2 \tag{1}$$

$$m_{particle} = \frac{4}{3}\pi(\frac{d}{2})^3\rho \tag{2}$$

$$m_{load} = 2(\frac{1}{d+l})^2\frac{4}{3}\pi(\frac{d}{2})^3\rho \tag{3}$$

In which d is the particle diameter, l is the distance between two particles, ρ is the density of Pt. Then n_{particle} is the particle number per cm^2 on the self-assembled membrane, m_{particle} is the weight of a Pt particle, m_{load} is the Pt loading per cm^2 on the self-assemble membrane. If we use the idealized date of d=2 nm, l=0 nm, ρ=21.4 g/cm^2, the Pt loading is 12.6 μg/cm^2. The actual loading was determined by Atom Absorption spectra, and was 2.8 μg/cm^2. It is almost the lowest Pt loading of the catalyst-coated membrane up to now.

Proton conductivity of self-assembled membrane was measured by using an impedance analyser. The assembled membrane was fixed in a four-point probe cell consisting of two platinum wire, outer current-carrying electrodes (distance 3 cm) and two platinum wire inner potential-sensing electrodes (distance 1 cm). Comparing with 0.0951 S/cm of pure Nafion membrane, the conductivity of the as-obtained CCM (assembled for 24 h) after protonation was 0.0932 S/cm.

Figure 6 shows the preliminary performance of a PEFC made of self-assembled Pt-PDDA nanoparticles MEA forwards H_2/O_2 at room temperature without a humidifier. In the Figure, the cathodic polarisation curve of the self-assembled Pt–PDDA electrode measured, in 1 M H_2SO_4 saturated with O_2 at 25°C, was also given. There is substantial

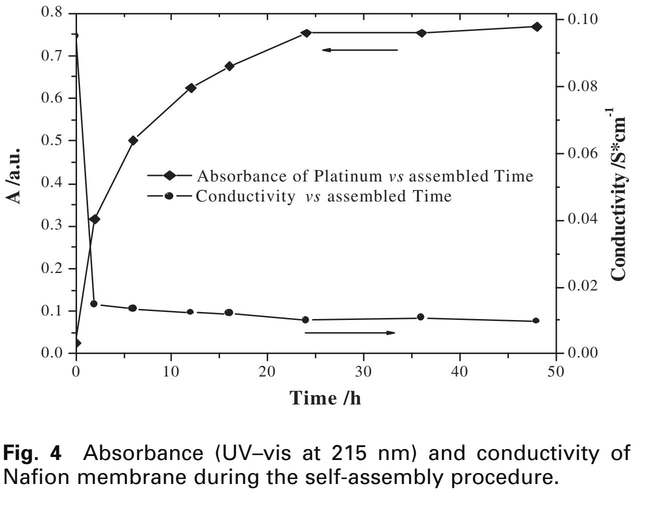

Fig. 4 Absorbance (UV–vis at 215 nm) and conductivity of Nafion membrane during the self-assembly procedure.

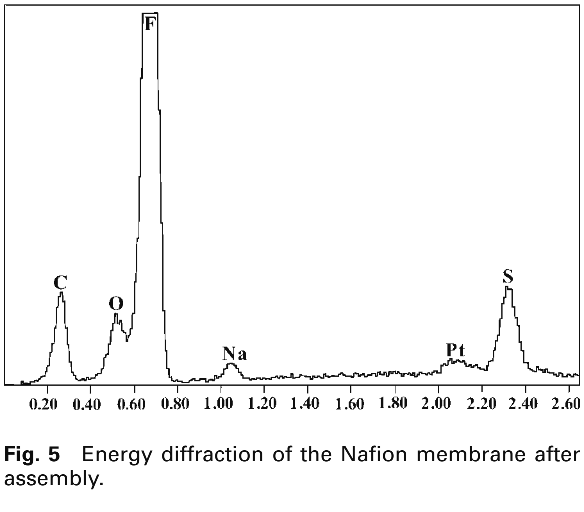

Fig. 5 Energy diffraction of the Nafion membrane after self-assembly.

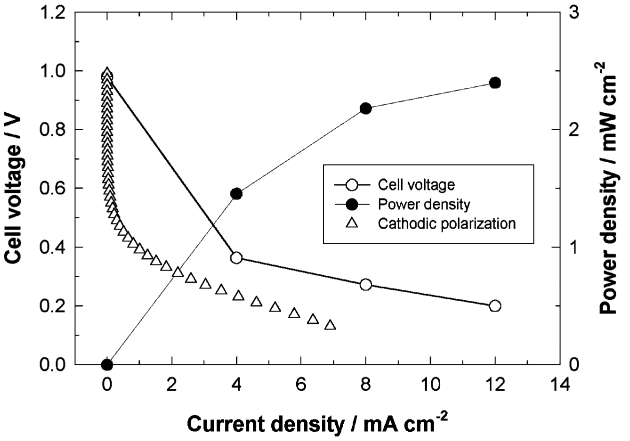

Fig. 6 Single cell performance of self-assembled Pt–PDDA MEA at H_2/O_2 at room temperature without humidifier. In the figure, the cathodic polarisation curve of the self-assembled Pt–PDDA electrode measured in 1 M H_2SO_4 at 25°C in saturated O_2 using half-cell test rig was also given.

reduction in the current density at the early stage of polarisation. The rapid reduction in the single cell performance is consistent with that of the O_2 reduction on the self-assembled Pt–PDDA electrode. This demonstrated that the rapid reduction in the cell performance is due to the limiting step of the O_2 reduction on the Pt–PDDA nanoparticle catalysts. The maximum power density obtained was 2.3 mW/cm^2. As the Pt loading of the self-assembled MEA was 2.8 µg/cm^2, the power output per 1 g Pt would be 821 W/g^1. O'Hayre *et al.*[6] prepared a MEA with Pt loading of 40 µg/cm^2 using a sputtering deposition technique and the power density achieved was 33 mW/cm^2 at H_2/O_2. This gives a power output of 825 W per 1 g Pt. This indicates that the performance of the self-assembled MEA in the present study is reasonable, despite being at a preliminary stage of the development of the self-assembled MEA in the present study.

Conclusions

A catalyst-coated membrane (CCM) with a Pt loading of 2.8 µg/cm^2 has been prepared by self-assembling charged Pt particles on sulfonic acid function group, SO_3^-, on the membrane surface. Proton conductivity of the as-obtained CCM is 0.0932 S/cm. Half-cell polarisation shows the CCM is electrochemical active. Electrochemical characterisation of the self-assembled electrode showed that the Pt-PDDA nanparticles were electrocatalytic active. The performance of the self-assembled MEA with Pt loading 2.8 µg/cm^2 achieved 2.3 mW/cm^{-2}. This corresponds to a Pt utilisation of 821 W per 1 g Pt. The results indicate the feasibility of the self-assembly technology in the preparation of low Pt catalyst loading. The most significant results from the present study is probably the possibility of the formation of monolayer Pt nanoparticle structure on the membrane interface. Such a monolayer structure could be potentially used for fundamental studies in the polymer electrolyte system.

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