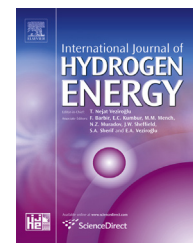


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A novel cathode architecture with a thin reaction layer alleviates mixed potentials and catalyst poisoning in direct methanol fuel cells

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ABSTRACT

Methanol crossover is a barrier that limits the widespread deployment of direct methanol fuel cell (DMFC) technology. As methanol crossover can be reduced, but cannot be completely eliminated, efforts should be focused on reducing the adverse impacts of permeated methanol on the cathode, i.e.: the problems of mixed potential and Pt poisoning. In this work, we propose a novel cathode structure involving an additional thin reaction layer that is interfaced with the membrane. The reaction layer, conducting ions but being insulated to electrons, is able to chemically consume permeated methanol to reduce the methanol concentration on the cathode. Experimental results show that the adoption of the proposed cathode not only increases the open-circuit voltage due to a reduced mixed-potential loss, but also decreases the desorption peaks of intermediates on the cathode catalyst (Pt) surfaces as a result of an alleviation in Pt-poisoning. Hence, the overall fuel cell performance exhibits a substantial improvement.

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Introduction

Direct methanol fuel cell (DMFC) is a promising technology for next-generation power sources in portable electronic devices [1–7], owing to its low operation temperature, high energy density, compact structure and safe operation. However, the widespread commercialization of DMFC technology is limited by several technical issues, among which methanol crossover is the most challenging [8–11]. Fuel crossover wastes fuel, but more importantly causes serious adverse impacts on the cathode: (1) the simultaneous oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) at the cathode

catalyst layer (CL) result in a mixed potential, hence, decreasing the cell voltage and deteriorating the performance [12]; (2) the cathode platinum catalyst becomes poisoned by carbon monoxide (CO), which is the main intermediate species formed during the MOR [13]. Extensive efforts have been made to lower methanol crossover via the modification of Nafion membrane [14–16] and the development of novel proton exchange membranes [17,18]. However, the issue cannot be eliminated by alterations of the membrane till now [19,20]. An alternative solution was proposed to develop methanol tolerable cathodes to alleviate the problems brought about by methanol crossover, but at the expense of the ORR activity [21,22]. In this work we propose another strategy that

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places a thin reaction layer (denoted as TRL hereafter), which conducts ions but insulates electrons, and is interfaced within the membrane at the cathode. The TRL is composed of PtRu nanocatalysts supported on silica and Nafion ionomer, in which the reaction between methanol and oxygen spontaneously takes place; hence the permeated methanol can be chemically consumed before it reaches the cathode CL.

Experimental

Preparation of PtRu catalysts support on SiO₂

Silica supported Pt–Ru (1:1) nanocatalysts were prepared by a conventional impregnation method [23]. Silica (SBA-15) was first suspended into DI water and magnetically stirred until it became a homogenous suspension. H₂PtCl₆·6H₂O (Aldrich, 7.4 mg Pt ml⁻¹) and RuCl₃·3H₂O (Aldrich, 4.87 mg Ru ml⁻¹) solutions were then dripped into the silica solution while continuously stirred. The amount of metal loading in the SiO₂ supported PtRu catalyst was adjusted to 20 wt.%. Sodium citrate was added to the solution as a surfactant, and 5 mM NaBH₄ solution was freshly prepared and added dropwise into the mixture while stirring for 5 h. The final product, denoted as PtRu/SiO₂, was collected via a Nylon membrane and dried in a vacuum at 60 °C overnight.

Preparation of membrane electrode assembly

The membrane electrode assembly (MEA) consisted of a pre-treated Nafion® 115 membrane, a commercially available anode from Johnson Matthey® and a cathode. A SGL® carbon paper with 5 wt.% Polyterafluoroethylene treatment and a MPL were used as GDLs for both the electrodes. The anode catalyst layer was made of carbon supported PtRu (50 wt.% Pt 25 wt.% Ru) catalysts with a loading of 4.0 mg cm⁻². The cathode catalyst layer was comprised of carbon supported Pt (60 wt.% Pt) with a loading of 2.0 mg cm⁻² and Nafion ionomer with a content of 20 wt.% at the cathode catalyst layer. A PtRu/SiO₂ based thin layer was fabricated and positioned between the cathode CL and the membrane which works as the reaction layer to consume the permeated methanol chemically. PtRu/SiO₂ and 5 wt.% Nafion ionomer suspension were mixed to form a slurry using ethanol as dispersant and the slurry was ultrasonic treated for 30 min in ice water. The fully dispersed slurry was directly coated onto the membrane using the catalyst-coated membrane (CCM) method [24]. The catalyst loading (PtRu) in the TRL was 0.3 mg cm⁻² and the mass ratio of Nafion ionomer in this layer was adjusted to 55 wt.% to ensure a high proton conductivity. Finally, the MEA formed by hot pressing under a temperature of 135 °C and a pressure of 4 MPa for 3 min with an active area of 1 cm × 1 cm.

Single cell test

The cell performance tests were conducted by using the MEAs with and without the TRL at 60 °C. During the discharging process, solutions of 1.0 M, 3.0 M or 5.0 M aqueous methanol was fed to the anode with a flow rate of 0.5 ml min⁻¹ and pure oxygen was supplied to the cathode at a flow rate of 50

standard cubic centimeters per minute (sccm) under atmosphere pressure. The discharging process was controlled and recorded by an Arbin BT2000 electrical load, and at each discharging current point, the voltage became stable after about 60 s. Prior to the tests, each MEA was fully activated.

To investigate the cathode catalyst behavior with respect to methanol oxidation, cyclic voltammetry tests were conducted on the cathode using the potentiostat (PARSTAT 2273). Prior to the CV test, nitrogen was passed through both electrodes for 0.5 h and then nitrogen was swapped with humidified hydrogen at the anode to serve as the reference hydrogen electrode (RHE) and the counter electrode. After the CV test, the fuel cell discharged at 50 mA cm⁻² for 0.5 h, the anode was supplied with 3.0 M methanol at a flow rate of 0.5 mL min⁻¹, and the cathode was supplied with oxygen at a flow rate of 50 sccm. Post-discharge, the CV test on the cathode was conducted again to investigate the cathode catalyst behavior. The cyclic voltammetric measurements were made in the potential range of 0.0–1.0 V vs. RHE at a sweep rate of 20 mV s⁻¹.

Results and discussion

Fig. 1 shows the schematic diagram of the novel cathode architecture with a thin reaction layer interfaced with the membrane. It should be noted that as the silica catalyst support is an electron insulator, triple-phase boundaries cannot be formed in the thin reaction layer. Permeated methanol will react with oxygen chemically on the PtRu surface which is highly methanol-tolerable, resulting in less methanol reaching the Pt catalyst particles at the cathode CL. Hence, the function of the thin reaction layer is to reduce the mixed potential loss and alleviate the probability of the Pt catalyst poisoning caused by methanol crossover.

The XRD spectra of the PtRu/SiO₂ is shown in Fig. 2b. The pattern exhibits diffraction peaks at 2θ value of 40.0°, 46.4°, 67.7° and 81.6°, respectively. These peaks show a slight shift toward a higher value compared with the standard diffraction peaks of Pt, which are at 39.7°, 46.2°, 67.4°, 81.2°, as shown in Fig. 2a. It is caused by the incorporation of the Ru atoms into Pt lattice and decreasing lattice constant of Pt, which indicates that the single phase PtRu was formed. The peaks of a typical hexagonal close-packed structure of pure Ru and RuO₂ were not present in the XRD patterns, suggesting the absence of metallic Ru and its oxides in the PtRu alloy. In addition, there is no diffraction peak of SiO₂, since the SiO₂ used is in amorphous form. Fig. 3 presents the TEM images of the PtRu/SiO₂ catalysts at different magnifications. Formation of PtRu nanoparticles on SiO₂ support was clearly observed.

After the fabrication of the MEA with the thin reaction layer, the cross-sectional morphology was examined by both the SEM and EDX which is shown in Fig. 4. It could be found that a thin layer interfaced with the membrane at the cathode exists which shows a different brightness with the catalyst layer. The thickness of the cathode CL is approximately 50 μm, in contrast with that, the value of the PtRu/SiO₂ reaction layer is 5–7 μm, indicating that the reaction layer is rather thin. The EDX mapping of Si element is also shown in Fig. 4; it clearly shows that the PtRu/SiO₂ based thin reaction layer was

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