Membrane electrode assembly with enhanced platinum utilization for high temperature proton exchange membrane fuel cell prepared by catalyst coating membrane method

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HIGHLIGHTS

- Low Pt loading MEAs for HT-PEMFC were prepared by CCM method.
- The CCM-based MEAs showed enhanced Pt utilization compared to GDEs at low Pt loading.
- Cell resistances can be decreased by CCM method at low Pt loading.
- Enhanced electrochemical surface area was obtained with CCM at low Pt loading.

GRAPHICAL ABSTRACT
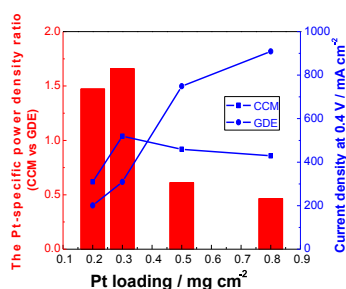
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ABSTRACT

In this work, membrane electrode assemblies (MEAs) prepared by catalyst coating membrane (CCM) method are investigated for reduced platinum (Pt) loading and improved Pt utilization of high temperature proton exchange membrane fuel cell (PEMFC) based on phosphoric acid (PA)-doped *poly*(2,5-benzimidazole) (AB-PBI) membrane. The results show that CCM method exhibits significantly higher cell performance and Pt-specific power density than that of MEAs prepared with conventional gas diffusion electrode (GDE) under a low Pt loading level. In-suit cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) show that the MEAs prepared by the CCM method have a higher electrochemical surface area (ECSA), low cell ohmic resistance and low charge transfer resistance as compared to those prepared with GDEs at the same Pt loading.

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1. Introduction

Compared to the low temperature fuel cells, the phosphoric acid (PA) doped polybenzimidazole (PBI) membrane based high-temperature proton exchange membrane fuel cells (HT-PEMFC) exhibit several unique advantages: excellence CO tolerance, enhance electrode reactions with especial relevance in the case of oxygen reduction reaction, no-dependency on intricate water management, higher utilization of residual heat and simple system without humidification system [1–3]. Hence, they are considered to be the promising energy conversion device and have attracted enormous attention in the last decades [1–6]. Membrane electrode assembly (MEA) is the most critical component of PEMFCs, which is comprised of anode and cathode catalyst layers (CL), gas diffusion layers (GDL) and proton exchange membrane (for PBI-based HT-PEMFC, proton conduction is rely on the PA doping level). The cell performance directly depends on the properties of the MEA [7–9].

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So far, MEAs for the PA doped PBI membrane based HT-PEMFCs were prepared by spraying catalyst inks on the surface of GDL with microporous layer (MPL) followed by hot-pressing, which is known as gas diffusion electrode (GDE)method [4–6,10–15]. This method is appropriate to fabricate the large-scale MEA and for mass production [9]. However, there may be a lot of Pt/C nanoparticles immersed into the gap of GDL, resulting in the waste of catalyst [16]. In addition, the contact between the CL and the membrane was weak due to the CL was combined with the GDL. Therefore, the interfacial resistances between the membrane and CLs could be high.

In the research of Nafion® based low temperature PEM fuel cell, MEAs were commonly fabricated by catalyst coated membrane (CCM) method, in which the CLs were directly coated on the surface of the membrane, the results indicated that CCM method can enhance the catalyst utilization efficiency and decrease the interface resistance between the CLs and the membrane compared to GDE method [17–20]. However, this method was seldom used to prepare MEAs for HT-PEMFCs due to the problems caused by introducing PA into the PBI membranes of the CCMs. When a pre-doped membrane is used for CCM, the surface of the membrane tends to keep wet even at high temperature because of the exudation and the strong moisture absorption of PA, which results the catalyst powder cannot effectively attach with the membrane. Possibly for this reason, Cho et al. [21] prepared a CCM with dry PBI membrane and then soaked it in 85% PA solution to doping enough PA in the membrane. Although a higher performance was observed in their work with this PA-doped CCM, it is very risky because the intense swelling of the PBI membrane due to the high acid uptake could cause serious dimensional change of the coated CL. Moreover, the CCM could serious distort due to the different PA absorption rates between the CL covered membrane and the bare membrane around, resulting in detachment of the CL and difficulties in MEA.

Recently, Wannek et al. [22] reported a novel strategy for introducing PA into HT-PEMFCs by using acid impregnated CLs instead of pre-doped membranes. They proved that the redistribution of PA in MEAs is a rather quick process whether PA is doped in the GDEs or pre-doped inside the membrane, which makes the use of un-doped PBI membranes for HT-PEMFCs possible. Inspired by their findings, we developed a novel method to prepare CCM-based MEAs for HT-PEMFCs by acid impregnated GDLs instead of pre-doped CCMs, through this way the deformation of the CCM can be suppressed and the integration of the CLs can be maintained. The performance and electrochemical properties of this MEA were characterized under normal operating conditions with different Pt loadings, and the availability of this CCM method was discussed.

2. Experimental

The membranes used in this study are AB-PBI (=poly(2,5-benzimidazole)), which were supplied by FuMA-Tech (fuma-pem®AM, ∼50 μm). Commercial Hispec4000 Pt/C (40 wt.% Pt, Johnson Matthey) was used for the CCM preparation, and the catalyst inks were mixed by adding catalyst and 5 wt.% PVDF/DMAc solution into the extra DMAc solvent. Before preparing the CLs, a homogeneous suspension of the catalyst inks was ultrasonicated for 50 min at room temperature. The dry PVDF content in the CL was adjusted to be 15 wt.%. In this work, we prepared and investigated a series of CCMs with different cathode Pt loadings of 0.2, 0.3, 0.5, 0.8 mg cm^{-2}, respectively. The Pt loadings of anodes were fixed at 0.5 mg cm^{-2}. The actual electrode area of the MEAs in this study was 2.3 × 2.3 cm^2.

2.1. Preparation of membrane electrode assemblies

All the MEAs were established by using an automated ultrasonic spraying machine (Ultrasonic Spray Coating System, Sono·TEK Corporation, USA). For the fabrication of CCM and GDE, the catalyst inks were uniformly sprayed onto the dry AB-PBI membranes (for CCMs) or on the MPL (for GDEs) of a commercially available GDL (H2315-CX196, Freudenberg, Germany). In order to make the solvent evaporated quickly during the spraying process, the membranes or GDLs were fixed on a 100 °C plate. The resulting CCMs or GDEs were dried at 140 °C under vacuum overnight to remove residual DMAc solvents.

For the GDE-type MEA, the PA-doping process was performed by immersing the membranes in 85% PA solution at 100 °C for 24 h, which gave the membrane an acid doping level of about 3.8 molecules of H$_3$PO$_4$ per polymer repeating unit [4–6]. For the CCM-type MEAs, the introduction of PA was conducted by impregnating the GDLs with predefined amounts of PA. A H$_3$PO$_4$/ethanol solution (0.2 mg μl^{-1}) was evenly dropped onto the top of commercial GDLs by several times. Afterwards the ethanol was allowed to evaporate overnight in an oven at 80 °C. The amount of PA pre-impregnated in the GDLs was calculated by the weight of the dry membrane (before CL coating) with the actual electrode area. Similarly, the PA doping level is also about 3.8 molecules of H$_3$PO$_4$ per polymer repeating unit with the actual electrode area.

2.2. Single-cell tests

The CCM- or GDE-based MEAs were assembled in a single cell fixture (BalticFuelCellsGmbH, Germany) together with fluorinated polymer gaskets without hot-press. This test cell consists of graphite plates with single serpentine gas channels and solid metallic endplates equipped with heating cartridges and then connected to a Cell Compression Unit (Pragma Industries, France). The cell performances were evaluated at 160 °C and under ambient pressure using an in-house HT-PEMFC setup, which consisted of a PC loaded with Labview software to control the electronic load (Höcherl&Hackl GmbH, Germany) and mass flow controllers (Bronkhorst, Netherlands). Pure hydrogen and compressed air were fed to the anode and cathode, respectively, at flow rates of 200 and 1000 mL min^{-1}. Before the polarization curve test, the cells were activated at 0.5 V and 160 °C until stable performance was obtained. The current–voltage polarization curves were obtained by measuring the voltage with stepwise increment of current density from 0 to 2000 mA cm^{-2} with intervals of 20 mA cm^{-2}, until the cell voltage approaches 0.2 V. At each current, the cell voltage was measured after a hold time of 2 min to allow the cell approaching steady state. For accuracy, single cell tests on each MEA prepared by CCM method or GDE with different Pt loading were performed at least three times, and then the average values (voltage) were determined. Normally, the relative standard deviations of these values were less than 4%.

2.3. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using an Autolab PGSTAT 30Potentiostat/Galvanostat (Metrohm) equipped with a 20 A booster and a frequency response analysis (FRA) module. To determine the resistance of the MEAs, the *in-suit* EIS were conducted at 0.6 V in potentiostatic mode. A signal amplitude of 5 mV in the frequency range of 100 mHz–20000 Hz was applied. Because of the much faster reaction kinetics of the H$_2$ oxidation reaction on the Pt electrocatalysts as compared to that of the O$_2$ reduction reaction, the cell impedance would be mainly dominated by the