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Development of membrane electrode assembly for high temperature proton exchange membrane fuel cell by catalyst coating membrane method

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HIGHLIGHTS

- MEA with low Pt loading for HT-PEMFC was developed by CCM method.
- The fabrication parameters were investigated for the performance optimization.
- The CCM-based MEA has good stability during a short-term fuel cell operation.

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ABSTRACT

Membrane electrode assembly (MEA), which contains cathode and anode catalytic layer, gas diffusion layers (GDL) and electrolyte membrane, is the key unit of a PEMFC. An attempt to develop MEA for ABPBI membrane based high temperature (HT) PEMFC is conducted in this work by catalyst coating membrane (CCM) method. The structure and performance of the MEA are examined by scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and I–V curve. Effects of the CCM preparation method, Pt loading and binder type are investigated for the optimization of the single cell performance. Under 160 °C and atmospheric pressure, the peak power density of the MEA, with Pt loading of 0.5 mg cm^{-2} and 0.3 mg cm^{-2} for the cathode and the anode, can reach 277 mW cm^{-2}, while a current density of 620 A cm^{-2} is delivered at the working voltage of 0.4 V. The MEA prepared by CCM method shows good stability operating in a short term durability test: the cell voltage maintained at ~0.45 V without obvious drop when operated at a constant current density of 300 mA cm^{-2} and 160 °C under ambient pressure for 140 h.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) are considered as a promising next generation of clean energy conversion technology due to its high power density, high efficiency, low emissions and fast start-up [1,2]. With increasing the operating temperature of fuel cell (100–200 °C), the Pt catalyst poisoning by CO impurities at the anode can be significantly mitigated and the cell performance also can be further enhanced because of the improved kinetics of cathode and anode reaction [3,4]. In addition, the humidification system is not necessary and water management become easier at a relatively higher temperature. Moreover, fuel cell operated at elevated temperature has high thermodynamic efficiency and simplified thermal management, which is ideal for combined heat and power (CHP) systems. Hence, researchers have made efforts to develop HT-PEMFCs based on phosphoric acid (PA) doped polybenzimidazole (PBI) membrane in the last decades [5–10]. However, to date, this promising technology has not yet been put on the market, resulting from the low cell performance caused by the slow oxygen reduction reaction (ORR) kinetics and the transport limitation of the reactants and proton, due to the presence of phosphoric acid [5,8]. Therefore, one of the most critical challenge in developing HT-PEMFCs is to enhance the cell performance [5,6,11].

The most important part of PEMFC is membrane electrode assembly, which is consisted of catalyst layers, electrolyte membrane and two gas diffusion layers (GDLs). In the MEA, the

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electrochemical reaction for both anode and cathode only take place at 'triple-phase boundaries', where reactant, catalyst particles and electrolyte contact together [12]. The fuel cell performance can differ greatly depending on the method of the MEA fabrication and other key parameters such as catalyst loading, binder and ionomer content [5,6]. Many methods have been developed to prepare MEAs, including gas diffusion electrode (GDE) method and CCM method [13,14]. As an alternative to the GDE method, in the CCM process, the catalyst inks are directly applied onto both sides of the proton exchange membrane. Hence, it is believed that the CCM method can avoid the loss of catalyst particles immersed into the pore network of gas diffusion layer (GDL) and establish a better interfacial contact between the catalyst layer (CL) and the electrolyte membrane, which can enhance the catalyst utilization and improve the cell performance [15,16]. However, one technical challenge is that the surface of the PBI-based membrane with pre-doped PA will remain moist state due to the strong moisture absorption and the exudation of PA, resulting in a poor adhesion of the catalyst particles on the wet surface of the ABPBI membrane. Wannek et al. [17–20] reported that PA redistribution is a quick process within the HT-MEAs consisted of dry ABPBI and PA pre-doped GDEs. A stable cell performance can be reached in several minutes after commissioning. Inspired by this line of thought, MEAs with enhanced Pt utilization prepared by CCM method and by acid impregnated GDLs have been reported by our group [21]. It was found that the serious distortion of the membrane can be avoided, then a good contact between the CL and the membrane can be kept. At low platinum loadings, the CCM method exhibited much higher performance and Pt utilization compared with the MEA fabricated by GDE method.

In this work, we prepared MEAs by the CCM method and the effects of different parameters, such as preparation method, binder type as well as the Pt loadings of the cathode and the anode, on the fuel cell performance of the so-prepared MEA were investigated. The cell performances were evaluate at 160 °C with pure hydrogen and air as the reactants under ambient pressure. Polarization curves (*I*–*V*) and electrochemical impedance spectroscopies (EIS) were used to characterize various potential losses and variation of electrochemical properties. The results provide a more complete understanding for MEAs prepared by using CCM method for ABPBI membrane-based HT-PEMFC.

2. Experimental

2.1. Preparation of catalyst inks and fabrication of MEAs

Before the CCM based-MEAs fabrication, homogeneous suspension of the catalyst inks were prepared by dispersing Pt/C catalyst (JM 40 wt.% Pt), binder (PTFE, PBI or PVDF) in extra solvent (DMAc for PVDF and PBI binder, IPA for PTFE binder) and then ultrasonicated for 1 h at room temperature. In the CL, the dry PTFE/PVDF content is ~15 wt.%, while the PBI content in the CL is ~10 wt.%.

In the work, all the MEAs with an active area of 2.3 × 2.3 cm^2 were prepared by using an automated ultrasonic spraying technique [9]. Three types of CCM-based MEAs were investigated using the above-prepared catalyst inks. For clarity, the differences in the preparation of the three types of MEA are presented in Table 1.

Table 1
The differences in the MEAs preparation based on CCM method.

MEA-type	Membrane status	CL fabrication	PA doping
Type-a	Dry	Directly on the membrane	GDL
Type-b	Wet, PA-doped	Decal transfer	Membrane
Type-c	Dry	Directly on the membrane	CCM

For the type-a MEAs, the catalyst inks were directly deposited onto the both sides of the dry ABPBI membranes (fumapem®AM, ~30 μm of thickness, FuMA-Tech). After the formation of CLs, the resulting electrodes were left in a vacuum oven for overnight drying. Finally, the MEAs were assembled by contacting CCM and two commercially GDLs (H2315-CX196, Freudenberg, Germany) impregnated with PA without a preceding hot-pressing step. The details of introducing PA can be found in our previous work [21]. 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 considering that PA redistribution mainly happened around the actual electrode area. The H_3PO_4 doping level is 3.8 molecules of H_3PO_4 per polymer repeating unit (PRU) [6].

Type-b MEAs were constructed by the decal transfer method [22–24], which is considered as a suitable way for CCM mass production. In this work, we are then motivated to examine its applicability on the preparation of HT-PEMFC MEAs. To prepare type-b MEAs (CCM-decal transfer), the CL was formed by spraying the catalyst inks onto the surface of a PTFE piece and then transferred onto the surface of the PA pre-doped ABPBI membrane by hot-pressing at 130 °C under the pressure of 200 kgf cm^{-2} for 5 min. The H_3PO_4-doping process was carried out by soaking the ABPBI membranes in 85 wt.% PA solution for several hours at 100 °C. The acid doping level in the membrane was about 3.8(±0.4) molecules of H_3PO_4 per PRU, which is similar with that for type-a MEA. The MEAs were assembled by contacting CCM and two commercially GDLs together without hot-pressing.

The type-c MEAs was fabricated by soaking the prepared CCMs in 85 wt % PA solution for several hours at 100 °C, then contact with two GDLs without hot-pressing. The PA doping level was also controlled at ~3.8(±0.4) molecules of H_3PO_4 per PRU of the membrane.

2.2. Single-cell tests

The prepared MEA was assembled with two gaskets made of fluorinated polymer into an HT-PEMFC cell fixture (BalticFuelCells GmbH, Germany) and then installed in a Cell Compression Unit (CCU, Pragma Industries, France). The cell fixture consists of two graphite plates with single serpentine channels (1.0 mm × 1.0 mm × 23 mm) and ribs (1.0 mm × 23 mm). The active area is about 5 cm^2 (23 mm × 23 mm). Electrical heaters and a thermocouple were embedded into the plates and connected to the CCU which controlled the cell temperature at 160 °C and the piston pressure at 1 N mm^{-2} in this study to minimize the electrical and thermal resistances of the GDLs [25]. A procedure and set-up details for fuel cell performance evaluation is referred in the previous work [21]. The flow rate of hydrogen and air is 0.2 and 0.5 L min^{-1}, respectively. The cell was activated at 160 °C and 0.5 V until the variation of current density was less than 5 mA in 5 min.

2.3. Physical and electrochemical characterization of the MEAs

The surface morphology and the cross-section images of the MEAs were obtained by scanning electron microscopy (SEM) (Oberkochen, Germany). The cross-section of the samples were prepared by freeze-fracturing the MEAs in liquid N_2.

To determine the resistances of the MEAs, the *in-suit* electrochemical impedance spectroscopy (EIS) was performed at 0.6 V with a 5 mV amplitude and the frequency range of 0.1 Hz–20,000 Hz.