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Short communication

A novel dual catalyst layer structured gas diffusion electrode for enhanced performance of high temperature proton exchange membrane fuel cell

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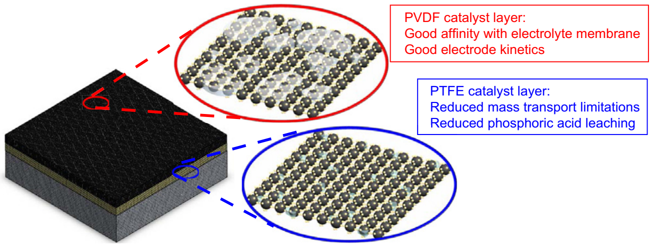
HIGHLIGHTS

- Novel dual CL structured GDE was prepared for high temperature PEMFC.
- Good electrode kinetics can be maintained by a PVDF outer CL.
- Reduced mass transport limitations can be realized by a proper PTFE inner CL.
- Superior performance was delivered by combining both merits of two binders.

GRAPHICAL ABSTRACT



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ABSTRACT

Gas diffusion electrode (GDE) based on a novel dual catalyst layer (CL) structure is designed to enhance the performance of poly(2,5-benzimidazole) (ABPBI)-based high temperature proton exchange membrane fuel cell (PEMFC). Differing from conventional GDE with simplex binder CL, the dual CL GDE is prepared using two different binders, in which a polyvinylidene difluoride (PVDF) CL works as the outer layer to obtain good electrode kinetics by intimately contacting with the electrolyte membrane, while a polytetrafluoroethylene (PTFE) CL works as the inner layer to reduce mass transport limitations. Single cell test and electrochemical analysis on both the dual CL GDE and conventional GDEs are performed to evaluate the effect of the novel CL structure on the fuel cell performance. The results show that significant reductions on both kinetics and mass transfer losses account for the enhanced performance of the novel dual CL structured GDE.

1. Introduction

Membrane electrode assembly (MEA) is the key part of proton exchange membrane fuel cell (PEMFC), which plays a major role in determining cell performance. At present, almost all MEAs for polybenzimidazole (PBI)-based high temperature PEMFC were prepared by catalyst coated gas diffusion layer (GDL) method, i.e., the MEA is the assembly of gas diffusion electrode (GDE) and acid-doped membrane. Therefore, the GDE characteristics, especially the structure of the catalyst layer (CL), have significant influence on the whole cell performance. Many studies have been devoted to improve GDE performance by optimizing CL structure [1–13], including selection of binder type [1–3], optimization of binder content [4–6], investigation of ink preparation [7], and

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introduction of porogens [8], etc. In early PBI-based PEMFC, PBI is the most commonly used binder for GDE preparation. Although PBI is a good membrane material due to its low gas permeability, addition of PBI as binder in the CL could impose mass transport limitation due to the film formed on the catalyst sites [13]. Alternative binders, such as polytetrafluoroethylene (PTFE) [13–15] and polyvinylidene difluoride (PVDF) [16–21], are recently considered good candidates for CL fabrication. Usually, the physicochemical properties of these binders are different from each other, consequently the electrodes based on these binders have their own advantages and shortcomings. For example, the GDEs prepared with PTFE binder usually have minimum mass transport limitations due to the high hydrophobicity and porous structure of the CLs, which can reduce the risk of PA flooding and increase the gases transport [1,14]. However, the PTFE binder which is inert and has no interaction with PA in the electrode results in a high kinetic overpotential [3]. In contrast, the GDEs prepared with PVDF binder give better electrode kinetics due to the good affinity with PA and electrolyte membrane, but the performance, especially at high current densities, is limited by the serious mass transport limitations due to the immersion of PA from PA-doped membrane [18].

In this work, a dual CL structured GDE for PBI-based high temperature PEMFC is designed by using two different binders (PTFE and PVDF), in which a PVDF-bonded CL works as the outer layer to obtain good electrode kinetics by intimately contacting with the electrolyte membrane, while a PTFE based CL works as the inner layer that was next to GDL to reduce mass transport limitations. It is envisaged that the new GDE will combine the merits of both binders; accordingly an enhanced performance can be delivered.

2. Experimental

2.1. Preparation of GDEs

Hispec 4000 Pt/C catalyst (40 wt.% Pt, Johnson Matthey) was used in this study. All GDEs were prepared by spraying method. To deposit the CL with PTFE binder, the catalyst ink was prepared by dispersing catalyst powder into a mixture of PTFE emulsion (60 wt.%, Electrochem Inc.) and isopropanol. For the CL with PVDF binder, the ink was prepared by using a lab-made 5 wt.% PVDF/DMAc solution and extra DMAc solvent. Before being used, these inks were ultrasonicated for at least 1 h for homogeneity.

All GDEs used in this study were prepared using a newly developed automatic catalyst spraying under irradiation (ACSUI) method [22]. The GDEs with dual CL structure were prepared by the following procedures. First, the catalyst ink containing PTFE binder was sprayed onto the microporous layer (MPL) of a commercially available GDL (H2315-CX196, Freudenberg, Germany), followed by calcining at 350 °C for 30 min in N_2 to form the inner CL. Then, the catalyst ink containing PVDF binder was sprayed onto the inner CL to form the outer layer. Last, the whole GDE were heat-treated at 165 °C oven overnight to evaporate the remaining DMAc. The binder contents in the inner and outer layers were 30 wt.% (PTFE) and 15 wt.% (PVDF), respectively. For simplicity, the dual CL structured GDE is denoted as DGDE. For comparison, conventional GDEs with single binder (PTFE or PVDF) CL were also prepared and denoted as PTFE GDE and PVDF GDE, respectively. The Pt loadings of all the GDEs in this study are 0.5 mg cm^{-2}.

2.2. Physical characterization of the GDEs

Pore size distributions of the GDEs were determined by using an Auto Pore IV 9500 Hg porometer (Micromeritics Instrument Corp., USA).

2.3. Single cell test and electrochemical characterization

The membranes used in this study are AB-PBI (poly(2,5-benzimidazole)), which were supplied by FuMA-Tech (fumapem® AM, ~50 μm). For doping with PA, the membranes were immersed in 85% acid solution for 24 h at 95 °C, which gave the membrane an acid doping level of about 3.8 molecules of H_3PO_4 per polymer repeating unit (PRU). The MEA was assembled by sandwiching the doped membrane between two 2.3 cm × 2.3 cm GDEs in a single cell fixture (BalticFuelCells GmbH, Germany) without a preceding hot-pressing step.

The cells were operated at 160 °C and 2 N mm^{-2} piston pressure in a FuelCon Evaluator C test station (FuelCon, Germany). Pure hydrogen was fed to the anode and air to the cathode respectively, with flow rates of 100 ml min^{-1} (hydrogen) and 250 ml min^{-1} (air), at ambient pressure, which are almost the minimum value allowed by our test system. Both hydrogen and air were used as dry gases, directly from the compressed bottles without external humidification. Prior to the recording of the polarization curves, the MEAs were activated by operating the unit cell at a constant voltage (0.55 V) under the cell temperature of 160 °C until a stable performance was obtained. The current–voltage polarization curves were obtained by measuring the current density with the stepwise decrement of voltage from 0.9 to 0.2 V, with an interval of 0.05 V. At each cell voltage, the current was measured after a hold time of 5 min to allow the cell approaching steady state. For better accuracy, single cell tests for each type were performed at least three times with different pairs of GDEs (cut from same batch), and then the average values (current densities) were determined. Normally, the relative standard deviations of these values were less than 4%.

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using an Autolab PGSTAT 30 Potentiostat/Galvanostat (Metrohm). EIS measurements were carried out at a cell voltage of 0.6 V with amplitude of 5 mV, and in the frequency range of 100 mHz–20 kHz. The impedance data were obtained by calculation and simulation with Autolab Nova software. Voltammetric measurements, undertaken to study the electrochemical active surface area (EASA), were conducted using dry N_2 at the cathode (working electrode) and dry H_2 at the anode (counter electrode and reference electrode) at room temperature (~27 °C). Cyclic voltammograms were recorded from 1.2 V to 0.05 V at a scan rate of 0.05 V s^{-1}.

3. Results and discussion

To reveal the structural differences among the CLs of the three GDEs, the pore sizes characterizations on these GDEs by mercury intrusion method were performed, as shown in Fig. 1. The distribution of pore sizes is an important parameter to GDEs since the reactant gases and water (liquid or vapor) transport are regulated by the specific volumes of small and large pores [23]. From Fig. 1, it can be seen that all three curves are similar except in the macropores zone (i.e. 5–100 μm), where the pore volume of the dual CL structured GDE is close to PTFE GDE, substantially increased comparing to pure PVDF GDE. This result is understandable considering PTFE remains insoluble in the catalyst ink, so big catalyst agglomerates are more likely formed, which would justify the larger macropores volume of the electrodes (PTFE GDE and DGDE) with PTFE CL. In the case of gas transport to the catalyst sites, the main contribution to gas transport will be due to Knudsen diffusion in the micropores and a molecular diffusion mechanism in the macropores [23]. Better mass transport would be expected for the electrodes with larger volume of the macropores, especially at high current densities.