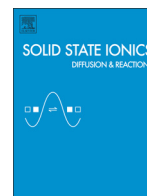




Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Design and investigation of dual-layer electrodes for proton exchange membrane fuel cells

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ARTICLE INFO

Article history:

Received 8 May 2013

Received in revised form 20 August 2013

Accepted 25 August 2013

Available online xxx

Keywords:

Catalyst-coated membranes

Proton exchange membrane fuel cell

Spray deposition

Catalyst layers

Water management

ABSTRACT

With an aim to develop a proton-exchange-membrane fuel cell (PEMFC) with improved water management, catalyst-coated membranes based upon Nafion 212 membrane with electrodes of dual-layer structure which consist of one hydrophilic layer of Pt/C + Nafion and one hydrophobic layer of Pt/C + PTFE arranged in a proper order, is specifically designed and successfully fabricated by a facile high-temperature spray deposition technique. Dual-layer structured anode and cathode are separately evaluated by electrochemical performance in single cells. Effect of relative thickness of the dual layers in the electrode on the cell performance is investigated. No improvement in cell performance is observed by adopting the dual-layer structure for the anode as compared to conventional anode with single hydrophilic catalyst layer. However, better cell performance is observed for the cell with dual-layer structured cathode, and the optimal cell reaches a peak power density of about 800 mW cm⁻² at 50 °C with humidified hydrogen and oxygen as fuel and oxidant respectively.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have received considerable attention recently as a potential power source for portable, mobile, and stationary applications because of their numerous inherent advantages, such as high efficiency, high energy density, low emissions, and fast start-up and shut-down capability [1]. Nafion-type perfluorosulfonic acid polymers are the most widely used electrolytes in PEMFCs due to their high chemical, mechanical and thermal stability [2]. However, the currently used perfluorosulfonic acid polymers in PEMFCs must be well hydrated to maintain high proton conductivity. As a result, the proper water management is of critical importance for achieving high cell performance. For the catalyst layers (electrodes), both water drying and flooding will exert unfavorable influence on the cell performance. Triple phase boundaries (TPBs) reduce and proton transfer becomes difficult as water drying in the catalyst layers, while the effective catalytic sites will also decrease for the water flooding in catalyst layers due to blocked gas passages.

There are several ways to control the water balance in PEMFCs including development of self-humidifying composite membranes [3–8], improvement of catalyst layer [9–20], and optimization of the gas diffusion layers (GDLs) [21–23]. Up to now, several researchers

have successfully improved the water balance in PEMFCs by optimizing the component and structure of catalyst layers. Adding hydrophilic oxides to the anode catalyst layer turns out to be an effective way in improving cell performance under low humidification and high temperature operation conditions [9–12]. Han et al. designed a self-humidified anode by adding silica (20–30 nm) into Nafion matrix of anode [10], and they observed that the cell performances increased with the increase of silica content in anodes from 0 to 6 wt.% at 60 °C under the condition of without external humidification. Chao et al. investigated the performance of PEMFCs by adding Pt/TiO₂ particle into the anode catalyst layer and they demonstrated the best cell performance was obtained with 5 wt.% Pt/TiO₂ particle addition at temperatures of anode humidifier ranging from 25 to 75 °C [11]. Since water is produced at the cathode side during the fuel cell process, the water flooding at the cathode may happen. To improve water management of the cathode, some hydrophobic materials such as polytetrafluoroethylene (PTFE) [13] and dimethyl silicone oil (DSO) [14,15], were added into the cathode catalyst layer. Optimizing the structure of electrode is also effective in mediating the water drying or flooding problem of PEMFCs. For example, it was confirmed that low Nafion content near the GDLs is beneficial for oxygen diffusion and water removal [17]. Su et al. also demonstrated that better Pt utilization and mass transfer thus cell performance can be realized by an appropriate cathode structure. Previously, Zhang et al. prepared a gas diffusion electrode (GDE) that contains a cathode with the structure of dual-bonded catalyst layers [18,19], and better cathode performance was achieved than conventional cathode with single layer PTFE or ionomer-bonded catalyst. They also investigated the Nafion content in the ionomer-bonded layer and Nafion loading

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in recast film between hydrophilic layer and hydrophobic layer, and found no obvious improvement in cell performance by changing Nafion content in the hydrophilic layer, while finding the cell without the recast film exhibited the best performance. However, they did not get optimal thicknesses of the respective layer for the best cell performance. Besides, there are two typical fabricating methods for PEMFC, the deposition of catalyst onto the GDL and the direct deposition of catalyst onto the electrolyte membrane surface. Due to their different structures, different water management may be required for them. The direct deposition of catalyst onto electrolyte surface has the advantages of high catalyst utilization. Previously we have successfully prepared a catalyst-coated membrane by direct high-temperature spray deposition of catalyst ink onto Nafion electrolyte membrane with high performance [24,25].

In this study, in order to optimize water management, catalyst-coated membranes (CCMs) with dual-layer electrodes including a hydrophobic Pt/C + PTFE catalyst layer and a hydrophilic Pt/C + Nafion catalyst layer were prepared by the high-temperature spray deposition technique. We evaluated the dual layer-structured anode and cathode separately by examining the electrochemical performance in single cells. A systematic study was also made on the effect of relative thickness of the dual layers while fixing Pt loading in whole electrode on cell performance, and an optimal layer thickness was developed.

2. Experimental

2.1. Preparation of the gas diffusion layer

The gas diffusion layer (GDL), composed of a PTFE modified carbon paper substrate and a PTFE bonded carbon micro-porous layer (MPL), was fabricated as follows. Firstly, the commercial carbon paper (Toray Inc., Japan) was modified with PTFE to increase its water-proof performance. An aqueous solution with 1 wt.% PTFE was prepared by diluting 60 wt.% PTFE emulsion (DuPont-TE-3893) in proper amount of deionized water, the carbon paper was then soaked in the PTFE aqueous solution for 1–2 min and dried on a hot-plate at 120 °C, the steps were repeated until the weight of PTFE reached around 10 wt.% of the carbon paper, the carbon paper was thermally treated at 250 °C for 30 min to remove the dispersion agent contained in PTFE and further sintered in air at 340 °C for 30 min. Secondly, the MPL was deposited on the carbon paper to increase the gas diffusion properties. To deposit the MPL onto the carbon paper substrate, a homogeneous slurry of 60 wt.% PTFE, carbon powder (Vulcan XC-72), alcohol was first prepared by ultrasonic dispersing and ball milling, then the slurry was coated onto the carbon paper substrate. Finally, the whole GDL was finally treated at 250 °C for 30 min and then 340 °C for 30 min. The amount of MPL on the carbon paper substrate was approximately 3 mg cm⁻² with the carbon to PTFE weight ratio of 4:1.

2.2. Fabrication of catalyst-coated membranes

Catalyst-coated membranes were prepared by a technique based on high-temperature spray deposition of catalyst directly onto the Nafion membrane [24–26]. Before spray deposition of the catalyst layers, polymer electrolyte membranes (Nafion 212) were pre-treated under the standard procedure of 1 h in 5 wt.% H₂O₂ solution at 85 °C, 1 h in deionized water at 85 °C, 1 h in 0.5 M H₂SO₄ solution at 85 °C, and 1 h in deionized water at 85 °C, in sequence. After the treatment, the membranes were stored in deionized water before use. A catalyst ink was prepared by ultrasonic dispersing of commercial 40 wt.% Pt/C (Pearl Hydrogen Technology Co., Ltd, Shanghai) and 5 wt.% Nafion solution (DuPont 520) at the catalyst to Nafion weight ratio of 3:1 in isopropanol media for about 1 h. To deposit the catalyst layers onto the electrolyte membrane to form CCMs, the pretreated Nafion 212 membrane was fixed onto a flat Pyrex glass by high-temperature adhesive tape over a hot plate. After the hot plate was heated up to around 150 °C, the

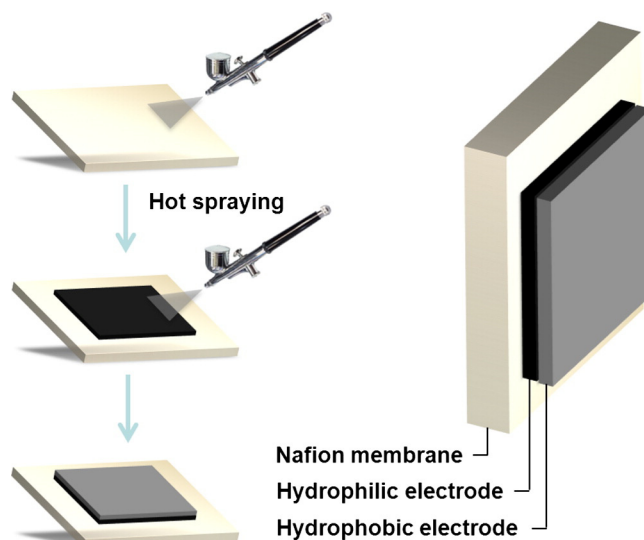


Fig. 1. Schematic preparing process and structure of dual-layer structured electrode CCM.

catalyst ink was air-driven spray deposited onto the Nafion 212 membrane surface. The catalyst ink was wetted by a small amount of deionized water to prevent burning during the spray deposition. Most of the liquid in catalyst ink was vaporized before reaching the membrane, thus just allowing the catalyst particle deposited onto the electrolyte membrane surface. The spray was conducted in a zigzag manner at a deposition rate of 0.3–0.5 mL min⁻¹. The same catalyst loading of 0.4 mg cm⁻² is adopted for both electrodes.

To prepare the CCMs with dual-layer structure of the electrode, as schematically shown in Fig. 1, a catalyst ink with Pt/C and PTFE was further sprayed on the hydrophilic catalyst layer (Pt/C and Nafion) on electrolyte membrane as the hydrophobic catalyst layer. The hydrophobic catalyst ink was prepared by ultrasonic dispersing 40 wt.% Pt/C with 60 wt.% PTFE suspension at the catalyst to PTFE weight ratio of 4:1 in isopropanol/water (4:1) media for 1 h. CCMs with different ratios of hydrophilic catalyst layer to hydrophobic catalyst layer thicknesses with fixed total Pt content were prepared and the corresponding parameters are listed in Table 1.

2.3. Fuel cell performance test and characterization

CCMs with 3 × 3 cm² active electrode area for both anode and cathode were sandwiched between two gas diffusion layers to form the PEMFC and assembled with Teflon gaskets and graphite blocks with a serpentine flow field for performance test. Hydrogen with purity higher than 99.99% was applied as the fuel at the flow rate of 250 mL min⁻¹ [STP] and industrial grade oxygen as oxidant at the cathode side at the flow rate of 300 mL min⁻¹ [STP]. Typically, the single cell was operated at 50 °C under ambient pressure and the reactant gas was humidified by

Table 1

CCMs with different ratios of hydrophilic catalyst layer to hydrophobic catalyst layer thicknesses.

	Pt loading of anode (mg cm ⁻²)		Pt loading of cathode (mg cm ⁻²)	
	PTFE-bonded catalyst layer	Ionomer-bonded catalyst layer	PTFE-bonded catalyst layer	Ionomer-bonded catalyst layer
CCM-N	0	0.4	0	0.4
CCM-A1	0.1	0.3	0	0.4
CCM-A2	0.2	0.2	0	0.4
CCM-A3	0.3	0.1	0	0.4
CCM-C1	0	0.4	0.1	0.3
CCM-C2	0	0.4	0.2	0.2
CCM-C3	0	0.4	0.3	0.1

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