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Improvement of PEMFC performance and endurance by employing continuous silica film incorporated water transport plate

Xiaoqian Guo^{a,b}, Yachao Zeng^{a,b}, Zhiqiang Wang^{a,b}, Lijuan Qu^{a,b}, Zhigang Shao^{a,*}, Zhanhui Yuan^{c,**}, Baolian Yi^a

^a Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China ^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

^c Fujian Agriculture and Forestry University, Fuzhou 350002, China

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ABSTRACT

An appropriate water balance between membrane dehydration and water flooding is essential to improve the performance and endurance of the polymer electrolyte membrane fuel cell (PEMFC). In this study, a novel hydrophilic porous carbon plate (HPCP) is employed as a water transport plate (WTP) to achieve the water balance by virtue of its humidification and water drainage functions. The HPCP is fabricated by electrochemically assisted self-assembly of a hydrophilic silica film on the pore surface of a porous carbon plate (PCP). To overcome the problem that the precursor is unable to enter the hydrophobic pores of the PCP, a novel electro-deposition device forcing the precursor to flow through the pores is designed. Consequently, continuous hydrophilic pores are obtained which promotes the ability of humidification and water drainage. Owing to the humidification function of the HPCP, at the current density of 1000 mA cm⁻², the voltage of the cell with HPCP is 270 mV higher than that with solid plate (SP) under no-humidity. Attributed to the water drainage function, the runtime of the cell is twelve times longer than that with SP under dead-ended cathode operation.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are attracting enormous interest as a primary power source for automotive applications by virtue of its high power density, facility of operation, high efficiency and zero pollution [1,2]. One of the critical issues associated with the high-power and endurance of PEMFCs is water management, which needs a delicate water balance scheme between membrane dehydration and water flooding [3,4].

Several approaches have been considered for dealing with the water balance. One of them is the modification of the membrane electrode assembly (MEA) [5–11]. Hydrophilic substances (e.g. SiO_2 , polyaniline et al) with the capacity of water absorption were added into the membrane, catalyst or gas diffusion layer to endow the MEA with self-humidifying, anti-flooding ability. Another pervasive approach refers to the employment of improved flow field structures [12–14]. Ge et al [14] integrated polyvinyl alcohol

E-mail addresses: zhgshao@dicp.ac.cn (Z. Shao), 2113569075@qq.com (Z. Yuan).

http://dx.doi.org/10.1016/j.electacta.2016.01.059 0013-4686/© 2016 Elsevier Ltd. All rights reserved. (PVA) wickings into the flow field to absorb generated water and transport it to moisten the inlet dry gas, which alleviated outlet water flooding and inlet membrane dehydration. Nevertheless, concerning the modification of the MEA and flow field, only internal water in cell could be adjusted to acquire the water balance. Ascribed to the complicated water transportation in cell operation, the optimal water balance is difficult to obtain.

A promising approach to achieve proper water management is the utilization of water transport plates (WTPs), designed by the United Technologies Corporation (UTC) [15–18]. Different from commercial bipolar plates, WTPs are made up of hydrophilic porous materials [18]. WTPs perform two main functions. When gas streams are not saturated, WTPs provide water in cooling water chamber to flow through the hydrophilic pores and evaporate into gas channels to moisten them. When excessive water existed, WTPs provide an escape path for liquid water such that it does not hinder reactant gases from transporting to the catalyst [17]. Due to the participation of external water in water chamber, WTPs decouple the inevitable relationship of performance and internal water transportation, which made it easier to achieve water balance [18].

As for the fabrication process of WTPs, only few patents [19–21] in the public literatures have disclosed them. One is to mix the





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^{*} Corresponding author. Tel.: +86 411 84379153; fax: +86 411 84379185. ** Corresponding author.

hydrophilic oxide or the modified carbon together with electronically conductive materials, resin and molded into a plate. Another is to generate hydrophilic substances in the PCPs by a precipitation method, whereas it can only partially cover the pore surface due to the precursor unable to enter the hydrophobic pores of the PCPs spontaneously. With regard to the approaches discussed above, hydrophilic materials exist in the form of particles and continuous hydrophilic pores are difficult to obtain, which resulted in inadequate water permeability.

In this study, a novel hydrophilic porous carbon plate (HPCP) was fabricated by an electrochemically assisted self-assembly method, which led to the generation of hydrophilic thin films rather than particles. To solve the problem of the precursor unable to enter the hydrophobic pores of the PCP, a novel electro-deposition device with pre-hydrolysed precursor flowing in the pores of the PCP was designed. Moreover, the effects of vapor water and liquid water permeability on cell performance and endurance were discussed.

2. Experimental

2.1. Preparation of hydrophilic porous carbon plates

HPCPs were fabricated by an electrochemically assisted selfassembly method. Pre-hydrolysed precursor composed of 1.04 g tetraethoxysilane (TEOS, Xilong chemical), 50 ml ethanol (98%), 50 ml sodium nitrite solution (0.1 mol L⁻¹) was added into 0.365 g surfactant template cetyltrimethylammonium bromide (CTAB, Kermel) and stirring for 1 h. If the precursor solution is alkaline, the TEOS would be prone to hydrolyze and form a precipitate (silica) immediately [22]. Therefore, the pH of the precursor solution was adjusted to 3 by titration with the hydrochloric acid solution $(1 \text{ mol } L^{-1})$.

Due to the hydrophobicity of PCPs, the precursor has no ability to enter into the pores of PCPs spontaneously. To solve this problem and form continuous hydrophilic pores, a novel electro-deposition device was designed. As shown in Fig. 1, the precursor solution was transported into the electro-deposition device and passed through the pores of PCPs by a peristaltic pump. Then a constant potential of -3.5 V was set on the PCP for 2 min in parallel to the precursor flowing process, with respect to the graphite counter electrode. The samples prepared at the pump rotation speed of 0.5, 1, 1.5 and 2 rpm, were marked as C-0.5, C-1, C-1.5 and C-2, respectively. The volumetric flow rates of the precursor flowing through the C-0.5, C-1, C-1.5 and C-2 is 0.135, 0.270, 0.405 and 0.540 ml min⁻¹, respectively.

2.2. Characterization of hydrophilic porous carbon plates

2.2.1. Microstructure characterization

In order to investigate the microstructure of HPCPs and the untreated carbon plate, hydrophilic pore fraction, porosity and pore size were measured. A weighing method was used to determine the hydrophilic pore fraction by immersing the HPCPs in water at $80 \degree C$ for 8 h [23]. and mercury porosimetry (PoreMasterGT 60) was adopted to measure the porosity and pore



Fig. 1. (a) 3D diagram of the electroplating device and (b) the flow chart of electro-deposition.

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