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

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\section*{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 \cite{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 \cite{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) \cite{5–11}. Hydrophilic substances (e.g. SiO\textsubscript{2}, polyaniline etc) 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 \cite{12–14}. Ge et al \cite{14} integrated polyvinyl alcohol (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) \cite{15–18}. Different from commercial bipolar plates, WTPs are made up of hydrophilic porous materials \cite{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 \cite{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 \cite{18}.

As for the fabrication process of WTPs, only few patents \cite{19–21} in the public literatures have disclosed them. One is to mix the
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 self-assembly 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 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 °C for 8 h [23], and mercury porosimetry (PoreMasterGT 60) was adopted to measure the porosity and pore size.
size. The generation of hydrophilic thin film was confirmed using a scanning electron microscope (SEM, JEOL JSM-7800F) and an energy dispersive X-ray (EDX, JEOL JSM-7800F) spectroscopy.

2.2.2. Contact angles measurement
To characterize the wettability property of varied HPCPs, contact angles were measured by a sessile drop method (KRUSS). Pure water droplets of 3 μL were dropped onto the surfaces of HPCPs, then the contact angles were acquired by analyzing the recorded water droplet images.

2.2.3. Bubble pressure measurement
The HPCPs, serving as WTPs, should have the ability to avoid the mixture of hydrogen and oxygen. To investigate the gas-blockage property of the HPCPs, a bubble pressure measurement was conducted using a home-made apparatus [24]. The sample with a thickness of 1 mm and a diameter of 30 mm was sealed into the apparatus. Firstly, HPCPs were saturated with water by immersing them in water at 80 °C for 8 h. Then nitrogen was fed into one side of the water-saturated sample and water was fed into the other side. The pressure of the gas side was gradually increased, until gas bubbles were observed in the water chamber. The pressure at which gas bubble forms on the water side is the bubble pressure.

2.2.4. Water permeability measurements
In order to evaluate the humidification and water drainage functions of HPCPs, vapor water permeability and liquid water permeability measurements were conducted respectively by a home-made water permeability test apparatus [24]. A 30 mm diameter sample with a thickness of 1 mm was sandwiched between the water chamber and gas chamber. The temperature of both water and gas chambers was 65 °C with the absolute pressure of the water chamber setting at 0.13 MPa. The water chamber was linked with a pipette and the decrement rate of liquid water in the pipette indicated the flow rate of water permeating through the samples. As for vapor water permeability measurement, to simulate the operating condition of PEMFC under no-humidity, the absolute pressure of the gas chamber was 0.15 MPa with dry nitrogen flow rate of 100 ml min⁻¹. While as for the liquid water permeability measurement, the gas chamber was exposed to the ambient air.

2.2.5. Single cell test
To characterize the effects of water permeability property of HPCPs on cell performance and endurance, single cell tests were conducted. Pt/C (Johnson Matthey, 70 wt.%) catalyst ink was sprayed onto a Nafion® 212 membrane as anode (0.4 mgPt cm⁻²) and cathode (0.4 mgPt cm⁻²) catalyst layers with 5 cm² active area. HPCPs, employed as cell plates, possess parallel flow channels with the following dimensions: thickness of 1.3 mm, channel width of 0.5 mm, rib width of 1 mm and channel height of 0.3 mm.

2.2.5.1. Humidification function test. In order to evaluate the humidification function, a HPCP was employed as an anode plate. The flow chart was shown in Fig. 2(a). Generally, under no-humidity, by increasing the gas flow rate, membrane dehydration will become more serious which will be detrimental to the cell performance. In order to better test the humidification function of HPCPs, dry hydrogen and air, with high flow stoichiometric ratios controlled as 1.4/4.8, were provided into anode and cathode sides respectively. The absolute pressures of both anode and cathode sides were set as 0.15 MPa. Circulating water at 65 °C was pumped into the water chamber with the chamber pressure (absolute pressure) fixed at 0.13 MPa. Subsequently, polarization curves were recorded with KFM 2030 (Kikusui, Japan).

2.2.5.2. Water drainage function test. In order to evaluate the water drainage function, a HPCP acted as a cathode plate. Due to the high flow rate of air, water flooding in PEMFC fed with air is not serious. So the pure oxygen was chosen to be supplied into the cathode side. Saturated hydrogen and oxygen were supplied with the stoichiometric flow setting as 1.4/1 for H₂/O₂ at 0.15 MPa (absolute pressure). The temperature and absolute pressure of the water chamber was set as 65 °C and 0.13 MPa, respectively. Furthermore, what’s the most promising application area for WTPs is the situation of undersea and aviation. Due to the lack of oxygen in these situations, the most important issue is to increase the oxygen utilization ratio. So the cathode outlet was blocked to prevent the loss of oxygen, which is called as dead-end cathode (DEC) operation. Then cell voltage at the current density of 2000 mA cm⁻² was recorded. When the voltage declined to 0.3 V, the valve at the cathode outlet would open to pulse purge. The flow chart was represented in Fig. 2(b).

3. Results and discussion
3.1. Characterization of hydrophilic porous carbon plates
HPCPs were fabricated by electrochemically assisted self-assembly of silica thin film on PCPs. Since the TEOS carries the positive charge under the acidic condition (pH = 3), it could be carried by cation surfactant template CTAB micelles. By applying a constant cathodic potential on the PCP, the micelles were induced to the pore surface by the electrical field, subsequently, the silica thin film generated. The reactions proceeding in the direction of silica generation are shown as follows [25–27]:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (1)$$

$$\text{NO}_3^- + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_3 + 9\text{OH}^- \quad (2)$$
\[
(C_2H_5O)_4Si + 3H_2O^{\text{OH}} \rightarrow 4C_2H_5OH + H_2SiO_3
\]  
(3)

\[
H_2SiO_3 \rightarrow SiO_2 + H_2O
\]  
(4)

In most cases, due to the application of the cathodic potential, the increase in pH could be driven by the reduction of water at the electrode-solution interface (Eq. (1)). Moreover, ascribed to the addition of sodium nitrate, pH will further increase as a consequence of nitrate reduction (Eq. (2)). The local pH increase induced the polycondensation of TEOS and the CTAB micelles caused the concomitant self-assembly formation of silica as thin films on the work electrode (Eq. (3)), as shown in Fig. 3. Consequently, the hydrophilic silica film was obtained by the heat-treatment of silica sol (Eq. (4)).

To confirm the generation of silica film in the pores of PCPs by the electrochemically assisted self-assembly method, SEM and EDX measurement of pores were performed. In Fig. 4(a), the EDX of the mouth and throat of a pore was depicted. It implies that the pore surface was covered by a thin film, which is composed of silicon and oxygen elements. As observed in the elemental mapping images of a pore cross-section (Fig. 4(b)), the extending area around the pore was covered by silica which further confirmed the generation of silica on the pore surface.

To determine if all the pores of HPCPs are completely covered by hydrophilic silica using the electro-deposition device, the bubble pressure and hydrophilic pore fraction were measured. The bubble pressure of the HPCPs will be discussed in detail below. With respect to the hydrophilic pore fraction, it was 100% for every sample, representing that all the pores were covered by the hydrophilic silica film and continuous hydrophilic pores had formed.

3.1.1. Microstructure

Porosity and pore size of the untreated carbon plate and the HPCPs with different volumetric flow rates of precursor solution were measured by a mercury intrusion method. As shown in Fig. 5, the porosity and pore size of the untreated carbon plate is 17% and 2.6 μm, respectively. Due to the generation of hydrophilic thin films on the pore surface, the porosity and pore size decreased accordingly. Furthermore, the porosity and pore size of the samples decreased correspondingly with the increase of the volumetric flow rate.

Refer to the constant-voltage electro-deposition process, it is composed of two key processes: the diffusion-convection process for the precursor transporting to the pore surface of PCPs and the electrochemical reaction process. As depicted in Fig. 6, the electro-deposition current density decreased apparently with time. It is because that the complementary precursor by the diffusion-convection process could not satisfy the quantity of the reaction, which made the diffusion-convection process be the rate-limiting step. With the increase of volumetric flow rate, the thickness of the diffusion boundary layer reduced such that the diffusion-convection process enhanced. Correspondingly, the reaction current density increased and more silica accumulated on the pore surface of HPCPs, which resulted in the decrease of the porosity and pore size.

3.1.2. Contact angles

The wettability characteristics of HPCPs were investigated by a sessile drop method. Fig. 7 displays the water droplet images on the surface of HPCPs prepared with different volumetric flow rates of pre-hydrolysed precursor solution. It reveals that attributed to the increasing accumulation of SiO2 in the pores, the hydrophilicity of HPCPs improved apparently with the increase of the volumetric flow rate.

![Fig. 3. Schematic of silica generation mechanism.](image)
pressures) of C-0.5, C-1, C-1.5 and C-2 is 0.11, 0.13, 0.17 and 0.18 MPa, respectively, which represents that all the samples have the ability to prohibit gas leakage under the operating conditions of the fuel cell efficiently.

Moreover, the bubble pressure measurement is reliable to determine if all the pores are hydrophilic and completely hydrophilic. Assume that all the pores are completely hydrophilic, in order to displace water out of the pore of carbon plate, the bubble pressure should overcome the resistance force (capillary force and viscous force) [28]. One can calculate the capillary force using the Young’s equation:

$$p_c = \frac{2\gamma \cos \theta}{r}$$

(5)

where \(p_c\) is the capillary force, \(\gamma\) is the surface tension, \(\theta\) the contact angle and \(r\) is the pore size. According to Eq. (5), the capillary force of C-0.5, C-1, C-1.5 and C-2 is 0.044, 0.065, 0.10 and 0.14 MPa, respectively. The bubble pressure (gauge pressure) is much greater than the capillary force, which is in line with the assumption. Therefore, all the pores are completely hydrophilic.

3.3. Water permeability

To investigate the humidification and water drainage functions of different HPCPs, permeated vapor and liquid water flux were measured, respectively, which were listed in Table 2.

3.3.1. Vapor water permeability

As for the vapor water permeability, it consists of two processes: liquid water capillary flow process and water evaporation process [17]. According to the Young’s equation, the capillary force of the four samples was greater than the pressure differential between gas and water chambers \((p_{\text{gas}}-p_{\text{water}}) = 0.02\) MPa. Thus, it is sufficient to enable liquid water in the water chamber to flow through the hydrophilic pores and reach the gas-channel interface. Then the permeated water evaporates to the gas chamber, which is taken away by inlet gas streams. Weber et al. [17] found that the quantity of flow-through water exceeded the maximum evaporation rate by eight times, meaning that the evaporation is the rate-limiting process. Thus, the permeated vapor water flux is determined by the Fick’s law, which is showed as follows:

$$J = D_v \frac{\Delta C}{h} A_s$$

(6)

$$A_s = \frac{A e}{h}$$

(7)

where \(J\) is the vapor water flux, \(D_v\) is the diffusion coefficient of water in the gas, \(\Delta C\) is the different water content between water and gas chambers, \(h\) is the boundary distance between water and gas, \(A_s\) is the active surface for water vapor evaporation, \(A\) is the sample surface and \(e\) is the porosity.

According to the Fick’s law, the vapor water flux is proportional to the active surface area for vapor water evaporation, which is determined by the porosity. As shown in Fig. 5, the higher volumetric flow rate was, the lower porosity was obtained. Correspondingly, with the increase of the volumetric flow rate, the vapor water flux declined, as shown in Table 2.

3.3.2. Liquid water permeability

As for the liquid water permeability, the experimental data is determined by the Darcy’s law. The equations are showed as follows.

$$Q = \frac{K A P}{\mu L} = \frac{K A (p_c + \Delta P_0)}{\mu L}$$

(8)

where \(Q\) is the volumetric flow rate, \(K\) is the permeability, \(A\) is the active area, \(\mu\) is the dynamic viscosity and \(L\) is the thickness of the membrane.
where \( Q \) is the permeated liquid water flux, \( K \) is the permeability, \( A \) is the area of samples, \( \mu \) is the viscosity, \( L \) is the height, \( \Delta P_p \) is the pressure differential between supplied water and gas chambers.

According to Eq. (8), the permeated liquid water flux is related to the permeability \( K \) and capillary force. The permeability \( K \), representing the water permeable ability, is determined by the geometric construction of porous media. Moreover, the porosity is the key factor determining the geometric construction. The increasing porosity provides more passageways for water transportation from water chamber to gas chamber. Therefore, the permeability \( K \) is proportional to porosity. Regarding to the capillary force, it is determined by the pore size and contact angle. Therefore, according to Eqs. (5) and (8), the liquid water flux is proportional to porosity and inversely proportional to pore size and contact angle.

With the increase of precursor flow rate, the porosity, pore size and contact angle decreased. Ascribed to the decrease of pore size and contact angle, the capillary force of the HPCP was improved with the increase of the volumetric flow rate. While with the increase of the volumetric flow rate, the porosity decreased and less passageways for water transportation from water chamber to gas chamber were supplied, which led to the decrease of \( K \). Therefore, take the porosity, pore size and contact angle into account, there is an extremum of the liquid water flux. As listed in Table 2, the experimental data show that the order of the liquid water flux is C-0.5 < C-2 < C-1.5 < C-1.

### 3.4. Cell performance and endurance

#### 3.4.1. Humidification function

To study the influence of vapor water permeability on cell performance, polarization curves of PEMFC by employing different HPCPs as anode plates with dry gases supply were evaluated. As shown in Fig. 8(a), it is noted that cell performance follows the sequence of \( \text{SP} < \text{C-2} < \text{C-1.5} < \text{C-1} < \text{C-0.5} \). The voltage of the cell with C-0.5 is 270 mV higher than that with SP at 1000 mA cm\(^{-2}\).

Ohmic resistance, mainly affected by membrane resistance, plays the dominant role to affect the cell performance under no-humidity. The more water exists in the membrane, the lower membrane resistance will be. Moreover, the water content of membrane is affected by the relative humidity of the inlet gases. By employing the SP, there is no access for water to permeate through the plate, which give rise to the serious water shortage of membrane. While by employing the HPCP as an anode plate, the membrane could be moistened sufficiently by virtue of the permeated water from the water chamber. Subsequently, the water-shortage of the membrane under no-humidity was addressed effectively and the membrane resistance decrease apparently. Therefore, by employing the HPCP, the cell performance was much higher than that with SP. The relative humidity levels corresponding to the additional water amount supplied by the HPCPs could be briefly calculated as follows [24].

\[
RH = \frac{P}{P_{sat}} = \frac{n}{n_{sat}}
\]  

\[
P_{sat}V = n_{sat}RT
\]  

\[
n = \frac{Q \times A \times t}{M_{sat}}
\]

SP stands for solid plate that water cannot permeate through.
water at 65 °C. Q is the permeated water flux of the HPCPs which was measured experimentally. A is the area of the HPCPs (5 cm²), \( t \) is the time in operation and \( M_{\text{water}} \) is the molar weight of water. According to the Eqs. (9)–(11), the humidity levels of the hydrogen corresponding to the additional water supplied by C-0.5, C-1, C-1.5 and C-2 from the water chamber are 81%, 78%, 67% and 58%, respectively. With the increase of the precursor flow rate, the humidity level decreased which caused the increase of the electric resistance. As shown in Fig. 8(a), the order of the electric resistance is C-0.5 < C-1 < C-1.5 < C-2. Therefore, the cell performance decrease with the increasing precursor rate, which is in accordance with the opposite trend of the electric resistance above.

### 3.4.2. Water drainage function

To test the influence of liquid water permeability on cell endurance, the variation voltage of PEMFC by employing different HPCPs as cathode plates was evaluated under fully-humidity condition and DEC operation, which is represented in Fig. 8(b).

Under the DEC operation, due to the absence of outlet for generated and electro-osmosis drag water to escape, liquid water will clog the oxidant channel and inhibit the access of oxidant gas to the catalyst, which resulted in the cell voltage drop. As for the cell with SP, due to a lack of passages to draw away excessive water, the voltage took about only 30 s to decline from 0.6 V to 0.3 V at 2000 mA cm⁻². Nevertheless, with regard to the cell with HPCP, owing to the existence of hydrophilic passages, the excessive water could flow through the HPCP to the water chamber, which resulted in the alleviation of voltage loss and the increase of the purge interval. The purge interval of the cell with HPCP follows the sequence of SP < C-0.5 < C-2 < C-1.5 < C-1, which is strikingly in line with the tendency of the liquid water permeability data shown in Table 2. The purge interval of the cell with C-1 is more than twelve times longer than that with SP. Thus, the reduction of liquid water in the flow field will be helpful to prevent the performance decay and correspondingly increase the utilization ratio of oxygen.

### 4. Conclusions

A novel hydrophilic porous carbon plate (HPCP) was fabricated by electrochemically assisted self-assembly of silica thin film in the pores of porous carbon plates. The HPCPs, acted as water transport plates, were employed to improve the PEMFC performance and endurance by virtue of the functions of humidification and water drainage. Attributed to the humidification function, by employing the HPCP as the anode plate, dry inlet gases were moistened by the permeated vapor water from water chamber which achieved the improvement of the cell performance under no-humidity. Owing to the water drainage function, by employing the HPCP as the cathode plate, the purge interval of the cell with HPCP was much higher than that with SP, which increase the cell endurance and the utilization ratio of oxygen under dead-ended cathode operation. The favorable performance and endurance of the cell indicates that the HPCP is a promising candidate for WTP's material.

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