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Improved properties of carbon fiber paper as electrode for fuel cell by coating pyrocarbon via CVD method

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Abstract: The fabrication of a pyrocarbon coated carbon paper and its application to the gas diffusion lay (GDL) of proton exchange membrane (PEM) fuel cell were described. This carbon paper was fabricated by using conventional carbon paper as the precursor, and coating it with pyrocarbon by pyrolyzing propylene via the chemical vapor deposition (CVD) method. For comparison, conventional carbon paper composites were also prepared by using PAN-based carbon fiber felt as the precursor followed by impregnation with resin, molding and heat-treatment. SEM characterization indicates that pyrocarbon is uniformly deposited on the surface of the fiber in the pyrocarbon coated carbon paper and made the fibers of carbon felt bind more tightly. In contrast, there are cracks in matrix and debonding of fibers due to carbonization shrinkage in the conventional carbon paper. Property measurements show that the former has much better conductivity and gas permeability than the latter. In addition, current density−voltage performance tests also reveal that the pyrocarbon coating can improve the properties of carbon paper used for electrode materials of fuel cell.

Key words: fuel cell; gas diffusion layer; carbon fiber paper; chemical vapor deposition; pyrocarbon coating

1 Introduction

The development of the fuel cell has attracted considerable attention in the world due to global warming as well as problems related to oil supply. As a key part of the fuel cell, the electrode substrate plays an important role in affecting the performance of the fuel cell, thus it is highly desirable to develop high quality electrode materials. As a thin, highly conductive, lightweight matrix with small pores, carbon paper substrate has been considered to be an ideal alternative conductive electrode for fuel cell[1−2].

The carbon paper made from carbon fiber felt displays good processing properties and is thought to be potential electrode material. However, after high temperature heat-treating the carbonization shrinkage becomes large, leading to the change of the structures of the fiber and matrix and the closing of porosity. In addition, resin carbon is difficult to graphitize. All these factors can deteriorate the conductive properties and the thermal performance as well as the mechanical properties of the carbon paper[3]. In order to further improve the comprehensive performance of carbon paper, considerable efforts have been devoted to the decoration and modification[4−7].

Generally, carbon paper is prepared by a conventional method, in which liquid resin materials are impregnated into carbon precursor and subsequently converted into carbon by heating in an inert atmosphere. Various carbon precursors, such as carbon black, carbon paper, in which carbon nanotubes (CNTs) were uniformly grown on carbon fibers via chemical vapor deposition (CVD) method, and its composites displayed significantly facilitated self-humidifying as the membrane of proton exchange membrane (PEM) fuel cells[8−10].

Recently, XIAO et al[11] developed a new method of preparing carbon fiber paper by CVD, in which the carbon fibers were first heated in an inert atmosphere, then exposed to gaseous organic compounds. Usually, hydrocarbons decompose to deposit a coating of pyrocarbon on the fiber surface. Compared with conventional impregnation method, the CVD method proposed by XIAO et al[11] has many advantages, such as increase of homogeneity, decrease of shrinkage and

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cracks and high conductivity.

In the present work, carbon fiber paper decorated by CVD method was reported and conventional carbon fiber paper was produced by impregnation; the properties of the two kinds of carbon fiber papers were examined and studied comparatively.

2 Experimental

2.1 Preparation procedures

To prepare the conventional carbon paper, PAN-based Toray carbon fibers (T300) and phenolic resin (from Ben Pu Plastic Co. Ltd.) were used as raw materials. The phenolic resin was mixed with carbon fibers to make sure that phenolic resin content was 15% (mass fration). The carbon fiber felt was prepared by dry papermaking technology. SEM micrographs of the surface (Fig.1(a)) and the cross-section (Fig.1(b)) of the carbon fiber felt are given in Fig.1, which had area density of 20 g/m^2 and width of 1 000 mm and thickness of 0.5 mm. The carbon fiber felt was cut into pieces of 40 cm×40 cm and then impregnated with phenolic resin mixture, and dried in an oven at a temperature of 50 °C for 30 min. Two carbon fiber felts were molded together to improve the pore size distribution in the carbon paper, and then they were pressed at 180 °C under 2.5 MPa, thus carbon fiber paper was formed. Finally, the carbon fiber paper was graphitized at 2 000 °C in argon with a heating rate of 5 °C/min.

Pyrocarbon was directly deposited on the conventional carbon paper substrates by CVD technology to form the pyrocarbon coated carbon paper. A new chemical vapor deposition set-up had been designed for the growth of pyrocarbon coating. Those samples of conventional carbon papers were placed in a furnace and heated to 1 100 °C at 5 °C/min in nitrogen and the holding time was 1 h. During the carbonization of phenolic resin, the reactive gas (propylene in the present study) was introduced simultaneously with nitrogen (in 1:1 of mass ratio) into the furnace for the pyrocarbon coating. These conditions were maintained for 2 h. Finally, the propylene flow was cut off and the furnace was cooled down to room temperature under flowing nitrogen. Graphitization was performed at 2 000 °C at 5 °C/min under argon gas flow.

In order to investigate the difference of performances between the pyrocarbon coated carbon paper and the conventional carbon paper, those samples with same bulk density (0.45 g/cm^3) and thickness (0.2 mm) were prepared in-house by adjusting preparation process as described above.

2.2 SEM analysis

Those samples were mounted on the sample holder and placed directly in a model Jeol JSM−5600LV to observe the surface morphology, fracture morphology and arrangement of carbon fiber in the carbon fiber paper.

2.3 Electrical resistivity analysis

Those through-plane resistance was measured with two goldplated copper plates by the universal testing machine (WDW−1010), where the sample was kept under an increasing pressure (0−10 MPa) (Fig.2). Samples with 20 mm in diameter were placed between two goldplated copper plates to simulate the

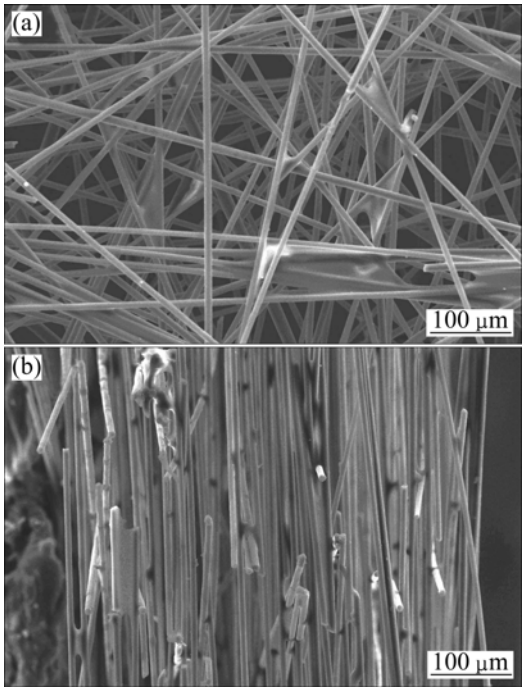

Fig.1 SEM micrographs of surface (a) and cross-section (b) of carbon fiber felt

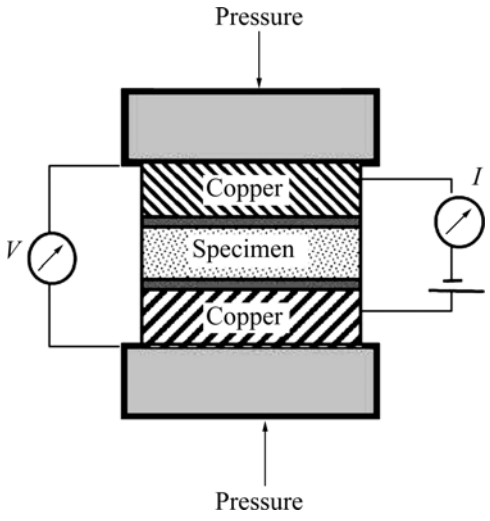

Fig.2 Scheme of experimental setup used in through-plane resistances measurement

interfacial contact in a fuel cell stack. A given current was produced by a programmable power supply (GW INSTEK PSP−2010) through the two gold-coated copper plates, and the resultant voltages were measured by multidisplay multimeter (ESCORT EDM−3150 PRO).

2.4 Gas permeability measurement

Air permeability measurements were carried out in a homemade test facility as shown in Fig.3. After the circular samples were mounted in the annular specimen chamber, the air was allowed to flow into the upper air chamber. The inferior air chamber was open to atmosphere. The pressure drop could be totally ascribed to the gas permeation across the specimen, thus the gas permeability could be calculated through the descending velocity of the pressure in the upper air chamber. The initial pressure in the upper air chamber was 0.03 MPa. The effective diameter of the sample was 35 mm.

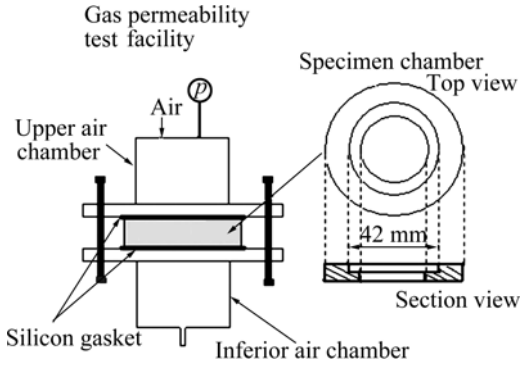

Fig.3 Scheme of gas permeability measurement

2.5 *J* −*V* performance of fuel cell

The cell performance was measured using H_2 as fuel gas and air as oxidant at 60 °C without back pressure. The external humidification temperatures of both H_2 and air were kept constant at 60 °C. H_2 and air flow rates were 300 cm^3/min and 2 000 cm^3/min, respectively. Before recording the performance curve, cells were activated by polarization at a constant current till the performance kept stable.

3 Results and discussion

3.1 Morphology of carbon fiber paper

Morphologies of the surface and cross-section of two samples were observed by SEM, which show obvious distinctions between the pyrocarbon coated carbon paper and the conventional carbon paper. Fig.4 shows the micrographs of the surface and the cross-section of the pyrocarbon coated carbon paper produced using the conventional carbon paper coated by CVD pyrocarbon. In Fig.4, it can be seen that pyrocarbon coating grown by CVD uniformly covered

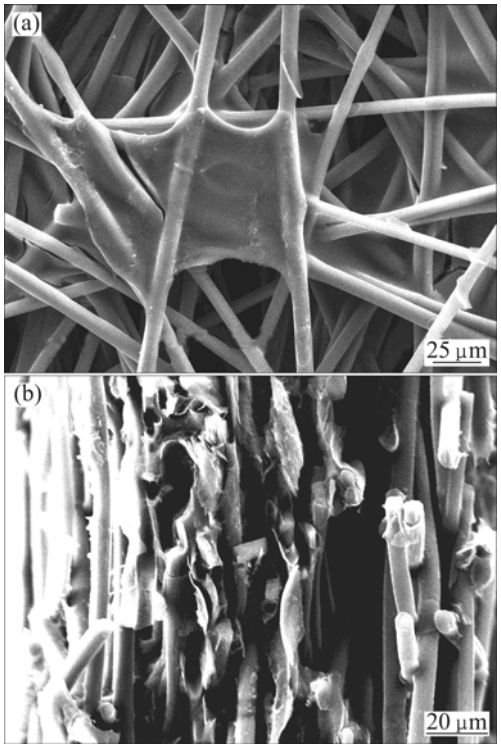

Fig.4 SEM micrographs of surface (a) and cross-section (b) of pyrocarbon coated carbon paper

the carbon fibers and no visible fraction of bare fibers was observed. It can be roughly estimated that the coating thickness ranged from 1 to 3 μm. SEM images show that fibers were encapsulated in pyrocarbon sheaths which were connected with each other. The pyrocarbon deposited at intersecting positions of the carbon fibers acted as binding adhesives between fibers, thus making fibers bind effectively and seamlessly. The matrix mainly formed by uniform pyrocarbon sheaths around each fiber ultimately resulted in a homogenous joint of fiber/matrix interface, which means that there were more routes for electron transmission. After graphitization, there was not cracking producing in pyrocarbon, which kept the fibers to bind tightly together, creating the desired carbon fiber paper. From this morphology analysis, it can be inferred that the pyrocarbon coated carbon paper would contribute to the improvement of mechanical property, electrical property and gas transport of the gas diffusion layer (GDL).

The matrix cracking and fiber-matrix interfacial debonding were observed for the conventional carbon paper in Figs.5 (a) and (b). Some visible fractions of bare fibers were also observed. The matrix carbon was not uniformly distributed in the conventional carbon paper. The carbonization shrinkage was found to be 15% at 1 000 °C and 39% at 2 000 °C. The conventional carbon paper was prepared from PAN-based carbon felt through impregnation with resin, molding and heat-treatment at

1 000 °C. This process eliminated volatile elements from the matrix and carbonized them. The appreciable matrix shrinkage that occurred during carbonization generated pores and cracks at fiber/matrix interface. Differences between the coefficient of thermal expansion of the fibers and matrix also generated internal stress cracks during cooling[12]. The carbonized solid, therefore, might exhibit a low mechanical property and electrical property.

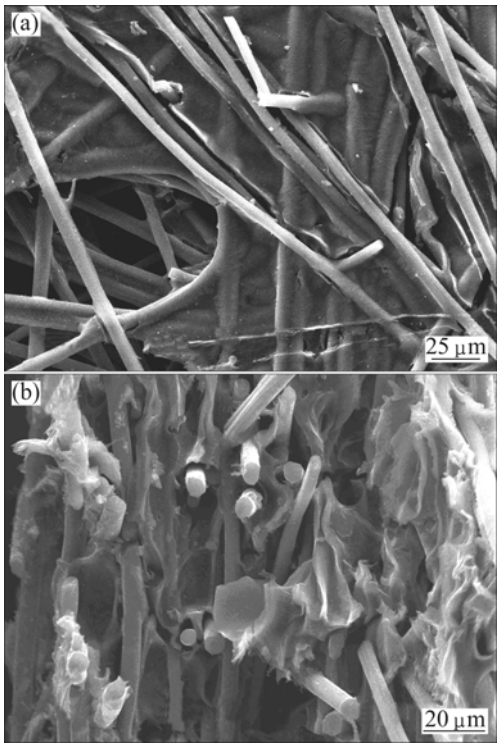

Fig.5 SEM micrographs of surface (a) and cross-section (b) of conventional carbon paper

3.2 Electrical resistivity

As shown in Fig.6, the through-plane resistances of both pyrocarbon coated and conventional carbon papers decreased with the increase of pressure and reached 3.9 and 10.4 mΩ·cm^2 at pressure of 0.98 MPa, respectively. The conventional carbon paper displayed through-plane resistance of 2.5 times higher than pyrocarbon coated carbon paper, indicating that fibers and matrix are electrically well connected with each other by CVD pyrocarbon coating resulting in the significant decrease of through-plane resistance for pyrocarbon coated paper. Due to the deposition of pyrocarbon, some matrix cracks were filled, and debonded fibers were rebounded. In addition, the pyrocarbon coated carbon paper may reduce the electric contact resistance due to the pyrocarbon deposition at intersecting positions of the carbon fibers. Therefore, despite that pyrocarbon coated carbon paper had less compact internal structure and higher apparent porosity than conventional carbon paper, carbon fiber and carbon matrix formed three-dimensional conductive network, leading to desired lower values of through-plane resistances[13]. These results show that the pyrocarbon coated carbon paper is significantly useful to improving the electrical performance of PEM fuel cells.

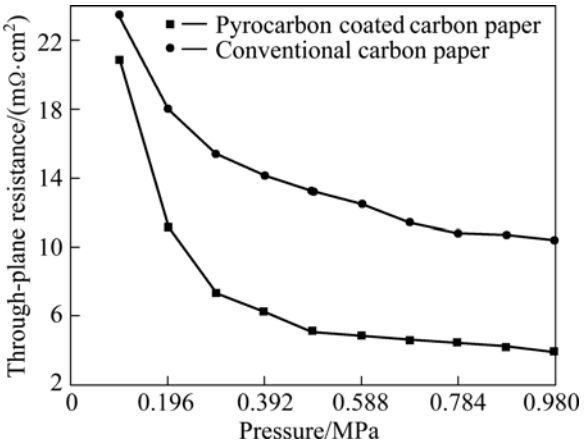

Fig.6 Variations of through-plane resistances of carbon fiber paper with pressure

3.3 Gas permeability

Fig.7 shows gas permeability and pressure difference curves for pyrocarbon coated and conventional carbon papers. This graph reveals that gas permeabilities of two carbon paper samples increase linearly with the increase in pressure difference. Regression relation expressions of two carbon samples between the gas permeability and pressure difference are: y=0.18x+1.23 and y=0.17x+1.08, respectively. It is clear that two slopes of the two lines are very close, while pyrocarbon coated carbon paper displays an increase in gas permeability of approximately 10% under the same operating condition. It is well known that carbon paper with high gas permeability has good electrochemical performance as a fuel cell electrode substrate. However, the pore size and its distribution in the carbon paper have been paid more attention to avoid the electrode flooded and electrochemically inactive. In the process of CVD, the reactant gas would take the path of least resistance to flow and deposit, i.e. a large pore of carbon paper. Thus, the size of the large pores and the number of large pores reduced effectively, leading to a more uniform distribution of gas. On the other hand, since fiber surface and matrix cracks possessed high chemical activity, carbon source gas might undergo prior decomposition and deposition of carbon coating or chemical reaction on fiber surface or matrix crack, especially on interface of fibers. Pyrocarbon coated carbon paper had less compact internal structure and higher apparent porosity than conventional carbon paper, increasing the gas permeability within the carbon paper. As has been

demonstrated by WANG et al[14] and LIANG and CHENG[15], highly tortuous structure of the carbon paper led to severe mass transport limitation under high-humidity operations. In contrast, in a modified process, most of the matrix was present in form of bulk matrix with lower gas permeability. Fig.7 reveals that increasing the ratio of CVD pyrocarbon to resin carbon can yield higher gas permeability.

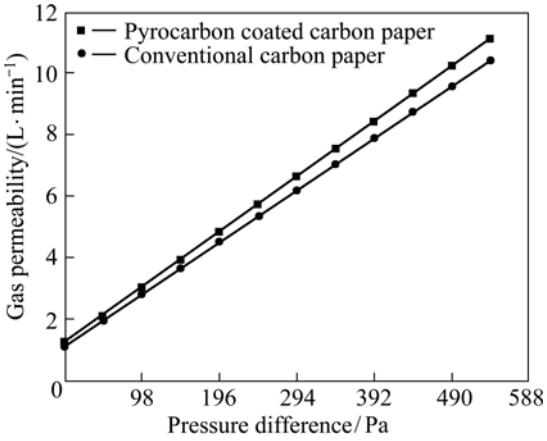

Fig.7 Variations in gas permeability of carbon fiber paper with pressure difference

3.4 Current density−voltage performance

Fig.8 presents the comparative performance of the fuel cell with pyrocarbon coated and conventional carbon papers at 60 °C and 100% relative humidity, and the excess coefficients of H_2 and air were 1.25 and 4 respectively. Under this operating condition, the pyrocarbon coated carbon paper shows a current density of 700 mA/cm^2 at 0.6 V, whereas a current density of 500 mA/cm^2 at 0.6 V was recorded for the conventional carbon paper, which is 70% that recorded for pyrocarbon coated carbon paper. The improvement in performance for pyrocarbon coated carbon paper is probably due to its higher conductivity, which helps to reduce the Ohmic resistance in Ohmic region. At higher current densities, the polarization curves of two samples displayed a decrease in voltage, and conventional carbon paper showed a more rapid decrease. This was probably because of its lower gas permeability leading to an increase of concentration losses due to mass transport[13, 16], and thus resulting in a decrease in the performance. These results indicate that the pyrocarbon coated carbon paper is promising to improve the electrochemical performance of PEM fuel cell.

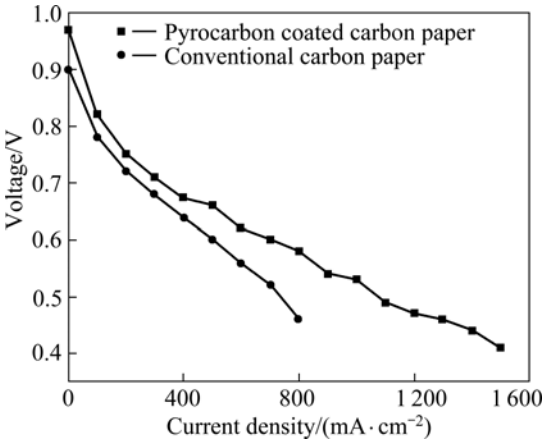

Fig.8 Polarization curves of carbon fiber paper samples

4 Conclusions

1) The pyrocarbon coated paper and conventional carbon paper were prepared in-house, and two samples were applied to the GDL of PEM fuel cell. Two samples with thickness of 0.2 mm and bulk density of 0.45 g/cm^3 were produced after heat-treatment above 2 000 °C.

2) Measurements of morphology, through-plane resistances, gas permeability and electrochemical behavior indicate that the deposition of pyrocarbon can eliminate the matrix cracks and rebond the debonded fibers to make carbon fiber and carbon matrix form an organic network, which is significant to electric conductivity, gas permeability and thus polarization performance of PEM fuel cells.

3) The polarization curve of the carbon fiber paper shows that the pyrocarbon coating by CVD is a promising approach to effectively improving the comprehensive performances of carbon paper for PEM fuel cells.

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References

[1] LEMONS R A. Fuel cells for transportation [J]. Journal of Power Sources, 1990, 29: 251−264.

[2] LIU C H, KO T H, CHANG E C, LYU H D, LIAO Y K. Effect of carbon fiber paper made from carbon felt with different yard weights on the performance of low temperature proton exchange membrane fuel cells [J]. Journal of Power Sources, 2008, 180: 276−282.

[3] MATHUR R B, MAHESHWARI P H, DHAMI T L, TANDON R P. Characteristics of the carbon paper heat-treated to different temperatures and its influence on the performance of PEM fuel cell [J]. Electrochimica Acta, 2007, 52: 4809−4817.

[4] LIU C H, KO T H, LIAO Y K. Effect of carbon fiber paper made from carbon felt with different yard weights on the performance of low-temperature proton exchange membrane fuel cells [J]. Journal of Power Sources, 2008, 178: 80−85.

[5] MATHUR R B, MAHESHWARI P H, DHAMI T L, SHARMA R K, SHARMA C P. Processing of carbon composite paper as electrode

for fuel cell [J]. Journal of Power Sources, 2006, 161: 790−798.

[6] SAHA M S, LI Ru-ying, SUN Xue-liang, YE Si-yu. 3-D composite electrodes for high performance PEM fuel cells composed of Pt supported on nitrogen-doped carbon nanotubes grown on carbon paper [J]. Electrochemistry Communications, 2009, 11: 438−441.

[7] SAHA M S, LI Ru-ying, SUN Xue-liang. Composite of Pt-Ru supported SnO_2 nanowires grown on carbon paper for electrocatalytic oxidation of methanol [J]. Electrochemistry Communications, 2007, 9: 2229−2234.

[8] DU Chun-yu, WANG Bao-rong, CHENG Xin-qun. Hierarchy carbon paper for the gas diffusion layer of proton exchange membrane fuel cells [J]. Journal of Power Sources, 2009, 187: 505−508.

[9] SUN X, STANSFIELD B, DODELET J P, DESILETS S. Growth of carbon nanotubes on carbon paper by Ohmically heating silane-dispersed catalytic sites[J]. Chemical Physics Letters, 2002, 363: 415−421.

[10] BORDJIBA T, MOHAMEDI T, Lê DAO H, AISSA B, EL-KHAKANI M A. Enhanced physical and electrochemical properties of nanostructured carbon nanotubes coated microfibrous carbon paper [J]. Chemical Physics Letters, 2007, 441: 88−93.

[11] XIAO Yong，HUANG Qi-zhong，CHANG Xin，WANG Xiu-fei，GUO Jun. Carbon fiber paper fabricated by CVD for application of proton exchange membrane fuel cell [J]. Journal of Central South University: Science and Technology, 2008, 39: 1119−1223.

[12] JULIUS J. Macroporosity and interface cracking in multi-directional carbon-carbons [J]. Carbon, 1986, 24: 603−613.

[13] O'HAYRE R P, CHA S W, COLELLA W, PRINZ F B. Fuel cell fundamentals [M]. New York: John Wiley and Sons Inc, 2006: 93.

[14] WANG Yun, WANG Chao-yang, CHENB K S. Elucidating differences between carbon paper and carbon cloth in polymer electrolyte fuel cells [J]. Electrochimica Acta, 2007, 52: 3965−3975.

[15] LIANG Hao, CHENG Ping. Lattice Boltzmann simulations of anisotropic permeabilities in carbon paper gas diffusion layers [J]. Journal of Power Sources, 2009, 186: 104−114.

[16] KONG C S, KIM D Y, LEE H K, SHUL Y G, LEE T H. Influence of pore-size distribution of diffusion layer on mass-transport problems of proton exchange membrane fuel cell [J]. Journal of Power Sources, 2002, 108: 185−191.

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