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Anode optimization based on gradient porous control medium for passive liquid-feed direct methanol fuel cells

Wei Yuan*, Zhiguo Yan, Zhenhao Tan, Aoyu Wang, Zongtao Li, Yong Tang

School of Mechanical and Automotive Engineering, South China University of Technology, Wushan Road 381, Guangzhou 510640, PR China

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ABSTRACT

The direct methanol fuel cell (DMFC) is a potential candidate to be used as a portable power source which still faces great challenges in structure optimization because of complex interactions and even conflicts between the reactant and product managements. This work presents an effective method for the anode optimization by using a gradient porous medium to realize more active control of the anode mass transfer mechanisms of a passive liquid-feed DMFC. This functional medium is made of a self-developed metal fiber sintered felt based on multi-tooth cutting and high-temperature sintering. Its structural features and processing parameters can be adaptively controlled according to the application requirement. Results indicate that the porosity, assembly pattern and thickness of this gradient porous medium have great effects on the cell performance. The DMFC is insensitive to the change of sintering process. The use of a gradient porosity promotes a higher cell performance than the uniform structure, especially when a lower porosity is used inward. How the methanol concentration affects the cell performance is also discussed in this study.

1. Introduction

With the rapid development of electronic products such as notebook, mobile phone and panel computer, a surge of demand for portable power sources with higher sustainability urges people to explore more advanced technology for power supply. Emergence of fuel cell technology sheds light on the likelihood of producing electricity with a longer endurance only if the fuel is continuously supplied. In this field, the direct methanol fuel cell (DMFC) is thought of as a promising candidate for portable applications owing to its high energy density, low emission, compact configuration and convenient operation [1,2]. Particularly, when the DMFC is operated in a fully passive manner with an open anode filled with liquid fuels and a self-breathing cathode exposed to the surrounding air, its energy density can be further enhanced for lack of auxiliary devices. However, a passive DMFC mostly suffers from severe power losses due to methanol crossover (MCO) [3], catalytic inactivity [4] and mass transfer inertia [5]. To address these issues, researchers and technicians have made great efforts to optimize its structure design [6,7] especially on the anode side.

Optimizing the anode structure is of great significance to improve the cell performance of a passive liquid-feed DMFC, because the mass transfer activities related to methanol, water and produced gas (i.e. CO_2) mostly take place at the anode. For a passive DMFC, methanol spontaneously permeates through the passages constructed by the flow field plate and diffusion layer, and arrives at the catalytic layer to take part in the reaction. The extra methanol tends to move across the membrane and reacts directly with the oxygen at the cathode, producing a mixed potential that necessarily drags down the voltage output. In this situation, how to minimize the effects of MCO comes to be an intractable issue regarding the anode optimization. To this end, some studies resort to methanol control layers by using permeable but resistant materials like the porous graphite [8–11], porous metals [12–14] and polymers [15–18] to mitigate the MCO. This functional layer acts as not only a methanol barrier but also a porous flow field that assists in regulating transport and distribution of the methanol fuel. Despite this, it is still imperative to supply sufficient methanol in order to prevent severe concentration polarization in the reaction area especially for high-current discharging. This matter also deserves attention when optimizing the anode structure and cell performance.

Another dominant problem for anode structure optimization is how to efficiently remove the gas bubbles from the electrode to the

* Corresponding author.
E-mail address: mewyuan@scut.edu.cn (W. Yuan).

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outside. In a passive DMFC, the produced bubbles are subject to spontaneous mass transfer and evolvement processes, making it more difficult to optimize the gas releasing behavior. What is worse, if the gas bubbles cannot be expelled in time, they may block the methanol flow paths and thus induce performance degradation due to methanol starvation. An effective method for improving the bubble removal behavior and also methanol management is to optimize the micro- and macro-structures of the diffusion medium [19–28].

Some researches focus on structural optimization of the catalyst layer, but such experiences are not always limited to passive DMFCs. Xie et al. [29] created a three-dimensional electrode by depositing the catalysts on polypyrrole treated polystyrene spheres in order to achieve a coexistent structure with big and small holes or channels which could cause a pressure difference inside the electrode. Suo et al. [30] attempted to use a double-catalytic layered electrode to construct catalyst concentration gradient, hydrophilicity gradient and porosity gradient. This structure was proven beneficial to MCO reduction. Wang et al. [31] designed a double-layer catalyst structure to reduce the MCO and assimilate mixed potential losses. Chen et al. [32] constructed a discontinuous hydrophobicity gradient distribution in the catalyst layer to enhance oxygen diffusion and water removal.

Now it is clear that it is quite essential to optimize the anode structure of a passive DMFC since it relates to whether the reactants and products can be properly controlled. In this regard, using a porous structure to make the flow field, diffusion layer and catalyst layer has been commonly validated [12]. The above background also suggests that there exist complex interactions and even conflicts among the involved mass transfer mechanisms such as methanol delivery, MCO control and gas bubble removal. Considering this, in this work, we introduce a porous medium for mass transfer control to the anode of a liquid-feed passive DMFC. This functional component owns a three-dimensional network structure with a gradient porosity through the thickness. The fabrication process for this component is based on the self-made metal fibers. This method helps easily realize effective control of the processing parameters and thereby the mass transfer characteristics, and also breaks through the limitation of using traditional chemical method to gain enough hydrophobicity because the cutting-based fibers naturally own very rough surfaces. As a mass transfer regulating medium, its gradient porosity can be formed within an integrated object with no need for using different layers to make multiple porosities. This is favorable to component assembly. A more outstanding merit of using this method is that the porosity gradient must yield a flow resistance difference along the bubble escaping passages so as to form a self-driven force to enhance bubble removal. Such a porous, gradient and rough structure provides adaptable functions to strengthen both reactant and product managements. However, how this special mass transfer medium affects the cell performance is still worthy of more in-depth investigation. In this context, in this study we aim to validate the feasibility of applying this functional component for anode optimization and disclose the influence mechanisms of a series of structural and operational factors.

2. Experimental

2.1. Fuel cell design and fabrication

The real appearance of the single DMFC passively fed with liquid methanol is illustrated in Fig. 1. For the convenience of visualization, the anode compartment was made transparent by using the acrylic material. A fuel reservoir with a size of 30 mm (length) × 30 mm (width) × 12 mm (depth) was built in the anode chamber. Two holes were drilled at the top of the chamber for fuel injection and gas escape. The anode and cathode current collectors were both made of SUS316L. The anode current collector used a thoroughly open pattern like a square frame, while the cathode used parallel through channels to form an air-breathing window with an open ratio of 63%. A metallic porous medium with a gradient porosity for active control of the mass transfer processes was embedded into the shallow groove of the anode current collector, which directly contacted the electrode. This functional layer acted as a flow field and also an enhanced diffusion medium to regulate the transport of both reactants and products. A seven-layer membrane electrode assembly (MEA) was sandwiched between the anode and cathode current collectors. A tailored polytetrafluoroethylene (PTFE) film was used to prevent leakage between the edged membrane and current collector while a silicon rubber gasket was used to seal the gap between the fuel chamber and current collector. All the components were laminated in series and fastened by using eight M4 bolts.

2.2. Manufacture and characterization of the gradient porous medium

The gradient porous component was made of a copper-fiber sintered felt (CFSF), as shown in Fig. 1. The whole process for CFSF fabrication included the fiber cutting and sintering stages. A copper rod fitted on the horizontal lathe (C6132A) was used to make continuous long fibers. A multi-tooth cutter was employed to simultaneously produce multi-threads of copper fibers. Detailed parameters for tool design and fiber cutting have been reported in our previous study [33]. Before sintering, the fibers were cleaned and segmented into small pieces with a certain length, e.g. 10 mm in this work. The shape and size of the CFSF could be controlled by using a mold assembly to make it compatible with the electrode profile, and its porosity could be controlled by setting the ratio of volume vs. weight. The CFSF thickness could be regulated by inserting one or more movable plates with a unit thickness of 1 mm. The copper fibers were filled into the mold cavity by hand, which were distributed randomly. In the sintering stage, the mold assembly was put into a programmable high-temperature atmosphere furnace. The sintering time and temperature in each substage followed the sequences shown in Fig. 2. The furnace chamber was purged with nitrogen before starting, and then filled with hydrogen gas to form a reductive environment at a constant pressure of 0.3 MPa. After the air-cooling treatment, the samples could be ready for use.

The amplified structure of the CFSF was characterized by using the scanning electronic microscopy (SEM). Fig. 3 depicts the morphological details of the CFSF samples with different porosities. It is clear that the use of a higher porosity yields a loose structure and thereby provides less resistance to the reactant and product transport. In order to construct a gradient structure, we must combine at least two layers with different porosities together to create an integrated porous medium. In this study, two types of gradient porous medium were produced by either one-step (#1) or two-step (#2) sintering. In the former case, the multi-layer structure of the porous medium was formed in the mold-filling stage. An alternative way is to separately fabricate the single-layer CFSFs with different porosities and subsequently sinter them together to form an integral porous sheet with a gradient porosity. Unless otherwise stated, the thickness of a single layer is 1 mm. For comparison, we prepared a reference sample with a homogeneous porosity and a thickness of 2 mm.

To inspect the flow characteristics of the gradient samples, permeability tests were conducted to quantify the relation between the flow rate and differential pressure. A schematic of the testing