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Effect of fabrication and operating parameters on electrochemical property of anode and cathode for direct methanol fuel cells

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ABSTRACT

A quick and simple method for optimizing assembly force of the direct methanol fuel cell has been introduced. Meanwhile, the effect mechanism of operating parameters on fuel cell performance and the properties of single anode and cathode have been intuitively investigated by a three-electrode system in this paper. The impedance curves indicate that internal resistance is the suitable intermediate to connect assembly torque and assembly force. The cathode polarization curve and limiting current density of methanol crossover are shown that the increasing methanol concentration markedly exacerbates the polarization in cathode due to serious methanol crossover phenomenon. Also, the higher cathode backpressure mainly improves cathode property, and lowers methanol crossover simultaneously. Finally, the summaries of peak power densities prove that the main factor that affected the optimal flow rates of methanol and oxygen is not the concentration or backpressure, but the working temperature.

1. Introduction

Direct methanol fuel cells (DMFCs) are topical interest as portable electric sources for portable multi-functional electronic devices and light-duty vehicles due to easy fuel storage, low operating temperature and simple structure [1]. Recently, many research teams have been concentrated on the catalyst with high activity, proton exchange membrane with good methanol resistance and dimensional stability, catalyst layer and diffusion layer with high mass transfer efficiency to improve the DMFC performance [2]. Thiam et al. [3] adopted Pd-SiO_2 fiber as inorganic fillers in Nafion recast membrane to effectively reduce methanol crossover in DMFC applications. Zainoodin et al. [4] introduced carbon nanofiber layer as porous layer in membrane electrode assembly for DMFC, and optimized Nafion content and the carbon loading. Chaisubanan et al. [5] modificated PtCo/C catalyst layer via TiO_2 to enhance the property for oxygen reduction reaction. But besides that, assembly force and operating conditions of a single cell are also major factors to influence the DMFC performance [6]. Unfortunately, until now, there have still been two shortcomings: (1) the methods for detecting assembly force have been still complex, and (2) the influence mechanisms of operating parameters on single cathode and singe anode have been also never presented directly.

As for detection of the assembly force for DMFCs, there have been two main methods. One is simulation using a finite element model [7]. And the other one is an *in-situ* detection technology though a pressure-sensitive paper [8]. Some researchers investigated the effect of assembly pressure distribution on the fuel cell performance, and also optimized structure of fuel cell and assembly parameters (for example, the number of screws) [9]. Combining both the two methods aforementioned, Lee et al. [10] verified the simulation result of the assembly pressure by a pressure-sensitive film. Obviously, the pressure-sensitive paper was used to provide the direct experimental evidence of assembly force as the key medium. Meanwhile, some researchers studied on the effect of the clamping pressure on the diffusion layer, stack performance and contact resistance [11]. Chang et al. [12] systematically analyzed the effect of assembly force on properties of the

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gas diffusion layer shach as porousity, gas permeability, electrical resistance and thickness. Oyarce et al. [13] studied on contact resistance between gas diffusion layer and bipolar plate under different assembly forces. Unfortunately, the value of assembly force couldn't be obtained quickly using the current methods. And all the explanations of the effect mechanism of assembly force were based on the whole polarization curve of fuel cell.

In respect of optimization of operating parameters, many effective works were analyzed and characterized by two-electrode test system. Some groups studied on the effect of operating parameters such as working temperature, methanol concentration, methanol flow rate and cathode flow rate on open circuit voltage (OCV) of DMFC and the integrated polarization curve of both anode and cathode [14]. By measuring limiting current density of methanol crossover, Seo et al. [15] determined the methanol crossover and efficiency of a DMFC under various operating conditions (for example, the cathode backpressure), and proved that the efficiency of the DMFC was closely related with methanol crossover. Combining modeling study, Falcao et al. [16] investigated the effect of important operating parameters by experimental polarization curves of the DMFC and confirmed that the simplified model was suitable for real-time simulation. Similarly, all of the analysis for operating parameters were also based on the whole polarization curve of fuel cell.

Therefore, to solve the two shortcomings, herein, a quick and simple method for detecting and optimizing assembly force, and the effect of operating parameters on the properties of the single anode and cathode were investigated by a three-electrode system, which intuitively revealed the influence mechanism of these assembly and operating parameters on anode and cathode, separately. Meanwhile, the key factor that affected the optimal flow rate of methanol and oxygen (O_2) was discovered in this paper.

2. Experimental

2.1. Perparation of membrane electrode assembly and single cell

The Nafion® 115 membrane and gas diffusion layers were pretreated by reported method [17]. The catalyst slurries consisting of Pt-Ru (1:1 atomic ratio of Pt to Ru, Johnson Matthey)/Pt black (Johnson Matthey), Nafion solution (5 wt% solution, EW1000, Dupont) and isopropanol were prepared in ice-bath with ultrasonic dispersion for 1 h and were uniformly sprayed by the sono-tek membrane electrode assembly (MEA) ultrasonic spray system onto Teflon decal blanks until the noble metal loadings reached to 4.0 mg cm^{-2} for anode/cathode catalyst layer, respectively. A catalyst coated membrane was obtained by transferring the catalyst layers from Teflon decal blanks to the pretreated Nafion115 via the decal method under the condition of 135 °C, 75 kg cm^{-2} for 3.5 min. Each MEA with working area of 5 cm^2 was assembled by sandwiching the resulting catalyst coated membrane between anode and cathode diffusion layers for multi-step activation and further test [18].

Principle part of the single cell was fabricated by sandwiching the MEA between two graphite plates with Teflon gaskets [19]. Copper plates that coated with gold were used as current collectors and located outside the graphite plates [20]. Two thick stainless-steel end plates with six bolts were used to compress the overall assembly. And the assembly force of the cell was controlled by a torque wrench.

2.2. Assembly force test of membrane electrode assembly

The fuel cell was assembled by a torque wrench (as shown in Fig. S1) after full wetting MEA. And then the internal resistance of DMFC was tested under various assembly torques. The test procedure of real stress state of MEA was described as follows. After wetted fully, MEA with saturated humidity was placed between two pieces of carbon plywoods without seals in the MEA assembly pressure test device shown in Fig. S2. Lifting jack and pressure sensor were used to pressure the MEA and detect the pressure value, respectively. Subsequently, two carbon plywoods were connected with working electrode and counter electrode, respectively, of an electrochemical integrated test system (VMP2, Princeton Applied Research) to test internal resistance of the MEA under different assembly forces. Finally, the corresponding relationship between assembly torque and assembly force could be obtained at the same internal resistance value.

2.3. Electrochemical measurements

Methanol solution and O_2 with various concentrations/backpressures and flow rate were fed to anode and cathode, respectively. Polarization tests were carried out with VMP2. With saturated calomel electrode as reference electrode, the three-electrode system was used to detect the polarization potential of work electrode, and saturated K_2SO_4 aqueous solution was used as electrolyte in salt bridge. The internal impedance measurements of MEAs were carried out at open circuit voltage with the frequency varying from 99 kHz to 9 Hz. Electrochemical impedance spectroscopy (EIS) test was carried out at 0.4 V with the frequency ranging from 99 kHz to 9 mHz.

The methanol crossover was measured by voltammetry with the scanning speed of 2 mV s^{-1} at 55 °C. The cathode of MEA was used as work electrode and fed humidified argon with a series of backpressures (i.e. 0, 0.1, 0.2 and 0.3 MPa), and the anode fed methanol solution as reference electrode and counter electrode.

3. Results and discussion

3.1. A simple method for detecting and optimizing assembly force

Due to easy operation, as shown in Fig. S1, the torque wrench has always been used to quantitatively fabricate DMFCs. However, the resulted assembly force inside of MEA is hard to measure. To determine it, a simple method, using the internal resistance of DMFC as an intermediate parameter to connect assembly force and torque, was introduced here. Fig. 1 presents the internal resistance curve along with assembly force and torque under different temperatures and the corresponding relationship between assembly force and torque based on the same internal resistance value. With assembly torque increasing from 3 to 8 N m, the resistance decreased at every temperature (for example, from 0.841 to 0.444 Ω cm^2 at 30 °C), and the declining rate gradually became slow at 5 N m. Meanwhile, the variation trend of internal resistance with assembly force was similar, for example, from 0.841 to 0.444 Ω cm^2 at 30 °C, and the turning point of the curve slope was 344.8 N, and the pressure was 689.6 kPa. The assembly force and torque value at the same internal resistance could be one-to-one correspondence to form a curve with the error less than 0.74% shown in Fig. 1. Therefore, the real stress force of MEA was 344.8 ± 2.8 N when the assembly torque was 5 N m.

Fig. 2 shows the polarization curves of the DMFC, anode and cathode under different assembly torques. As shown in Fig. 2a, the highest power density peak was 75.41 mW cm^{-2} at 5 N m of assembly torque. When current density was larger than 150 mA cm^{-2}, the most serious ohm polarization appeared in the DMFC assembled by 4 N m. While the torque was up to 6 N m, concentration polarization phenomenon emerged observably at more than 480 mA cm^{-2}. It can be seen from Fig. 2b that assembly