A gradient activation method for direct methanol fuel cells

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ABSTRACT

To realize gradient activation effect and recover catalytic activity of catalyst in a short time, a gradient activation method has firstly been proposed for enhancing discharge performance and perfecting activation mechanism of the direct methanol fuel cell (DMFC). This method includes four steps, i.e. proton activation, activity recovery activation, H_2-O_2 mode activation and forced discharging activation. The results prove that the proposed method has gradually realized replenishment of water and protons, recovery of catalytic activity of catalyst, establishment of transfer channels for electrons, protons, and oxygen, and optimization of anode catalyst layer for methanol transfer in turn. Along with the novel activation process going on, the DMFC discharge performance has been improved, step by step, to more than 1.9 times higher than that of the original one within 7.5 h. This method provides a practicable activation way for the real application of single DMFCs and stacks.

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1. Introduction

The direct methanol fuel cell (DMFC), as one of the most prospective fuel cells, is attracting considerable attention and research due to its easy fuel storage, simple assembly process, low running temperature [1]. As shown in Fig. S1, DMFCs possess wide application prospects, especially, as power source for portable multi-functional electronics within several hundreds watt (for example, a 50 W level of home-made DMFC stack exhibited in Fig. S2). Although plenty of resultful works have been studied and reported, low discharge performance has also been one of the biggest challenges for commercialization [2].

To enhance the performance of DMFCs, some research teams focused on fabrication of novel proton exchange membranes with high proton conductivity and low methanol crossover [3]. And, lots of works were done to develop many methods for preparing new catalysts with high activity, and novel catalyst layers with three-dimensionally ordered structure [4]. Also, many effective results focusing on diffusion layers with suitable hydrophobicity-hydrophilicity, and good flow field plate with excellent mass trans-

fer property have been obtained [5]. The rest of researchers analyzed the effect of assembly and operating parameters on the DMFC performance [6]. Meanwhile, it's well known that the activation process is an important factor affecting discharge performance of proton exchange membrane fuel cells (PEMFCs) [7]. Likewise, the activation process is also needed to improve the discharge performance and realize the optimal discharge state in a short time for DMFCs [8]. Unfortunately, until now, to the best of our knowledge, few reports have focused on development of the activation method for DMFCs.

Regarding activation procedures for DMFCs, current studies have focused on the single activation method or comparison of single activation procedures [9]. Combining with boiling pretreatment for different proton exchange membranes (PEMs), Silva et al. [10] designed an *in situ* discharging activation protocol at 200 mV for more than 15 h, and found that their activation process improved proton conductivity of PEM and activity of catalyst layer. After comparing four kinds of activation methods such as methanol circulation, methanol circulation and electric load, methanol circulation plus gas evolution, and H_2-O_2 PEMFC mode, Zhao et al. [11] believed that the combination of methanol circulation and electric load is a convenient and effective *in situ* way to activate the fresh membrane electrode assemblies (MEAs) for DMFCs, and the hydra-

tion in MEA is the maximum benefit. Also introducing the H_2-O_2 PEMFC mode into an activation process for DMFCs, Inoue et al. [12] reported a two-step activation method by using the PEMFC mode for 3 h and DMFC mode for 27 h, and obtained more than 1.4 times higher maximum power density than that of the one activated through a conventional method. The problems of the aforementioned activation methods for DMFCs are their long activation time and less influence on the catalytic activity of catalyst.

It's clear that the reduced Pt-metal catalyst possesses the highest catalytic activity [13], and the single Pt-based catalyst is easily poisoned by alcohols [14]. Sad to say, micromolecule alcohols have been usually used as disperser in catalyst slurries. Therefore, we believe that the recovery of catalytic activity of the Pt-based catalyst should be added into the activation process for DMFCs.

Herein, to realize gradient activation effect and introduce recovery function of catalytic activity of catalyst in a short time, we firstly investigated a novel gradient activation method for enhancing the DMFC discharge performance, perfecting the activation mechanism, and shortening the activation time.

2. Experimental

2.1. Preparation of membrane electrode assembly and fuel cell

Du Pont™ Nafion® 115 membrane was boiled in 5 wt.% H_2O_2 solution, distilled water, 0.5 mol L^{-1} H_2SO_4 solution and then distilled water, respectively, at 80 °C for 1 h per step [15]. Commercial carbon paper with micro-porous layer (H2315T10AC1 NOL, Japan) was pretreated through the methods reported in [16] for serving as diffusion layers. The catalyst layers were prepared as follow our previous paper [17] by a sono-tek MEA ultrasonic spray system shown in Fig. S3. The dispersant in the catalyst slurries was isopropanol. A catalyst coated membrane presented in Fig. S4, was obtained by transferring the catalyst layers from Teflon decal blanks to the pretreated Nafion115 via a decal method under a 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 to fabricate a fuel cell (shown in Fig. S5). 6 MEAs prepared under the same conditions were entitled as H-1 ∼ H-6 for different activation processes. The operation details of the activation processes and the corresponding MEAs were shown in Table S1.

2.2. Activation design for DMFCs

In this paper, four kinds of single activation methods and the gradient activation procedure were designed and carried out at 55 °C.

(1) Single proton activation

As for the proton activation method, two ways including water activation and acid activation, were explored. Water was fed to anode of the H-1 based DMFC with 2.5 mL min^{-1} at 25, 55, and 80 °C by a peristaltic pump, respectively, for 7 h, which was named as water activation. Acid activation was operated for H-2 as follow: 0.5 mol L^{-1} of H_2SO_4 was fed to anode of fuel cell instead of water at 55 °C for 3 h.

(2) Single activity recovery activation

Cathode fed with water was used as working electrode, and anode fed with H_2 of 360 mL min^{-1} under atmospheric pressure

as counter electrode and reference electrode. A cyclic voltammetry technology was used to scan the cathode of H-3 with potential window of 0–0.6 V (or 0–1.2 V) and scanning rate of 50 mV s^{-1}.

(3) Single H_2-O_2 mode activation

Humidified H_2 and O_2 with flow rate of 360 mL min^{-1} and atmospheric pressure were fed into anode and cathode of H-4, respectively, to assembly H_2-O_2 fuel cell. The discharging voltage range was 0.8–0.5 V.

(4) Single forced discharging activation

0.2 MPa O_2 with 670 mL min^{-1}, and 1.5 mol L^{-1} methanol with 5 mL min^{-1} were fed into cathode and anode of H-5, respectively, for discharging at a continuous current of 200 mA cm^{-2} for 2 h.

(5) Gradient activation

The gradient activation process was performed for H-6 at 55 °C as follow: firstly, acid activation step was carried out by 0.5 mol L^{-1} H_2SO_4 solution for 3 h; secondly, activity recovery activation step with potential range of 0–1.2 V was performed for cathode by feeding distilled water and H_2 to cathode and anode, respectively; subsequently, H_2-O_2 mode activation step and forced discharging activation step were done according to part (3) and (4) in order.

2.3. Measurement and characterization

Anode and cathode of the DMFC were provided with methanol solution (2.5 mL min^{-1}) and O_2 (670 mL min^{-1}), respectively. Polarization tests were carried out at a VMP2 system (Princeton Applied Research) at 55 °C. The electrochemical impedance spectroscopy (EIS) was obtained at 0.4 V with the frequency ranging from 99 kHz to 9 mHz. Surface morphologies of the anode catalyst layer in this experiment were observed by a Cambridge S-360 scanning electron microscope (SEM).

3. Results and discussion

All the MEAs (H-1∼H-6) were prepared at the same condition. Fig. S6 shows the polarization curve and internal resistance of the MEAs without any activation. The average peak power density and internal resistance of these MEAs were 61.12 mW cm^{-2} with a deviation of less than 3.75% and 0.799 Ω cm^2 with an error within 2.69%, respectively. The variations of the performance and internal resistance of the MEAs were quite minor. Therefore, the consistency of the MEAs was good enough to be used for a parallel contrast experiment.

3.1. Single proton activation

Reducing the MEA internal resistance is of great important to cut down ohmic loss during discharge process for DMFCs in the activation process, especially at high current density. The internal resistance is mainly composed of the migration resistance of electron and ion in MEA, and the contact resistance between components. And, establishing transfer channels of electrons and protons in MEAs is a prime way to reduce the internal resistance. Because proton conductivity is much lower than that of electron, building up of the transfer channel for protons is the main target of the proton activation in PEMs and catalyst layers. Meanwhile, supplying enough water and protons is a foundation for establishing the proton channels in MEAs. As to this, two proton activation