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Design of 3-electrode system for *in situ* monitoring direct methanol fuel cells during long-time running test at high temperature

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HIGHLIGHTS

- A design of a 3-electrode system with a solution-type salt bridge is reported.
- *In situ* monitoring is realized for DMFC long-time running test at high temperature.
- Effect of temperature and running time on anodic and cathodic polarizations are analyzed.
- Effect of temperature on cathodic performance is more significant than that of anode.
- Performance attenuation mainly comes from anode during long-time running at 80 °C.

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ABSTRACT

To understand the effect mechanisms of long-time running and high operation temperature on performance of the direct methanol fuel cell (DMFC) more clearly and directly, in this paper, a new design of 3-electrode system with a solution-type salt bridge has been developed to distinguish the integral polarization into anodic and cathodic polarizations at various temperatures and explore the attenuation mechanism by *in situ* monitoring the potential of anode during long-time running process at 80 °C, for the first time. The results indicate that the optimized 3-electrode system consists of a standard calomel electrode (SCE) and a solution-type salt bridge placed in the anode hole filled by 0.5 mol L^{-1} H_2SO_4 solution. By utilization of the 3-electrode system, the effect mechanisms of the running temperature and time on electrochemical parameters of the DMFC have been found: (1) The increasing operation temperature improves cathodic performance more significantly than that of anode; (2) the attenuation of fuel cell performance mainly comes from that of anode during the 20-h running test at 80 °C, resulting from the sharp drop of electrochemical active surface area of anode. More important, the new 3-electrode system has simplified the detection equipment and reduced the operating difficulty in a practical application for DMFCs, resulting in its portability.

1. Introduction

Increasingly stern environment and energy crises force people to eagerly develop new sustainable energies [1]. The direct methanol fuel cell (DMFC) has been recognized as one of the most promising green power generation technologies for portable multi-functional electronic devices due to its simple fabrication process and easy running operation [2]. For commercialization, there are two main problems including high power density and good long-time running property, to solve. To improve the power density, many explorations such as developments of the high-activity catalyst [3], the good methanol-resistance proton exchange membrane [4–6] and efficient flow field plate [7,8], microstructure optimization of membrane electrode assembly (for example, diffusion layer and catalyst layer with suitable por-

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ous structures and hydrophilic-hydrophobic property) [9–12], and design of activation process and operation condition [13–15], have been carried out. As for long-time running test, plenty of scholars have employed the degradation mechanism which mainly concentrated in destruction of structure and composition of anodic and cathodic catalyst layers [16–18], and performance retention and restoration measures [19–21]. It's worth noting that operation temperature is a key factor to affect the discharge power density and long-time running stability [7,22,23]. For example, the discharge performance has reached up to over 200 mW cm^{-2} at high temperature (80 °C) [24].

The polarization curve of a single electrode (cathode or anode) is the most important evidence to directly characterize the electrochemical behavior of DMFCs. However, most of the polarization curves in current reports are the integral polarization curves including both cathodic and anodic polarizations. To understand the effects of long-time running test and high operation temperature on performance of DMFC more clearly and directly, it's urgent to develop a 3-electrode system to distinguish the integral polarization to cathodic and anodic polarizations and realize *in situ* monitoring the potential variation of single electrodes for DMFCs.

Unfortunately, among the aforementioned literatures, only a few research groups adopted the 3-electrode system to analyze the cathodic and anodic polarizations, respectively, at low temperature [15,18]. Kuver et al. [25] firstly realized the distinction of the cathodic and anodic polarizations by using a new dynamic hydrogen reference electrode (DHRE) for DMFCs. And then, many researchers, for example, Lim et al. [26], used the anode polarization characteristics tested through this DHRE to *ex situ* represent their modified membrane electrode assemblies. To close to the electrode, avoiding any slight misalignment, Hinds et al. [27] and Brightman et al. [28] prepared a through-plate configuration with the salt bridge piercing the end plate, insulating plate, filed flow plate and diffusion layer to modify the DHRE with Nafion/H_2SO_4 tubing sheath salt bridge (shown in Fig. S1) for PME fuel cells and water electrolysers, respectively. Last year, they [29] introduced this modified DHRE to analyze the anode overpotential dynamics of DMFCs. Smith et al. [30] invented a reference electrode sandwiched between two pieces of solid polymer electrolytes to use in solution environment. Moreover, the lifetime of this reference electrode still needs to further extend. To use the 3-electrode system into DMFCs, Wu et al. [31] reported a reversible hydrogen reference electrode with 1 cm^2 of Pt-based catalyst layer installed in the DMFC fixture to enable discrimination of the anodic and cathodic potentials below 50 °C during 3-h running test. It's worth noting that the reference electrode attached inside of solid polymer electrolyte not only increases difficulty in both preparation and operating, but also degrades ion transfer performance [27]. As another hydrogen electrode, the driven mode DMFC with humidified hydrogen fed to cathode is significative to investigate the ruthenium crossover for Pt-Ru black anode [32]. But the driven mode DMFC, actually, is a two-electrode system and can't be used for *in situ* monitoring. Meanwhile, the hydrogen electrode mentioned in the above literature needs an additional hydrogen source supply to work, leading to complex test equipment and limitation of scope and place for real application. Relatively, the saturated calomel electrode (SCE, shown in Fig. S2) is also popular in the DMFC field due to its simpleness, safety, and portability [13,15,18,33]. But the application of the agar-type salt bridge leads to difficulty in high temperature running environment and long-time test, because the contact point between Nafion membrane and agar salt bridge is easy to dry up and break. Moreover, almost current reports only adopted the 3-electrode system to *ex situ* analyze the cathodic and anodic polarizations.

Herein, an easy-to-use design for 3-electrode system based on a SCE and a solution-type salt bridge has been developed to analyze the effect mechanism of operation temperature on discharge performance of DMFCs. Moreover, as far as we know, this is the first time to explore the attenuation mechanism by *in situ* monitoring the potential of anode/cathode during long-time running process at 80 °C.

2. Experimental

2.1. Preparation of membrane electrode assembly and fuel cell

The Nafion 115 pretreated by 1 mol/L H_2SO_4 solution at 80 °C for 1 h was employed as a proton exchange membrane [34]. According to our previous report [35], the commercial carbon cloth coated by microporous layer (H2315T10AC1 NOL, Japan), Pt-Ru (1:1 atomic ratio of Pt to Ru, Johnson Matthey)/Pt black (Johnson Matthey) were used as diffusion layer and anodic/cathodic catalysts, respectively. The membrane electrode assembly was obtained by transferring the catalyst layers to the pretreated Nafion115 by the decal method under the conditions of 135 °C, 75 kg cm^{-2} for 3.5 min [36]. As shown in Fig. 1a, the DMFC was fabricated by sandwiching the membrane electrode assembly with 5 cm^2 between anodic and cathodic graphite flow field plates and stainless steel end plates for activation and test.

2.2. Design of a new 3-electrode monitoring system

As shown in Figs. S3, S4 and 1b, a thin white PTFE tube ($\varphi \approx 1$ mm) filled with the saturated KCl solution is used as the solution-type salt bridge to connect with the SCE and the adapter tube located in anode (/cathode) hole instead of traditional agar-type salt bridge. The anode (/cathode) hole presented in Fig. S5 crosses over the stainless steel end plate, insulating film, Cu collector plate and graphite flow plate in anode (/cathode) side. The anode (/cathode) adapter tube filled with 0.5 mol L^{-1} H_2SO_4 (or saturated KCl) solution connected with Nafion 115 membrane via the anode (/cathode) hole. The connect site between the adapter end and Nafion membrane is signed in Fig. S6. And a thick rubber gasket is used to fix the adapter tube and seal the solution between Nafion membrane and the adapter.

2.3. Measurements

Methanol solution (1.5 mol L^{-1}, 4 mL min^{-1}) and oxygen (0.3 MPa, 670 mL min^{-1}) were injected into anode and cathode of DMFC, respectively. Polarization and electrochemical impedance spectroscopy (EIS) curves were obtained from a VMP3 system (Princeton Applied Research) at various temperatures. Consecutive long-time running test and electrochemical impedance spectroscopy (EIS) measurement were carried out at constant voltage of 0.4 V. The operation temperature was heated to 80 °C by the temperature control system (shown in Figs. S7–S9) during the long-time running test process. A cyclic voltammetry measurement was used to characterize the electrochemical active surface area of catalyst layers, and was carried out by feeding water to working electrode, humidified hydrogen of 360 mL min^{-1} to the reference and counter electrode. The working potential was cycled from 0 V to 1.2 V with a scanning rate of 50 mV s^{-1}.

3. Results and discussion

The traditional agar-type salt bridge consists of saturated KCl solution gelatinized in agar shown in Fig. S2. When the DMFC runs for long time at high temperature, the solution gelatinized by agar in salt bridge is easy to dry up, resulting in interrupt and failure of the detection circuit. To solve this problem, herein, a solution-type