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Determination of ionic resistance and optimal composition in the anodic catalyst layers of DMFC using AC impedance

Xinsheng Zhao, Xiaoying Fan, Suli Wang, Shaohua Yang, Baolian Yi, Qin Xin, Gongquan Sun*

Dalian Institute of Chemistry Physics, Chinese Academy of Science, Direct Alcohol Fuel Cell Laboratory, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

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Abstract

In the present study, a method based on transmission-line mode for a porous electrode was used to measure the ionic resistance of the anode catalyst layer under in situ fuel cell operation condition. The influence of Nafion content and catalyst loading in the anode catalyst layer on the methanol electro-oxidation and direct methanol fuel cell (DMFC) performance based on unsupported Pt–Ru black was investigated by using the AC impedance method. The optimal Nafion content was found to be 15 wt% at 75 °C. The optimal Pt–Ru loading is related to the operating temperature, for example, about 2.0 mg/cm^2 for 75–90 °C, 3.0 mg/cm^2 for 50 °C. Over these values, the cell performance decreased due to the increases in ohmic and mass transfer resistances. It was found that the peak power density obtained was 217 mW/cm^2 with optimal catalyst and Nafion loading at 75 °C using oxygen.

Keywords: DMFC; Ionic resistance; Catalyst loading; Impedance spectra; Methanol electro-oxidation

1. Introduction

Direct methanol fuel cells (DMFCs) are receiving a great deal of attention as alternative power sources for electric vehicles and portable electronic devices, due to their positive characteristics such as a simple system structure and a higher energy density. The status of research and development of DMFC was reviewed [1,2]. Recent advances in power densities of DMFC have been mainly attributed to improvements in preparation and optimization of electrode. To optimize the electrode structure, there are many parameters like composition of the catalyst itself, catalyst loading, ionomer content in the catalyst layer; porosity of the electrode, etc., which should be evaluated. The performance of DMFC anode catalyst layer is mainly affected by the catalytic activity of the catalyst, the mass transport of MeOH/CO_2 and the electrical conductivity, including ionic and electronic conductivity. The catalyst loading and the ionomer content affect the structural properties of the catalyst layer; hence, the mass transport and electrical conductivity are influenced by the two parameters.

Since the polymer membrane like Nafion 117 used as the electrolyte is solid phase, it cannot penetrate deeply into the electrode as a liquid electrolyte does. To increase the contact surface area, impregnation of ionomer into the catalyst layer enables the electro-catalyst to integrate into the electrolyte for extending the three-dimensional reaction zone. Extensive and intensive research on Nafion content was conducted in previous works [3–5]. The Nafion phase mainly influences the electrical conductivity, including ionic and electronic

* Corresponding author. Tel./fax: +86 411 84379063.
E-mail address: gqsun@dicp.ac.cn (G. Sun).

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conductivity. For estimating the ionic resistivity of the catalyst layer, the following methods have been proposed: (1) fitting of the models to polarization curves [6,7]; (2) fitting of a transmission line model to transverse impedance response to determine a distributed resistance [8]; (3) measuring the resistance of a membrane electrode assembly (MEA) containing inert layers composed of XC-72 carbon [9] and (4) combining DC polarization with AC impedance to compute ionic resistance of the catalyst layer [10,11].

Some work has been reported on catalyst loading in the electrode [12–15]. From the literature [12–14], the Pt–Ru black with loading more than 8 mg/cm^2 did not improve cell performance. On the contrary, Liu [15] pointed out that MEAs fabricated with unsupported Pt–Ru black still showed improvement even with the metal loading exceeding 8 mg/cm^2, and the "upper limit" for Pt–Ru black catalyst was not attained.

In this paper, a method was proposed to determine the ionic resistance of DMFC anode catalyst layer, and the effect of Nafion content and catalyst loading in the anode catalyst layer on the performance of the DMFC was investigated to optimize the catalyst layer.

2. Experimental

2.1. Preparation of MEA

Prior to fabricating electrodes, the Nafion 117 (DuPont) membrane was boiled in 5 wt% H_2O_2 solution for 1 h, then it was rinsed in boiling deionized (DI) water for 2 h. In order to remove metallic contaminants on the membrane surface and exchange Na^+ for H^+ in the membrane, it was boiled in 0.5 M H_2SO_4 for 1 h. Finally, it was rinsed again in boiling deionized (DI) water for 2 h.

In order to fabricate MEAs, the electrocatalysts and 5.0 wt% solubilized Nafion (Du Pont) were thoroughly mixed in an ultrasonic bath. Several kinds of anode catalyst inks having different Nafion contents or catalyst loadings were deposited onto the cleaned PTFE films by the spraying–drying method; they were used as anodes after being dried in a vacuum oven at 80 °C for 1 h. The anode catalyst used was Pt–Ru black (Pt:Ru = 1:1 in atomic ratio, Johnson Matthey Corp.). To prepare the cathode catalyst layer, the ink containing unsupported Pt black (Johnson Matthey Corp.) and 5.0 wt% Nafion solution was applied to a piece of PTFE film as described above, the Pt loading was 2.46 mg/cm^2 and the Nafion weight percent in the cathode catalyst layer was 10 wt%. In this case, the Pt loading was kept constant at the value for each cathode. The catalyst-coated PTFE films were cut into a rectangle shape of 2×2 cm^2, placed on both sides of Nafion 117 membranes, and hot-pressed at 140 ° for 90 s. The PTFE films were peeled off and the catalyst-coated membranes (CCM) were obtained; then the anode and cathode diffusion layers were placed on the corresponding side of the CCM to form MEAs.

2.2. Single cell test

The MEAs were sandwiched between two stainless-steel plates with parallel channels. Electrical heaters and thermocouples were embedded in the holes of the plates for controlling the desired operating temperature. A peristaltic pump was employed to supply aqueous methanol solution from a reservoir. Oxidants were supplied from an O_2 cylinder and the pressure was regulated by pressure regulating valves. In all the experiments, 1.0 mol/L methanol solution was pumped through the DMFC anode chamber at a rate of 1 ml/min. In fuel cell mode, the cathode was fed with oxygen at 2 atm pressure and a flow rate of 150 standard cubic centimeters per minute (SCCM).

The new MEA was conditioned for 4 h at 75 °C and ambient pressure with a continuous feed of 1 mol/L methanol solution in the anode chamber. The current–voltage curves were measured by employing an Arbin fuel cell test system (USA).

2.3. Electro-chemical measurements

To investigate anode catalyst layer performance for the electro-oxidation of methanol, the MEAs were first tested in a driven cell mode using 1.0 mol/L aqueous methanol fed to the anode. The cathode was fed on hydrogen, which served as the dynamic hydrogen electrode (DHE), and the overpotential of the DHE is negligible according to the previous work [16]. These anode polarization data provide a direct tool for comparing the activities of these anode catalyst layers.

The experimental setup and procedures to measure the DMFC anode impedance have been described in detail in an earlier paper [17,18]. The anode was supplied with 1.0 M methanol solution with a flow rate of 1 ml/min. All anode impedance spectra reported here were measured between the anode and the DHE in the complete fuel cell. The electrochemical impedance spectra (EIS) were recorded in the frequency range of 100 mHz to 4 kHz using a lock-in amplifier (EG&G Model 5210) controlled by a personal computer and coupled to a potentiostat/galvanostat (EG&G Model 273A) that allowed modulation of DC potential, in automatic sweep mode from high to low frequency with 10 steps per logarithmic decade, the amplitude of the sinusoidal modulation voltage did not exceed 10 mV.

3. Results and discussion

3.1. Effect of Nafion content on ionic resistances

According to the theory [19,20], the impedance of the catalyst layer can be modeled using the transmission line shown in Fig. 1. This is a classical model for the charging of a porous electrode, in which one resistance rail (R_e) represents electron conduction in the electrode material (the