A study on fuel additive of methanol for room temperature direct methanol fuel cells

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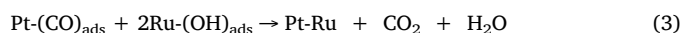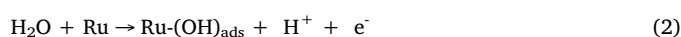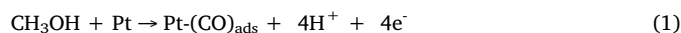
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ABSTRACT

Hydrogen peroxide is added into the anode methanol fuel as a pro-oxygenic agent to improve the electro-oxidation reaction rate of methanol in low-temperature direct methanol fuel cell. Cyclic voltammetry, electrochemical impedance spectroscopy and steady-state polarization with three-electrode system are used to test the catalytic efficiency with different concentrations of hydrogen peroxide additive. The mechanism of pro-oxygenic activity is revealed by cyclic voltammetry method. The results of electrochemical analysis show that the peak current density and peak power density are the highest when the concentration of hydrogen peroxide additive is 0.1 M at room temperature, increase 12.2% and 34.1% than those of pure methanol solution, respectively. The anode charge transfer resistances reduce gradually as the concentrations of hydrogen peroxide increase from 0 to 0.3 M. The tests under different temperature indicate that the promotion effect of hydrogen peroxide additive is significant at room temperature rather than at high temperature. The results show that hydrogen peroxide can be an effective pro-oxygenic agent for methanol electro-oxidation to improve the anode methanol electro-oxidation reaction of direct methanol fuel cell at room temperature.

1. Introduction

Direct methanol fuel cell (DMFC) is an active research topic of proton exchange membrane fuel cell [1]. Because DMFCs possess excellent characteristics of small size, light weight, low working temperature, high energy density, convenient fuel storage and so on [2]. It has received more and more attention as a new portable clean power sources [3]. However, the slow kinetics of methanol electro-oxidation and catalyst poisoning in the anode reduce the performance and durability of DMFC, which hinders its further commercialization and real application [4]. Therefore, one key objective of the current DMFC research is to optimize anode methanol electro-oxidation reaction [5].

Until now, Pt-based catalysts are still regarded as most effective for methanol electro-oxidation [6]. However, Pt is easily poisoned by the intermediates CO_{ads}, which strongly adsorbs on the Pt surface and occupies the re- action active sites [7]. The main measure to solve this problem is to use Pt-based alloy-based bimetallic electrocatalyst to enhance the anti-poisoning ability of catalysts at relatively high temperature [8]. For example, PtRu catalyst, Ye et al. enhanced the catalytic activity for fuel cells through developing a new electrodeposition method [9]. As is known to all, Ru promotes methanol oxidation reaction mostly by the bifunctional mechanism: water molecular dissociates into oxygenated species on Ru surface at much lower potential (0.2–0.3 V) compared to Pt [10]. As a result, CO_{ads} could be removed through oxidation more easily as follow reactions:

$$CH_3OH + Pt \rightarrow Pt\text{-}(CO)_{ads} + 4H^+ + 4e^- \tag{1}$$

$$H_2O + Ru \rightarrow Ru\text{-}(OH)_{ads} + H^+ + e^- \tag{2}$$

$$Pt\text{-}(CO)_{ads} + 2Ru\text{-}(OH)_{ads} \rightarrow Pt\text{-}Ru + CO_2 + H_2O \tag{3}$$

However, the low catalytic efficiency of PtRu bimetallic catalyst at room temperature reduces the portability of direct methanol fuel cells [11]. And the Ru is easy to run off as the reaction goes on, which will reduce the anti-poisoning ability of catalyst and limit the longtime running stability of the cell [12]. Therefore, it is essential to accelerate the process of CO_{ads} desorption and further improve the performance of the cell at room temperature [13].

As discussed before, it is expected that the catalytic efficiency of methanol electro-oxidation reaction will be improved and furthermore the performance and stability of the cell will be promoted if the process of CO_{ads} desorption can be accelerated via additive [14]. In cathode side, as pointed by Karim et al., hydrogen peroxide (H_2O_2) produced in oxygen reduction reaction is disadvantageous for DMFC performance [15]. In contrast, in anode side, Park et al. reported that the introducing of H_2O_2 to methanol solution can improve the efficiency of methanol-steam reforming reaction [16]. Furtherly, Papavasiliou et al. considered that the reaction mechanism was similar to the bifunctional mechanism of Ru [17]. Thus the H_2O_2 may be an effective pro-oxygenic agent for methanol electro-oxidation to accelerate the process of CO_{ads} desorption. In addition, H_2O_2 may product O_{ads} on the Pt surface and this kind of adsorption will oxidize CO_{ads} and help it desorbed from catalyst surface [18]. The reaction equation of the assisted-oxidation process of hydrogen peroxide can be described as follows:

$$H_2O_2 + Pt \rightarrow Pt^-(O)_{ads} + H_2O \quad (4)$$

$$Pt\text{-}(CO)ads + Pt^-(O)_{ads} \rightarrow CO_2 \quad (5)$$

Therefore, the potential advantage of using H_2O_2 in DMFC is worth to study. Our idea is to reveal the effect mechanism of the H_2O_2 additive with different concentrations on fuel cell performance with three-electrode system.

In this paper, based on PtRu bimetallic catalyst as methanol electro-oxidation, adding proper amount of additives in methanol solution, the performance of the cell can be further improved by the synergistic action of the additive and the anode catalyst. The experimental results show that H_2O_2 is used as a pro-oxygenic agent for methanol electro-oxidation to DMFC which can eliminate the adverse impact of CO_{ads} and significantly improve the performance of the cell.

2. Experimental

Electrochemical experiments were carried out in a conventional three electrode system in $0.5\,M\ H_2SO_4$ and $1.0\,M\ CH_3OH$ aqueous solutions at room temperature using a VMP-2 electrochemical analysis instrument. A platinum plate and saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. A glassy carbon electrode with a 4 mm diameter was used as the working electrode, and it was prepared by dispersing 2 mg commercial Pt black in 1 ml deionized water and 15μL of 5 wt% Nafion® solution (Dupont) and pipetting out 20μL of slurry. The cyclic voltammetry (CV) tests with different concentrations of H_2O_2 additive were performed in a range of -0.2 to $1.0\,V$ at a scan rate of $50\,mV\,s^{-1}$ to characterize the catalytic performances.

To investigate the reaction mechanism about methanol oxidation with H_2O_2 as additive, the relationships between peak current density (I_p) and peak potential (E_p) obtained from forward CV scans with different sweep rates (v) were also studied. The test solution and the scan window were the same as above while the scan rates were from 25 to $500\,mV\,s^{-1}$.

The membrane electrode assembly (MEA) consisting of electrodes and the electrolyte membrane were prepared by the heat spray method as reported in our previous work [19]. The catalysts of anode and cathode were PtRu Black (Johnson Matthey, Hospice 1000) and Pt Black (Johnson Matthey, HiSPEC 6000), respectively, with the loads of anode and cathode at both $4\,mg\,cm^{-2}$. Nafion adhesive (5 wt% DuPont, US), as proton conductor, was 15 wt% at anode and 10 wt% at cathode

[20]. Nafion115 (DuPont, US) was chosen as electrolyte membrane. Carbon cloth (H2315T10AC1 NOK, Japan) was used as diffusion layer material. MEA was treated with the method of multistep activation before testing [21].

The evaluation of the cell performance was conducted on the self-made fuel cell performance testing and monitoring platform. VMP2 electrochemical workstation (Bio-logic, France) was used as the electronic load. The steady state polarization curve of the cell was recorded with constant potential method whose potential step was 30 mV and settling time was 60 s. The mercury-mercurous sulfate (Hg/Hg_2SO_4) reference electrode was selected as reference electrode during the testing process. By using three-electrode system, the polarization curves of anode and cathode were recorded independently. The three-electrode system was also used for the electrochemical impedance spectroscopy (EIS) test [22], in such a way that anode impedance spectra could be analyzed.

The anode catalyst layer was additionally characterized by methanol-stripping voltammetry [23]. The methanol flow (1.5 M) at the anode was set to 2.5 ml/min, and the cathode was first purged with N_2 for 30 min and then fed with hydrogen at a flow rate of 50 ml/min. The cell was set to a fixed voltage of 100 mV (vs. the hydrogen fed cathode side) under potentiostatic control for a period of 10 min to adsorb methanol on the active sites of the anode. The anode was then purged with water for 30 min to flush the non-adsorbed methanol while the cell was still under potentiostatic control at 100 mV. Finally, the stripping scan was recorded at 10 mV/s from 100 to 800 mV.

3. Results and discussion

The CV curves of methanol electro-oxidation with different concentrations of H_2O_2 additive were recorded as shown in Fig. 1(a). The forward peak current density is $59.81\,mA\,cm^{-2}$, $62.12\,mA\,cm^{-2}$, $67.11\,mA\,cm^{-2}$, $55.7\,mA\,cm^{-2}$, $48.64\,mA\,cm^{-2}$ which correspond to 0, 0.05, 0.1, 0.2, 0.3 M H_2O_2 as additive, respectively. The results show that electro-catalytic properties of commercial Pt black firstly improve and then reduction with the increase of hydrogen peroxide concentration. In particular, when H_2O_2 concentrations is 0.1 M, forward peak current is increased by 12.2% compared to pure electrolyte without H_2O_2 additive. However, as the H_2O_2 concentration increases to 0.3 M, a drop on peak current densities by 18.7% is observed. Meanwhile, there are many bubbles on the surface of the electrode, which meant the solution became unstable at high H_2O_2 concentrations. The ratio of forward peak current density (I_f) to the backward peak current density (I_b) represents a crucial index [24,25] in evaluating electro-catalysts ability to complete oxidation of methanol to CO_2 and H_2O. As seen from Fig. 1(b), the value of I_f/I_b without H_2O_2 is only 0.95, which is far less than 1.03 obtained for the concentration of H_2O_2 additive with 0.1 M, which confirms that hydrogen peroxide can be used as pro-oxygenic agent for methanol electro-oxidation to eliminate the adverse impact of CO_{ads}. The above results show that peak current densities can be significantly improved by introducing certain amount of H_2O_2.

To investigate reaction mechanism with H_2O_2 as additive, the plots of forward peak current density (I_p) versus square root of sweep rates ($v^{1/2}$) and the relation of peak potential (E_p) for methanol oxidation upon the ln(v) [26] were shown in Fig. 1(c) and (d), respectively. In Fig. 1(c), it is clear that there is a linear relationship [27,28] between I_p and $v^{1/2}$ for pure electrolyte without H_2O_2, indicating that the process of methanol oxidation is controlled by diffusion process of methanol, which may be due to CO_{ads} strongly adsorbs on Pt sites and block the diffusion toward active sites and continuous adsorption of methanol molecules during the methanol electro-oxidation process. When adding 0.1 M H_2O_2, the linear relationship between I_p and $v^{1/2}$ is broken, which indicates that the process of methanol oxidation is controlled by electrochemical polarization, and electrochemical reaction process is changed. In Fig. 1(d), E_p of the methanol oxidation shifts positively with the increase of v and the linear relationship between Ep and ln(v)