

Effect of cations in solution on the oxidation of methanol on the surface of platinum electrode

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Abstract

The effect of metal cations in solution on the oxidation of methanol on the electrode surface of platinum is a neglected aspect to direct methanol fuel cell (DMFC). In this paper, a smooth platinum electrode absorbing metal cations as the working electrode was applied to investigate the methanol oxidation with the cyclic voltammetry (CV) in 1.0 mol L⁻¹ H₂SO₄. From the analysis of experiment, it is found that the cations, Li⁺, Ce⁴⁺, Mn²⁺, Ni²⁺, Cu²⁺, have some negative effect on the catalytic oxidation of methanol on the surface of platinum. The degree of the effect from different cations was analyzed.

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1. Introduction

DMFC is the candidate to the power source in static and portable applications due to its inherent simplicity of operation [1–3]. It is obvious that the problems, lifetime, price, optimization of the system and the components [4] and so on, must be studied before widely application. The effect of ions is one of them, which can affect DMFC's performance. However, the study of the effect of cations in solution on the oxidation of methanol on the surface of platinum is seldom carried out.

There are many ion sources in DMFC operation. In the progress of operation, all kinds of ions including cations and anions accumulate in the DMFC system. First, ions may come from the fuel, methanol. In the lifetime several years or longer time, thousands kilogram methanol will be consumed and the ions will accumulate in the system, though the concentration of the ions in the fuel is very low. For example, many corporations and laboratories proposed the prototypes [5–7] and studied the feasibility [8,9]. In these prototypes, pure methanol was pumped into mixing chamber to keep the methanol concentration con-

stant. As a result, the nonvolatile materials will accumulate in fuel cell system because the methanol solution circulates in an isolated system, which includes fuel cell stack and mixing chamber. The accumulated ions may reach high concentration after several years or longer time, though the concentration in pure methanol is very low. Second, ions may come from the composition of the system. For example, if the material of bi-plane is steel, it will be corroded for the long time and bad operation condition. Third, ions may come from air. Especially, when the DMFC system is operated near or in the sea, the air filled with gas-colloid that forms from spray of seawater will bring a lot of ions to the system. According to the reasons above, a filter and an ion exchange column are necessary to fix in the methanol cyclic system and an air filter is also necessary.

The effect of cations on the fuel cell may be in two ways. Firstly, they may exchange with H⁺ in PEM and accumulate in it to reduce the conductance of PEM. This is the negative effect of ions. Secondly, the ions may adsorb on the catalyst surface, and affect the progress of catalyzing. In this paper, several familiar cations were selected to study the effect. Electrochemical tests and single cell test were carried out to explore the effect of cations in solution on the oxidation of methanol on the surface of platinum electrode.

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2. Experimental

Experiments were carried out in a standard three-electrode electrochemical cell. Pt electrode (1 mm diameter) was used in the experiments. Before the experiment, Pt surface was polished with an Al₂O₃ water suspension, particle size 0.05 μm and cleaned ultrasonically three times in high purity water for 5 min. The counter electrode was a large area Pt plane. The reference electrode was Ag/AgCl/sat KCl, and all potentials were referred to the potential of Ag/AgCl electrode. Cyclic voltammograms for the catalyst were recorded in 1.0 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ H₂SO₄ with cations at 25 °C. The cations were introduced by sulfate such as Li₂SO₄, Ce(SO₄)₂, MnSO₄, NiSO₄, CuSO₄ to have same anion. In order to avoid the electro-reduction of the adsorbed cations to metal, we selected the metal cations whose O/R potential is at least 0.2 V lower than the oxidation potential of methanol. The electrolyte was saturated with purified N₂ gas. Water was purified in a Mili-Ro/Milli-Q (Millipore) system. The electrochemical experiments were performed using Parc 273 potentiostat, under control of Powersuit software. The potential was scanned between -0.2 and 1.0 V at a scan rate of 20 mV s⁻¹. Before recording, the potential was repeatedly scanned in the same range to remove residual impurities.

The experiments in the single DMFC were done at a cell temperature of 24 °C and an oxygen pressure of 1 atm. The area of the single cell electrodes was 4 cm². The commercial materials Pt/C (2.0 mg Pt cm⁻²) and PtRu/C 50:50 E-TEK (2.0 mg Pt cm⁻²) were used. A Nafion[®] 117 membrane was used as the electrolyte. The membrane and electrodes assemblies (MEA) were prepared by hot pressing at 130 °C and 50 atm for 2 min as described previously [10]. MEA was placed between Stainless Steel 316 plates with the flow of oxygen 100 mL min⁻¹ and the 1.0 mol L⁻¹ methanol solution 2.5 mL min⁻¹.

3. Results and discussion

3.1. Effect of cations on the oxidation of methanol on electrode of Pt

In this paper, several familiar cations of Li⁺, Ce⁴⁺, Mn²⁺, Ni²⁺ and Cu²⁺ were studied. Cleaned Pt electrode was put into 20 mL solution of 1.0 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ CH₃OH without cations, and then scanned with CV to a constant current curve before recording data. After recording, different volume solution with one cation was added orderly to study the effect of cation at different cation concentrations. The test process would be repeated when the cation was replaced.

Fig. 1 shows CV result of the oxidation of methanol without cations. Peak 1 was got from the positive direction scan and Peak 2 was got from the reverse direction.

Fig. 2 shows the effect of cations on the oxidation peak potential 1. From Fig. 2, we can divide the cations into three kinds. The first kind includes Mn²⁺ and Cu²⁺, which increase the peak potential up to a maximum value about 710 mV. The second kind includes Li⁺ and Ni²⁺, they change the peak potential slightly at low concentration and increase potential at last, but the increased value is much lower than the first kind. When Li⁺ was added into

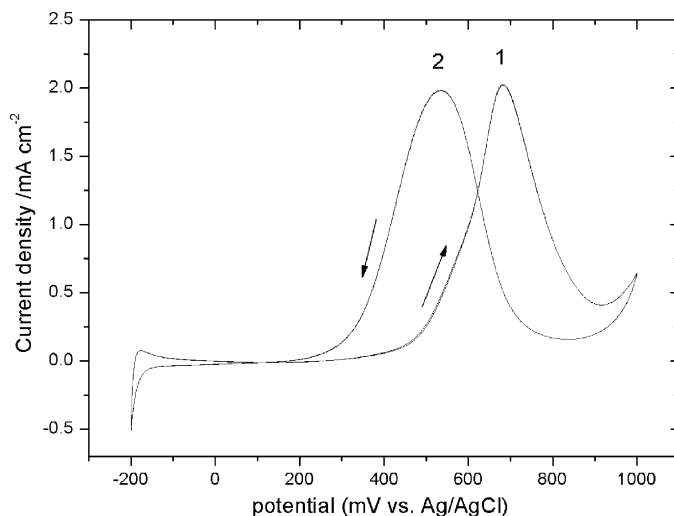


Fig. 1. Cyclic voltammogram obtained on Pt electrode in H₂SO₄ (1 M) + CH₃OH (1 M) with potential sweep rate of 20 mV s⁻¹.

the solution, the peak potential 1 is slightly lower than the virgin solution. The third kind includes Ce⁴⁺, it makes the potential increase slightly at first and decrease when the volume exceeds 0.5 mL. The effect of this kind cation on the current density is the weakest among the three kind cations seeing from Fig. 3.

Fig. 3 shows the effect of cations on the peak current density 1. From Fig. 3, we can see that the first kind of cations can reduce the current density to a very low degree, that is to say they can adsorb on the Pt electrode intensely and occupy the active sites. The second kind of cation has a relative weak effect. Li⁺ is good to low the oxidation potential, but the current density decreases very much even 0.5 mL Li⁺ was added. The third kind of cation has a worst effect on the peak current density 1.

The effect of cations on the oxidation of methanol may be in two ways. First, the cations adsorb on the electrode surface and occupy the active sites. This adsorption of cations may compete with that of the methanol on the electrode surface. As a result, the area of active surface decreases and the current den-

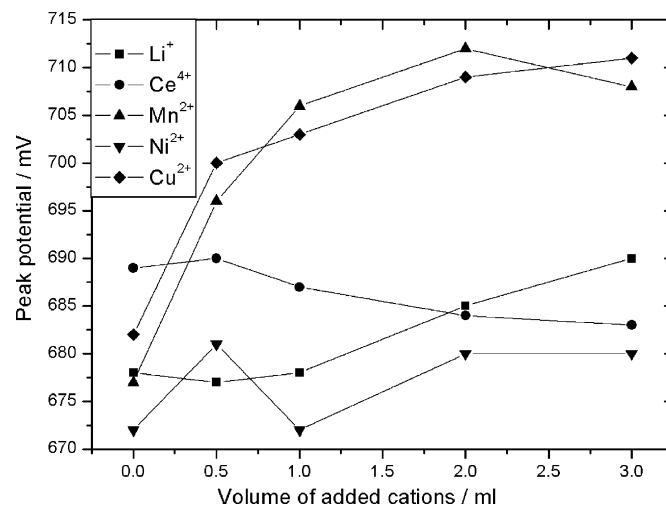


Fig. 2. Effect of added cations on the peak potential 1 of methanol oxidation.

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