

Selective Oxygen Reduction on Platinum by Additives in the Presence of Methanol

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Introduction

Methanol crossover effect is one of the most serious problems for direct methanol fuel cell (DMFC). This causes not only negative shift of cathode potential but also useless consumption of methanol [1]. The performance of DMFC significantly decreases when high concentration methanol is used in order to improve the energy density per unit volume of the fuel in particular.

In this paper, we report some additives that can suppress methanol oxidation reaction (MOR) on platinum significantly but have little effect on the oxygen reduction at the cathode. The negative potential shift of the cathode potential in the presence of methanol can be significantly reduced by adding such compounds in the electrolyte. This approach would be a first step to develop new compounds that can solve the methanol crossover effect of DMFC [2].

Experimental

2,2'-bipyridine (abbreviated as bpy), 1,10-phenanthroline (phen), 2,2':6',2''-terpyridine (terpy), 4,6-diphenyl-1,10-phenanthroline (dpphen) and their metal complexes were used as additives.

Electrochemical measurements were carried out with a conventional three electrode system equipped with a Pt disk-Pt ring working electrode, a Pt wire counter electrode and a saturated calomel reference electrode separated from the working electrode compartment. Electrochemical measurements and data acquisition were conducted by a homemade measurement program. All potentials shown in this paper are quoted with respect to the reversible hydrogen electrode (RHE).

In-situ ATR surface-enhanced infrared spectroscopy (SEIRAS) measurements were carried out in order to investigate effect of the additives in more details. A Fourier transform infrared spectrometer equipped with a MCT detector (Digilab FTS7000) was used for the measurements which were conducted by un-polarized infrared radiation at the angle of incidence of 65°. The platinum working electrode was a thin film, 15mm ϕ (1.5 cm²), of ca 50 nm thick formed by chemical deposition on the bottom of a 20 x 25mm Si ATR prism window. The collected spectrum at a given potential was represented as a ratio against the spectrum at the same potential in 0.1 M HClO₄ without additives and methanol. The platinum electrode surface was cleaned by cycling the potential between 0.05 V and 1.5 V before the measurements. After the spectrum was measured at each potential, an additive and methanol was separately added to the spectro-electrochemical cell. Potential of the working electrode was maintained at 0.1 V for 30 min after adding an additive or methanol.

Results and Discussion

Figures 1(d), (e) and (f) depict polarization curves for oxygen reduction using a platinum disk electrode at various methanol concentrations without 2,2'-bipyridine (abbreviated as bpy) during the positive scan. The onset potential of cathodic current E_c , which is defined as the

potential at the cathodic current of 1×10^{-5} A cm⁻²_{real}, drastically shifted by -0.207 V (0.1M MeOH) and -0.295 V (1M MeOH), respectively, compared to that without methanol. The diffusion limiting current for oxygen reduction slightly decreased to 98.4% (0.1 M MeOH) and 93.1% (1 M MeOH), respectively. Figures 1(a), (b) and (c) show polarization curves for oxygen reduction with 0.1 mM bpy at various methanol concentrations. In the absence of methanol, E_c moved from 0.968 V to 1.002 V. This is because bpy hindered the formation of platinum oxide species on the surface. The diffusion limiting current hardly changed compared to that without bpy. In the presence of methanol, E_c shifted by -0.06 V (0.1 M MeOH) and -0.177 V (1 M MeOH), respectively. E_c improved more than +0.13V compared to that without bpy. Thus, it was demonstrated that bpy adsorbed on platinum suppresses methanol oxidation.

Figure 2 shows a series of SEIRA spectra of the electrode surface in 0.1 M MeOH – 0.1 M HClO₄ during potentiostatic condition with or without bpy. Bpy strongly inhibits formation of the methanol adsorbate, CO, and formate, the intermediate for a non-CO path of methanol oxidation [4].

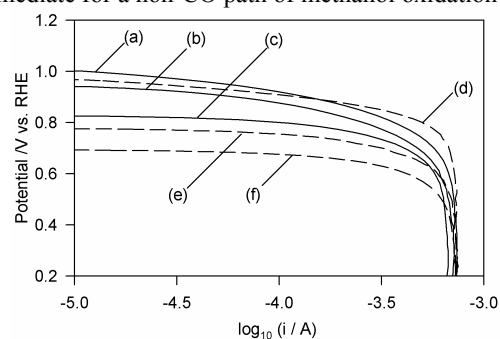


Figure 1 Polarization curves for oxygen reduction in 0.05M H₂SO₄. Scan rate is 5 mV s⁻¹. Rotating speed is 300 rpm. (a) 0.1mM bpy-0M MeOH; (b) 0.1mM bpy-0.1M MeOH; (c) 0.1mM bpy-1M MeOH; (d) 0M bpy-0M MeOH; (e) 0M bpy-0.1M MeOH; (f) 0M bpy-1M MeOH.

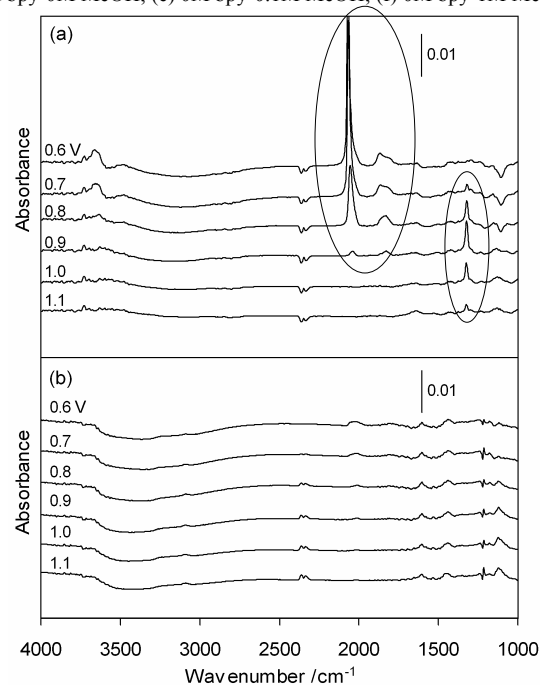


Figure 2 Series of SEIRA spectra of the Pt plating electrode in 0.1 M HClO₄ – 0.1 M MeOH at various potentials under N₂ (a) without additives, (b) 0.1 mM bpy. Acquisition time of each spectrum was 30 s.

References

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