Effect of Additives on Electrochemical Reduction of Oxygen in the Presence of Methanol

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Methanol oxidation on platinum has been suppressed and selective oxygen reduction was achieved in sulfuric acid – methanol aqueous solution by adding organic ligands or their complexes which have pyridyl structures.

Direct methanol fuel cell (DMFC) is expected for portable devices since power consumption of such devices has been increasing rapidly in recent years. However, there are two major subjects to be solved for commercialization of DMFC: the development of an active catalyst for methanol oxidation and methanol crossover through a membrane. Methanol permeates through the membrane to the cathode side of DMFC, and is oxidized to lower potential of the cathode and the fuel efficiency.[1] When a high-concentration methanol fuel is used to improve energy density per unit volume, influences caused by the methanol crossover become more serious. Many studies have been performed to cope with the subjects in two ways. One is the improvement of membrane properties such as hybrid membranes[2] and new membranes.[3] However, it is difficult to develop a membrane satisfying all requirements of proton conductivity, mechanical strength, and low methanol permeability. The other method is the development of oxygen reduction catalysts which are inactive to methanol oxidation such as $Pt_{70}Ni_{30}$ alloy,[4] transition metal chalcogenide,[5] and heat-treated porphyrins.[6] However, long term stabilities of these catalysts are not verified in the acidic membrane systems.

Herein, we report for the first time that compounds which have pyridyl structures inhibit methanol oxidation on platinum and hardly affect oxygen reduction, which is expected to reduce the methanol crossover effect of DMFC.

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.

When a cyclic voltammogram[7] of platinum was measured with bpy in the absence of methanol (Figure 1(A)), the charge of the hydrogen adsorption/desorption region decreased to 50%, suggesting that bpy was adsorbed on the surface of platinum. The formation potential of platinum oxide species shifted positively compared to that without bpy.

Figure 1(B) shows cyclic voltammograms of a platinum disk electrode with or without bpy in 0.1 M methanol–0.05 M H_2SO_4 ($M = mol\,dm^{-3}$). In the absence of bpy, methanol oxidation on platinum started at 0.5 V, the maximum current reached to $3\,mA\,cm^{-2}$ at 0.85 V around which methanol oxidation interfered with the O_2 reduction current. Whereas in the presence of 0.1 mM bpy, the peak current of methanol oxidation decreased by 86%, indicating that methanol oxidation on platinum is impeded by bpy. Since diffusion current caused by oxygen reduction with bpy hardly decreased compared to that without bpy, it is suggested that bpy adsorbed onto platinum suppresses methanol oxidation much more than oxygen reduction.

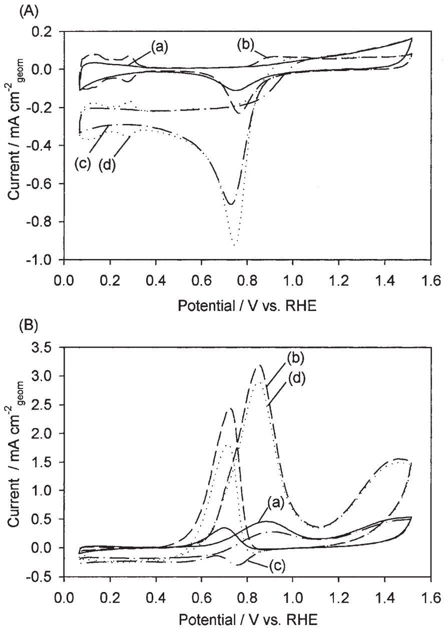

Figure 1. Cyclic voltammograms of a Pt-disk electrode in (A) 0 M methanol–0.05 M H_2SO_4 (B) 0.1 M methanol–0.05 M H_2SO_4 at room temperature. Scan rate is $20\,mV\,s^{-1}$. (a) with 0.1 mM bpy under N_2; (b) without bpy under N_2; (c) with 0.1 mM bpy under O_2; (d) without bpy under O_2.

Figures 2d–2f depict polarization curves for oxygen reduction using a platinum disk electrode at various methanol concentrations without bpy during the positive scan. The onset potential of cathodic current E_c, which is defined as the potential at the cathodic current of $1 \times 10^{-5}\,A\,cm^{-2}{}_{real}$, drastically shifted by -0.207 V (0.1 M MeOH) and -0.295 V (1 M 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 2a–2c show polarization curves[7] for oxygen reduction with 0.1 mM bpy at various methanol concentrations. In the absence of methanol, E_c moved from 0.968 to 1.002 V. This is because bpy hindered the formation of platinum oxide species on the surface as mentioned above. 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 $+0.13$ V compared to that without bpy. Thus, it was demonstrated that bpy adsorbed on platinum suppresses methanol oxidation selectively and interferes with the formation of the platinum oxide species.

Table 1. Effect of additives on polarization curves for oxygen reduction and methanol oxidation[a]

additive[b]	0 M MeOH			0.1 M MeOH			1 M MeOH		
	E_c/V[c]	$j_L/\mathrm{mA\,cm^{-2}}$[d]	%H_2O[e]	E_c/V[c]	$j_L/\mathrm{mA\,cm^{-2}}$[d]	$j_m/\mathrm{mA\,cm^{-2}}$[g]	E_c/V[c]	$j_L/\mathrm{mA\,cm^{-2}}$[d]	$j_m/\mathrm{mA\,cm^{-2}}$[g]
—	0.968	2.58	99.7	0.775	2.63	0.465	0.692	2.53	1.02
bpy	1.002	2.62	99.1	0.942	2.54	0.063	0.825	2.37	0.23
bpy (0.4 mM)	0.987	2.54	98.4	0.943	2.50	0.028	0.837	2.49	0.12
phen	0.991	2.58	99.1	0.932	2.52	0.042	0.826	2.43	0.11
terpy	0.958	2.47	98.4	0.881	2.43	0.039	0.789	2.39	0.17
dpphen	0.952	2.27	99.3	0.798	1.99	0.064	0.729	1.67	0.09
$Cr_2(phen)_4OH$	0.976	2.47	99.8	0.887	2.47	0.084	0.792	2.31	0.27
$Fe(terpy)Cl_x$[f]	0.851	2.41	96.7	0.817	2.35	0.003	0.784	2.30	0.02
$Ni_2(bpy)_4OH$	0.991	2.55	98.1	0.918	2.53	0.057	0.810	2.45	0.23
$Cu_2(phen)_4OH$	0.962	0.65	95.9	0.886	0.60	0.022	0.783	0.55	0.06

[a] Measurements were performed in 0.05 M H_2SO_4 at room temperature under 1 atm oxygen or nitrogen. Scan rate is 5 $\mathrm{mVs^{-1}}$. Rotating speed is 300 rpm. [b] The concentrations of additives are 0.1 mM. [c] Potential at cathodic current of $1 \times 10^{-5}\ \mathrm{A\,cm^{-2}}_{\mathrm{real}}$. [d] Diffusion limiting currrent of oxygen reduction at 0.3 V vs RHE normalized by the geometrical area of a Pt disk electrode. [e] Efficiency of O_2 to H_2O at 0.8 V. [f] $x = 2$–3. [g] Anodic current of methanol oxidation at 0.8 V under 1 atm N_2.

Table 1 shows the summary of polarization data for oxygen reduction with various additives. The efficiencies of O_2 reduction to H_2O were hardly affected by these additives. In the presence of methanol, E_c with additives were much more positive than that without additives. The limiting current densities for oxygen reduction (j_L) with additives were slightly lower than that without additives except $Cu_2(phen)_4OH$. The anodic currents for methanol oxidation (j_m) with additives were significantly less than that without additives. Consequently, it is revealed that these additives suppress methanol oxidation on platinum and E_c shifts to more positive potentials. In the absence of methanol, the order of E_c does not correspond to that of j_m. This is because E_c is affected by two opposing phenomena arising from the adsorption of additives. The additives adsorbed onto platinum suppress the formation of platinum oxide species to shift E_c positively, while the additives occupy active sites for oxygen reduction on platinum to shift E_c negatively. The extent of these counter-acting effects may depend on the structure of the additives and interaction between the additives and platinum surfaces. The limiting current density for oxygen reduction decreased only slightly except $Cu_2(phen)_4OH$, where it was decreased by 75%. This might be attributed to the inhibition of oxygen diffusion to the surface of platinum probably due to barrier formation, since E_c with $Cu_2(phen)_4OH$ is similar to that for other additives.

Methanol oxidation might be suppressed by the inhibition of free sites for adsorption of water species as well as that for methanol adsorption. Further investigation by SEIRAS[8] is in progress to study the nature of the adsorbed additives on platinum.

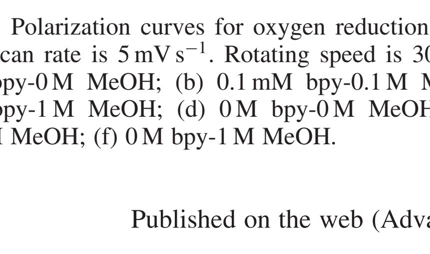

Figure 2. Polarization curves for oxygen reduction in 0.05 M H_2SO_4. Scan rate is 5 $\mathrm{mV\,s^{-1}}$. Rotating speed is 300 rpm. (a) 0.1 mM bpy-0 M MeOH; (b) 0.1 mM bpy-0.1 M MeOH; (c) 0.1 mM bpy-1 M MeOH; (d) 0 M bpy-0 M MeOH; (e) 0 M bpy-0.1 M MeOH; (f) 0 M bpy-1 M MeOH.

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7 Cyclic voltammograms and RRDE measurements were performed with a two compartment cell equipped with a platinum ring-platinum disk (6-mm diameter) working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode using a dual potentiostat with a function generator. The electrochemical data were collected by a homemade automatic measurement program. All potentials are referred to RHE. A Pt disk electrode was cleaned by sweeping voltage from 0 to 1.5 V in 0.05 M H_2SO_4 before each measurement. The collection efficiency of the ring disk electrode was determined to be $N = 0.4$ with the $[Fe(CN)_6]^{3-/4-}$ couple. The efficiency of the O_2 reduction to H_2O, %H_2O, was calculated from the equation, %$H_2O = 100 \times (i_D - i_R/N)/(i_D + i_R/N)$, where i_D is the disk current, i_R is the ring current. 2,2′-bipyridine was purchased from Wako Pure Chemical Industries Ltd. 1,10-phenanthroline, 2,2′:6′,2″-terpyridine and 4,7-diphenyl-1,10-phenanthroline were purchased from Aldrich Inc. Hydroxobis(1,10-phenanthroline)copper(II) was synthesized according to the following literature: M. S. Haddad, S. R. Wilson, D. J. Hodgson, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **103**, 384 (1981).

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