

Electrooxidation of benzylalcohol derivatives in aqueous solution

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Direct methanol fuel cells are expected to be a small and lightweight electric-power generator in the near future. However, methanol as fuel has some shortcomings, for instance, relatively toxic, a low boiling point (65°C), sluggishness oxidation kinetics and methanol crossover from the anode side to the cathode side. In order to overcome above disadvantages, alternative liquid fuels such as ethylene glycol, 2-propanol and dimethyl ether have been proposed. In this paper, we present electrooxidation of benzylalcohols in aqueous solutions for an alternative fuel comparing with methanol oxidation.

As water-soluble benzylalcohol derivatives, hydroxy benzylalcohol (**1**), hydroxymethoxy benzylalcohol (**2**) and their derivatives were used. For electrochemical measurement, a conventional three-electrode electrochemical cell was employed with a Pt working electrode (1.6 mm diameter), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode.

Figure 1 shows typical cyclic voltammograms of **1** at a Pt working electrode in an acidic, basic and neutral aqueous solutions. Each voltammogram had one irreversible oxidation peak and after subsequent potential sweep it decreased, indicating the adsorption of oxidized species. Electrochemical properties of **2** in a basic and neutral solution at a Pt working electrode were in a similar manner as above. In Fig. 2, solid line shows cyclic voltammogram of **2** in 0.5 M H₂SO₄ at a Pt working electrode. The oxidation peak (1150 mV vs. RHE) and coupled reduction peak (652 mV) were observed. In this case, the voltammetric wave shape was maintained after subsequent potential sweep. Dotted line is for methanol oxidation at the same working electrode as a reference. As compared with methanol, **2** indicates a large oxidation current though concentration of **2** is smaller than that of methanol. From Fig.3, oxidation of **2** expected to be diffusion controlled process, which is distinct from methanol oxidation process at a Pt electrode. As we consider a proposed mechanism of electrooxidation of benzylalcohols in aprotic solvents^{1,2}, electrode reaction of **2** in an acidic solution seems to be quite different from methanol oxidation for which a platinum or platinum-based electrocatalyst is indispensable because of slow electrode kinetics. Since similar electrochemical property has been observed when a glassy carbon electrode was used as the working electrode, benzylalcohol derivatives has potentiality for a direct liquid fuel cell which makes it possible not to use a platinum-based electrocatalyst.

References

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2. O. R. Brown, S. Chandra, and J. A. Harrison, *J. Electroanal. Chem.*, **34**, 505 (1972).

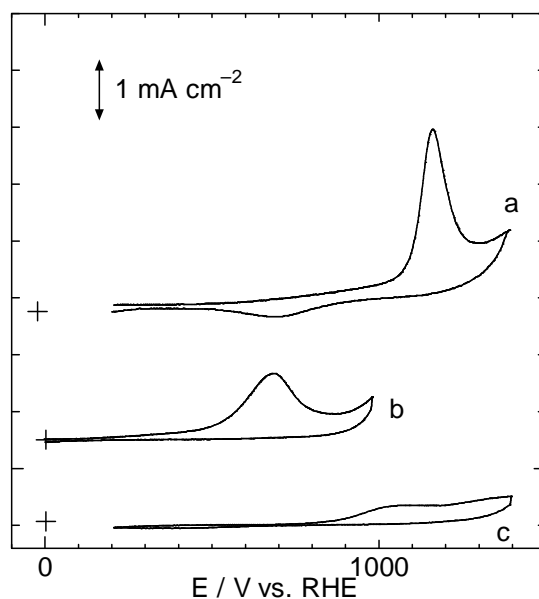


Fig.1 Cyclic voltammograms for 10 mM 4-hydroxybenzyl alcohol in (a) 0.5 M H₂SO₄, (b) 0.5 M KOH and (c) 0.1 M TEAP aqueous solutions at Pt electrodes. Sweep rate : 50 mV s⁻¹

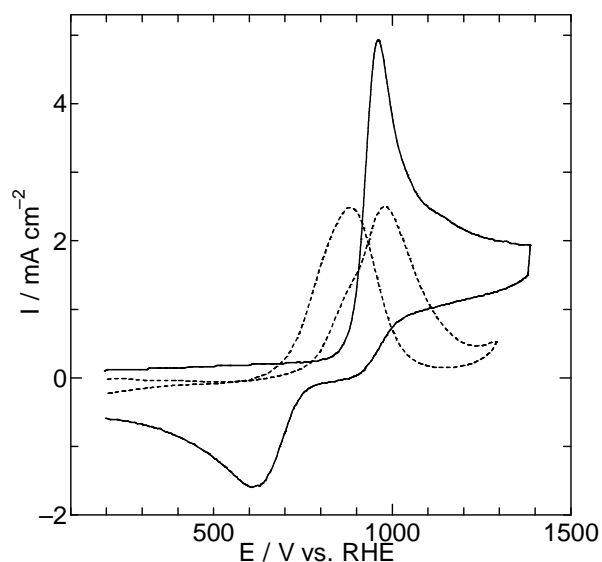


Fig.2 Cyclic voltammograms for 10.1 mM 4-hydroxy-3-methoxybenzyl alcohol (solid) and 0.5 M CH₃OH (dot) in 0.5 M H₂SO₄ at Pt electrodes. Sweep rate : 50 mV s⁻¹

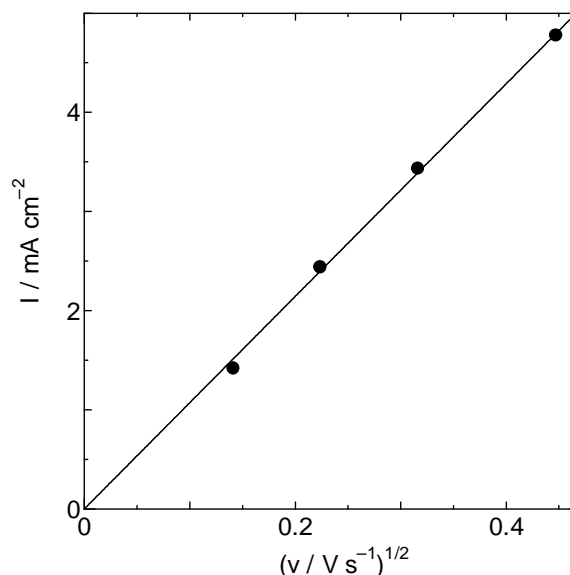


Fig.3 Anodic peak current density vs. $v^{1/2}$ plot for the oxidation of 4-hydroxy-3-methoxybenzyl alcohol in 0.5 M H₂SO₄ at a Pt electrode.