

SHORT COMMUNICATION

Mixtures of methanol and 2-propanol as a potential fuel for direct alcohol fuel cells

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Abstract: The electrochemical oxidation of methanol, 2-propanol, and their mixtures was investigated on a Pt/C thin film electrode in acid solution. It was confirmed that the oxidation of 2-propanol commences at less positive potentials than that of methanol and exhibits significantly higher oxidation current densities at low potentials. When both methanol and 2-propanol were present in the solution, the onset of the oxidation current was the same as for the oxidation of pure 2-propanol. Although both alcohols inhibit the oxidation reaction of each other to a certain extent, steady-state polarization measurements showed that their mixture provides higher current densities than single alcohols over the entire potential region from the hydrogen region to oxide formation on the Pt surface. This implies that the addition of 2-propanol into the fuel may extend the operational range of direct methanol fuel cells.

Keywords: electrochemical oxidation, 2-propanol, methanol, platinum supported catalyst, fuel cell.

INTRODUCTION

Solid polymer electrolyte fuel cells (SPEFC) which use directly alcohols as the fuel are promising power sources for portable electronic devices. Methanol has been considered as the best choice because it is readily available at low cost and has a high energy density. However, the kinetics of the methanol oxidation is slow and leads to high anodic overpotentials.^{1–4} This essential drawback of direct methanol fuel cells (DMFC) induced extensive investigations of the electro-oxidation of other alcohols. Ethanol is an attractive alternative⁵ because it is non-toxic and can be produced from biomass. Although the cleavage of a C–C bond is necessary to achieve complete oxidation of ethanol, the oxidation commences at less positive potentials than methanol oxidation,^{6,7} yielding acetate and CO as the

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adsorbates⁸ and acetaldehyde, acetic acid, and CO₂ as the main products.⁹ The oxidation of C₃ alcohols on Pt was also examined. It was revealed that the adsorbed intermediates and products depend on the position of the OH group in the molecule. Thus, during the oxidation of 1-propanol, adsorbates with one (*e.g.*, linearly bonded CO), two, and three C atoms were found and propionic acid and CO₂ were detected as the main products.^{10,11} Oxidation of 2-propanol produced acetone and CO₂, but no adsorbed CO was found and all adsorbates retained three C-atoms.^{10,12,13} When the onset potentials for oxidation of different alcohols were compared, the performance of 2-propanol was superior to that of methanol,⁷ ethanol^{7,14} and 1-propanol.¹⁰ Also, several researchers conducted parallel studies on direct alcohol fuel cells with 2-propanol as the fuel (DPFC) and DMFC. Wang *et al.*¹⁵ reported that a DPFC operating at 190 °C with either 1- or 2-propanol showed a much worse performance than a DMFC. However, recent studies which were performed at 25 to 90 °C concurred that the performance of the DPFC using 2-propanol was substantially higher than that of a DMFC at current densities lower than 100–200 mA cm⁻², while the DMFC was better at higher current densities.^{16–19} Considering these facts, in this study an attempt was made to combine the good characteristics of both alcohols. The results of the electrochemical oxidation of mixtures of methanol and 2-propanol on carbon supported Pt nanoparticles are reported here.

EXPERIMENTAL

The catalyst used in the experiments was platinum supported on XC-72R high-area carbon (Pt/C). Platinum was deposited on the support by a modified ethylene glycol method. The details of the preparation were given elsewhere.²⁰ The Pt loading of the catalyst was 16.6 mass %.

The catalyst was applied to a gold substrate (5 mm diam.) in the form of a thin film.²¹ Two milligrams of Pt/C was mixed with 1.0 ml of water and 50 μl of Nafion solution (5 mass %, Aldrich). The suspension was agitated in an ultrasonic bath for 60 min and 12.5 μl of it was placed on the gold electrode using a micro-pipette and left to dry over night. The amount of Pt on the electrode was 4.15 μg.

A standard glass cell was used with a Pt wire spiral as the counter electrode and a saturated calomel electrode as the reference electrode. All the potentials reported in this paper are expressed on the scale of the reversible hydrogen electrode (RHE). The electrolyte contained 0.1 M H₂SO₄ as the supporting electrolyte and various concentrations of methanol and 2-propanol. All solutions were prepared with high purity water (Millipore, 18 MΩ cm resistivity) and p.a. grade chemicals (Merck). The electrolyte was deaerated with high purity N₂. The cell was thermostated at 30.0 °C. A Pine RDE4 Potentiostat and a Philips PM 8143 X-Y recorder were used in all experiments.

After immersing a Pt/C electrode in the supporting electrolyte, the potential was cycled between the H₂ and O₂ evolution regions at a rate of 50 mV s⁻¹ until a steady-state voltammogram was obtained. Then in the positive-going sweep, the potential was held at 0.1 V *vs.* RHE, the alcohols were added into the electrolyte and sweep was continued at 50 mV s⁻¹. After attaining a steady-state curve for the oxidation of alcohol, the potential was again held at 0.1 V *vs.* RHE and a polarization curve was recorded at a slow sweep of 1 mV s⁻¹.

The real surface areas of the Pt electrocatalysts were determined using the hydrogen adsorption/desorption charge from the steady-state cyclic voltammograms in the supporting electrolyte

and assuming a charge of $210 \mu\text{C cm}^{-2}$ for a monolayer hydrogen adsorption. The anodic part of the voltammograms corresponding to hydrogen desorption was integrated and the double-layer charging current was subtracted. The average of fifteen experiments resulted in a specific surface area of $84.6 \pm 8.2 \text{ m}^2 \text{ g}^{-1}$, which is the equivalent of a particle diameter of $3.3 \pm 0.3 \text{ nm}$ (assuming that they were ideal spheres). Current densities for the oxidation of the alcohols were calculated per surface area determined for this particular thin film.

RESULTS AND DISCUSSION

The cyclic voltammogram of the Pt/C electrocatalyst, given in Fig. 1a, shows the usual characteristics of a Pt surface, except that current peaks for the adsorption/desorption of hydrogen are not as sharp and well-resolved as on a smooth Pt electrode. The hydrogen region is followed by a double layer charging current, adsorption of oxygen-containing species and their reduction.

The potentiodynamic polarization curves of the oxidation of 0.1 M methanol, 0.01 M 2-propanol, and their mixture are presented in Fig. 1b, while the same curves but with 0.1 M 2-propanol are presented in Fig. 1c. Methanol oxidation shows familiar features, *i.e.*, the onset of the reaction requires the complete desorption of adsorbed hydrogen atoms and the adsorption of OH particles, but the reaction slows down when the formation of Pt oxide commences. On the contrary, the oxidation of 2-propanol commences at the surface which is partially covered with adsorbed hydrogen and has no OH particles attached on it. The difference in the onset potentials of the oxidation of methanol and 2-propanol is caused by the different reaction mechanisms. Methanol adsorbs on the Pt surface dissociatively, CO_{ads} develops, and the oxidation reaction cannot begin until OH species are formed, either on Pt or on some other atoms in a case of a bi-metal catalyst (*e.g.*, Pt–Ru).^{1–3} During the adsorption of 2-propanol, not one C–C bond is broken and there are no strongly adsorbed intermediates, such as CO_{ads} .^{10,13} This implies that OH species are not necessary for the reaction, which was proven by experiments in which modification of the Pt surface by Ru did not influence the onset potential of 2-propanol oxidation.¹¹

When both methanol and 2-propanol were present in the electrolyte, the oxidation current appeared at approximately the same potential as in the electrolyte containing only 2-propanol (Figs. 1b and 1c). It should be noted that the onset potential of the oxidation of the mixture is the same regardless of which alcohol was added first to the electrolyte. In the potential region before the maximum of the 2-propanol oxidation rate, the mixture with 0.01 M 2-propanol (Fig. 1b) exhibits slightly lower current densities than the solution containing only 2-propanol at the same concentration, while in the mixture containing 0.1 M 2-propanol (Fig. 1c), the current densities practically overlap with those obtained with the solution containing only 0.1 M 2-propanol. Oxidation of the first mixture shows that CO_{ads} originating from methanol adsorption slightly hinders the adsorption of 2-propanol, which is consistent with a coverage by CO_{ads} of about 0.2.²² It seems that the oxidation of methanol is suppressed until the oxidation of 2-propanol reaches

its maximum, especially when the concentration of 2-propanol in the mixture was 0.1 M (Fig. 1c). This is probably due to adsorption of large 2-propanol molecules, which delays the adsorption of OH species necessary for the oxidation of CO_{ads} generated by the dissociation of methanol molecules.

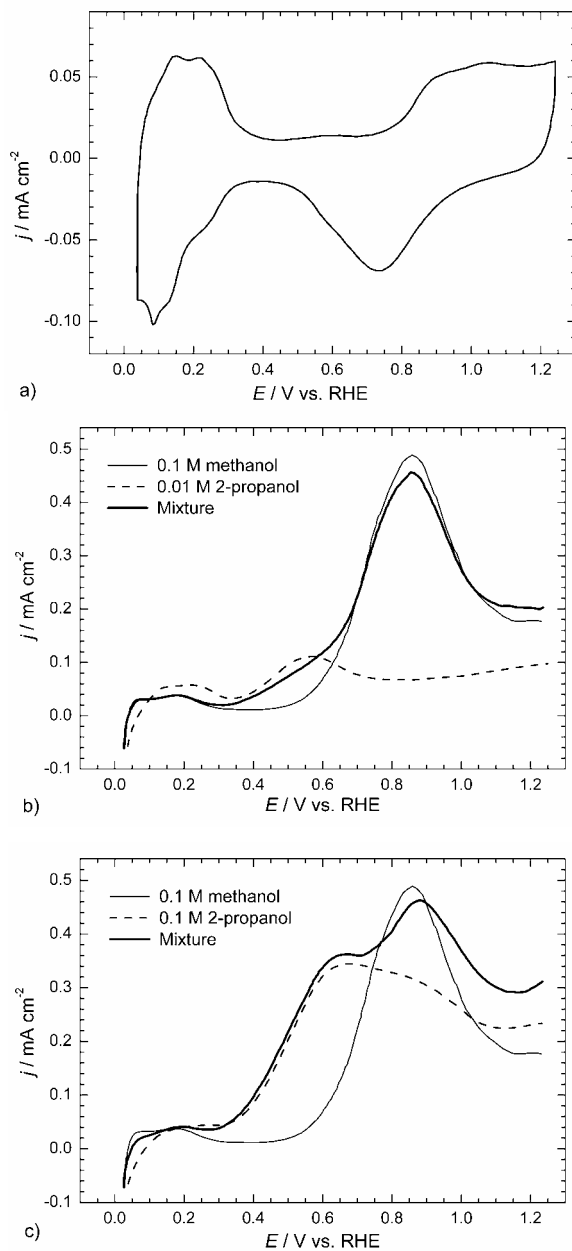


Fig. 1. a) Cyclic voltammogram of Pt/C electrocatalyst, b) potentiodynamic curves for the oxidation of 0.1 M methanol, 0.01 M 2-propanol and their mixture, and c) potentiodynamic curves for oxidation 0.1 M methanol, 0.1 M 2-propanol and their mixture. Supporting electrolyte 0.1 M H_2SO_4 , temperature 30 °C, scan rate 50 mV s^{-1} .

At the potentials more positive than 0.7 V, the oxidation current densities of the mixtures trace the methanol oxidation curve when the concentration of 2-propanol was low (Fig. 1b). At the high concentration of 2-propanol in the mixture (Fig. 1c), the potential of the maximum is shifted by about 30 mV with respect to pure methanol and the current densities are higher after the maximum, indicating a hindrance of the formation of Pt oxide in the presence of 2-propanol.

The applicability of the mixture of the alcohols as the fuel in a fuel cell was estimated from the steady-state polarization curves recorded at 1 mV s^{-1} . Since DMFCs with a Pt–Ru alloy as the anode electrocatalyst are the only direct alcohol fuel cells already in use, the oxidation of methanol and 2-propanol on the Pt/C electrocatalyst was compared with the oxidation of methanol on PtRu/C electrocatalysts (data taken from Ref. 23). All the currents are expressed as mass activities, *i.e.*, the current per mass of metal or alloy. The Tafel plots in Fig. 2 show the remarkably better performance of both pure 2-propanol and the mixtures, compared to methanol, at potentials up to about 0.6 V. At higher potentials, pure methanol and the mixtures are superior to 2-propanol. Therefore, only a mixture of methanol and 2-propanol can deliver a significant anodic current over the entire potential range from 0.2 to 0.8 V.

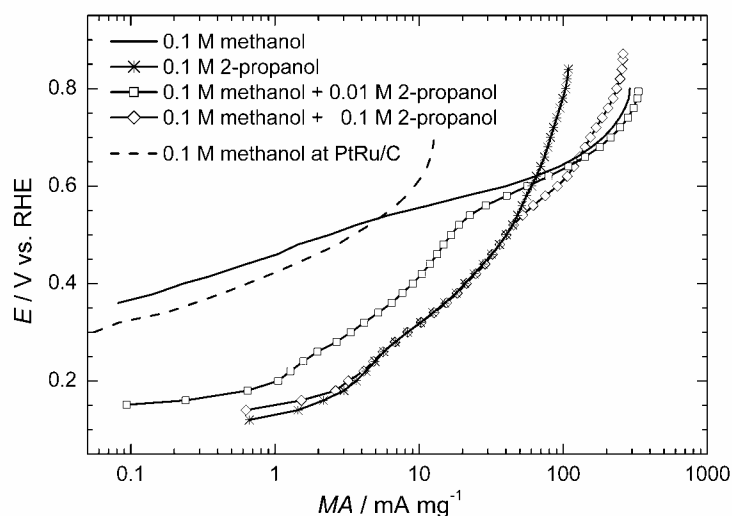


Fig.2. Polarization curves for the oxidation of 0.1 M methanol at Pt/C and PtRu/C catalysts, oxidation of 0.1 M 2-propanol and the oxidation of the mixtures of 0.1 M methanol with 0.1 and 0.01 M 2-propanol at a Pt/C catalyst. Supporting electrolyte 0.1 M H_2SO_4 , temperature 30 °C, scan rate 1 mV s^{-1} .

CONCLUSIONS

Investigation of the simultaneous oxidation of methanol and 2-propanol on a Pt/C electrocatalyst showed that 2-propanol exhibits significantly higher oxida-

tion current densities than methanol at low potentials, despite the fact that 2-propanol oxidizes incompletely, yielding acetone as the main product and only two electrons per molecule. When both alcohols are present in the electrolyte, methanol slightly suppresses the oxidation of 2-propanol, but only if the mixture contains a low concentration of 2-propanol. On the other hand, a high concentration of 2-propanol in the mixture delays OH adsorption and shifts the methanol oxidation towards more positive potentials. Although both alcohols inhibits the oxidation reaction of each other to a certain extent, steady-state polarization curves recorded at a slow sweep rate clearly showed that their mixture provides higher current densities than the single alcohols over the entire potential region from the hydrogen region to oxide formation on the Pt surface.

The results imply that a direct alcohol fuel cell operating with a mixture of methanol and 2-propanol should give higher voltages than a DMFC with a Pt–Ru anode. According to literature,¹⁶⁻¹⁸ when pure 2-propanol was used as the fuel (DPFC), a rapid drop at high current densities was observed. With a mixture of methanol and 2-propanol, this failure should be overcome because methanol can take on the anodic reaction. This statement requires verification under fuel cell conditions.

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ИЗВОД

СМЕША МЕТАНОЛА И 2-ПРОПАНОЛА КАО ПОТЕНЦИЈАЛНО ГОРИВО У ГОРИВИМ СПРЕГОВИМА СА АЛКОХОЛОМ

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Испитивана је електрохемијска оксидација метанола, 2-пропанола и њихових смеша на танком филму Pt/C катализатора у киселој средини. Потврђено је да оксидација 2-пропанола почиње на мање позитивним потенцијалима него оксидација метанола и да даје знатно веће густине струја при нижим потенцијалима. Када су и метанол и 2-пропанол присутни у раствору, струја оксидације се појављује на истом потенцијалу као у случају чистог 2-пропанола. Мада оба алкохола инхибирају оксидацију оног другог у извесној мери, стационарна мерења су показала да њихова смеша даје веће густине струја од појединачних алкохола у целој области потенцијала од водоничне области па до формирања оксида на платини. То указује да се радни опсег горивог спрега са метанолом може повећати додатком 2-пропанола у гориво.

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