Electrochemical oxidation of ethylene glycol on Pt-based catalysts in alkaline solutions and quantitative analysis of intermediate products

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**A B S T R A C T**

Electrocatalytic activities of Pt/C, Pt-Ru/C, and Pt-Ni/C for the oxidation of ethylene glycol in a basic solution are evaluated by cyclic voltammetry and quasi-steady state polarization. Based on the results of Tafel slopes from quasi-steady state polarization, the catalytic activities for ethylene glycol oxidation are in the order of Pt-Ru/C > Pt-Ni/C > Pt/C. The analysis of intermediate products for ethylene glycol oxidation by higher performance liquid chromatograph (HPLC) demonstrates that the degree of ethylene glycol oxidation is dependent on catalysts. Pt-Ru/C shows the highest current densities for ethylene glycol oxidation, but shows lower fuel utilization. On the other hand, Pt-Ni/C shows higher ability to cleavage C–C bonds, but is suffered from catalyst poisoning. To improve the tolerance for catalyst poisoning, we construct a novel Pt-Ni-SnO\(_2\)/C catalyst, compare its catalytic activities, and evaluate the intermediates. Pt-Ni-SnO\(_2\)/C shows superior catalytic activities for ethylene glycol oxidation, resulting in the highest degree of complete electro-oxidation of ethylene glycol to CO\(_2\).

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1. Introduction

Direct oxidation of alcohols in polymer electrolyte fuel cells has received much attention over the last years. These direct alcohol fuel cells (DAFCs) are expected as a potential alternative power source for portable electric devices, since DAFCs have some advantages in terms of energy densities and easy transportability, as compared with hydrogen fuel. Among direct alcohol fuels, methanol has been most widely studied. However, in an acid medium, there is an obstacle of sluggish kinetics in methanol oxidation \([1,2]\). Therefore, alkaline direct methanol fuel cells, in which methanol oxidation proceeds under basic conditions, have been intensely studied to realize fast kinetics of methanol oxidation.

Our group has been focusing on ethylene glycol as a direct fuel in anion-exchange membrane fuel cells (AEMFCs). Ethylene glycol has superior energy density (7.56 kWh dm\(^{-3}\)) and higher boiling point (471 K) than some typical alcohol fuels such as methanol and ethanol \([3]\). The oxidation of ethylene glycol in alkaline medium is faster than that in acid medium. And, surprisingly, ethylene glycol provides larger oxidation currents than methanol and polyols such as glycerol, erythritol, and xylitol in basic solutions \([4]\). Thus, ethylene glycol is a promising fuel for AEMFCs, which overcomes a conventional direct methanol fuel cell (DMFC).

Ethylene glycol has the above-mentioned advantageous features as DAFCs’ fuel, but it has a crucial problem derived from its inherent molecular structure. Ethylene glycol is a C2 molecule having a C–C bond in its structure. C–C bond is a stumbling block for electro-organic chemists since thus C–C bond is comparatively strong and cannot be easily cleaved \([5]\). As well as ethanol oxidation, ordinal Pt catalyst cannot achieve the complete oxidation of ethylene glycol (as shown in Eq. (1)), and leaves some intermediate products (Scheme 1):

\[(\text{CH}_2\text{OH})_2 + 100\text{H}^+ \rightarrow 2\text{CO}_2 + 8\text{H}_2\text{O} + 10e^- \quad (1)\]

Therefore, in order to increase the efficiency of fuel utilization, active catalysts, having sufficient ability to break C–C bond in ethylene glycol, are strongly required. As for ethanol oxidation, Adzie and co-workers \([6]\) reported that Pt-Rh-SnO\(_2\) catalyst oxidized ethanol and facilitated its oxidation to CO\(_2\) at lower potentials. However, to our best knowledge, there is no available literature concerning the oxidation of ethylene glycol to CO\(_2\) from an electro-catalytic view point.

Here we report an effective C–C bond cleavage electrocatalyst for ethylene glycol, and discuss the intermediate products through ethylene glycol oxidation using HPLC.
2. Experimental

2.1. Catalysts preparation and characterization

Carbon-supported Pt, Pt-Ru (1:1), and Pt-Ni (1:1) alloy catalysts (Pt/C, Pt-Ru/C, and Pt-Ni/C, respectively), purchased from E-TEK with metal loading of 40 wt%, were used as received. The procedure used in preparing SnO$_2$ nanoparticles was similar to that described by Jiang et al. [7]. In a mixture of 50 mL ethylene glycol and water (1:50 by mole), 100 mg of hydrochloric acid (35%, Nacalai Tesque, GR) and 200 mg of SnCl$_2$-2H$_2$O (Nacalai Tesque, GR) were dissolved. After the solution was fluxed at 463 K for 50 min, we obtained a SnO$_2$ colloid solution, whose clear color turned into slight yellow. Catalyst powder of 50 mg Pt-Ni/C was added into 10.8 g of SnO$_2$ colloid solution (SnO$_2$: 3.15 mg mL$^{-1}$), and this mixture was stirred for 30 min and further sonicated for 30 min to deposit SnO$_2$ nanoparticles on Pt-Ni/C. X-ray diffraction (Rigaku, RINT-2500), transmission electron microscopy (Hitachi, H-9000NAR), and X-ray photoelectron spectroscopy (ULVAC-PHI Model 5500) were used for characterizing Pt-Ni-SnO$_2$ catalysts.

2.2. Electrochemical measurements and HPLC analysis

Evaluations of electrochemical activities of each catalyst were performed by using catalyst-coating glassy carbon disk electrodes. Catalysts in 1-hexanol solutions were deposited on a glassy carbon disk electrode (Ø 6 mm) and fixed with Nafion ionomer solutions. Metal loading was uniformed at 25.5 µg cm$^{-2}$. A three-electrode electrochemical cell was equipped with Pt wire and reversible hydrogen electrode (RHE) as counter and reference electrodes, respectively. All potentials were referred to RHE throughout this study. An aqueous electrolyte solution of 1 mol dm$^{-3}$ KOH and 1 mol dm$^{-3}$ ethylene glycol was deaerated by Ar bubbling. A disk electrode was rotated at 900 rpm in cyclic voltammetry and chronoamperometry to achieve the steady-state diffusion of ethylene glycol solutions. We defined currents after 800 s beginning from a potential step as quasi-steady state currents.

In order to analyze the intermediate compounds, HPLC analysis of electrolyte solutions was performed. A three-electrode cell was used. Catalyst ink, which contains catalyst, Nafion ionomer (5 wt% Nafion, Aldrich), and ethanol, was coated on carbon cloth (Electrochem, EC-CC1-060) to serve as a working electrode. Pt wire and RHE were used as counter and reference electrodes, respectively. A solution of 1 mol dm$^{-3}$ KOH and 0.5 mol dm$^{-3}$ ethylene glycol was used. Potential holding was conducted at 0.50 V to obtain intermediates during the electro-oxidation of ethylene glycol. The method and a set of equipments for HPLC analysis were described previously [8,9].

Fig. 1. (a) Cyclic voltammograms and (b) Tafel plots on Pt/C, Pt-Ru/C, and Pt-Ni/C catalysts in an aqueous solution of 1 mol dm$^{-3}$ KOH and 1 mol dm$^{-3}$ ethylene glycol.
3. Results and discussion

3.1. Ethylene glycol oxidation on Pt-based catalysts

Fig. 1a shows cyclic voltammograms (CVs) of ethylene glycol oxidation. At the potentials of 0.30–0.60 V, the order of oxidative current densities was found to be Pt-Ru/C > Pt-Ni/C > Pt/C. Tafel plots calculated from the steady-state currents show the same order as CVs for ethylene glycol oxidation (Fig. 1b). In particular, Pt-Ru/C showed the highest catalytic activities for ethylene glycol oxidation. Generally, Ru easily forms oxygen-containing species on its surface. Such oxygen-containing species formed on the surface of Ru are effective to suppress CO poisoning of Pt catalysts, and therefore Pt-Ru/C work efficiently for the oxidation of alcohols such as methanol and ethanol [10,11]. Similarly, Pt-Ru/C was effective for the oxidation of ethylene glycol. In contrast, Pt-Ni/C had a slight increase in catalytic activities for ethylene glycol oxidation, as compared with Pt/C. Therefore, Ni alloying is not sufficient to prevent CO poisoning of Pt catalysts.

In HPLC analysis, two intermediate products of formate and glycolate were detected for ethylene glycol oxidation in KOH solution. Fig. 2 shows current efficiencies for formate and glycolate, obtained after 50 C passing at 500 mV. Glycolate is an intermediate product...
via 4-electron oxidation, in which C–C bond remains, as given by the following reaction:

\[
(\text{CH}_2\text{OH})_2 + 5\text{OH}^- \rightarrow \text{CH}_2\text{OHHCOO}^- + 4\text{H}_2\text{O} + 4\text{e}^- \quad (2)
\]

Formate is generated via 6-electron oxidation, which involves the C–C bond cleavage of ethylene glycol:

\[
(\text{CH}_2\text{OH})_2 + 8\text{OH}^- \rightarrow 2\text{HCOO}^- + 6\text{H}_2\text{O} + 6\text{e}^- \quad (3)
\]

In Fig. 2, “Others” refer to the rest of electric charges consumed for ethylene glycol oxidation, and mainly corresponds to the amount of CO₂ production, which indicates the degree of complete oxidation of ethylene glycol. According to HPLC analysis, the most produced product was glycolate for all catalysts, which is in good agreement with our previous report [8]. As compared with Pt/C, it is noted that Pt-Ru/C showed higher production of glycolate instead of formate, whereas Pt-Ni/C showed the highest production of formate instead of glycolate. These results can be understood from the two aspects: the tolerance for poisoning and the ability of C–C bond cleavage. Since formate is one of the species that initiate the poisoning of Pt catalysts [1,12] and Pt-Ru/C exhibited smaller amount of formate, it is indicated that Pt-Ru/C catalyst had higher tolerance for catalyst poisoning. However, Pt-Ru/C had poor catalytic activity for C–C bond cleavage, which resulted in larger amount of glycolate production. In contrast, Pt-Ni/C showed larger amount of formate and smaller amount of glycolate. The former indicated that Pt-Ni/C had less tolerance for poisoning, but the latter showed higher catalytic activities for C–C bond cleavage.

In order to utilize effectively an organic fuel, catalysts must be highly capable to break C–C bonds and highly tolerant for poisoning. Therefore, we added SnO₂ nanoparticles to Pt-Ni/C catalyst to obtain a catalyst with both high catalytic activity for C–C bond cleavage and concomitant tolerance for poisoning.

**3.2. Characterization of Pt-Ni-SnO₂ catalysts**

Fig. 3a–c shows TEM images of SnO₂ nanoparticles and Pt-Ni-SnO₂ catalysts. Solely SnO₂ nanoparticles, prepared by sol–gel method, had a diameter of 10–15 nm (Fig. 3a). TEM image of Pt-Ni-SnO₂ catalyst (Fig. 3b) shows that some particles co-existed having fringes with different d-spacing values. Therefore, we performed the filtration of fast Fourier transform (FFT) using the (2 0 0) lattice of SnO₂ and the (1 1 1) lattice of Pt-Ni alloy [13,14]. Two different groups of particles (Pt-Ni alloy particles and SnO₂ nanoparticles) were clearly distinguished in Fig. 3c. Pt-Ni alloy particles existed adjacent to SnO₂ nanoparticles, thus we can expect the significant interplay between Pt-Ni alloy particles and SnO₂ nanoparticles and their synergetic catalytic activities. XPS analysis showed that an approximate atomic ratio of Pt/Sn was 5/4, and therefore the catalyst consisted of about 16 wt% SnO₂ in Pt-Ni-SnO₂/C. In addition, based on the results of XRD patterns (Fig. 4), we confirmed that each catalyst had the same crystalline size (ca. 4 nm) and the addition of SnO₂ nanoparticles did not alter the crystal structure of Pt-Ni alloy.

**3.3. Ethylene glycol oxidation on Pt-Ni-SnO₂ catalysts**

Electrocatalytic activities of the resultant Pt-Ni-SnO₂/C were studied by cyclic voltammograms and Tafel plots as shown in Figs. 5 and 6. Pt-Ni-SnO₂/C showed superior catalytic activities for ethylene glycol oxidation to Pt-Ni/C and Pt/C. Therefore, it is confirmed that the addition of SnO₂ nanoparticles is effective to improve the tolerance for catalyst poisoning of Pt-Ni/C. The HPLC
analysis for intermediates for ethylene glycol oxidation show that the amount of formate production decreased, and the degree of complete oxidation increased by Pt-Ni-SnO2/C. However, SnO2 nanoparticles did not reduce the formation of glycolate. These results indicate that the addition of SnO2 nanoparticles had a specific effect of improving the tolerance for catalyst poisoning.

In this study, we explored the Pt-based catalysts with high activities that realize complete electro-oxidation of ethylene glycol to CO2. Pt-Ni/C was found to possess catalytic activities for C–C bond cleavage of ethylene glycol. According to the previous studies using in situ infrared spectroscopy, bulk Ni catalysts have ability to decompose C2 molecules into CO2 [15]. Therefore, the alloying Ni element is reasonably an effective way to C–C bond cleavage of C2 fuels in fuel cells. However, Pt-Ni/C is not efficient to oxidize ethylene glycol completely. Another stumbling block is catalyst poisoning. In order to improve the tolerance for catalyst poisoning, we attempted to add SnO2 nanoparticles to Pt-Ni/C catalysts. As a result, the Pt-Ni-SnO2/C catalyst showed higher electrocatalytic activities for the complete oxidation of ethylene glycol than Pt/C, Pt-Ni/C, and Pt-Ru/C. When we consider the effects of each element of Pt-Ni-SnO2/C catalysts, it was found that every element might play each different role cooperatively; the dehydrogenation of C–H bonds by Pt, the cleavage of C–C bonds in ethylene glycol by Ni, and the suppression of the poisoning of Pt catalysts by SnO2.

4. Conclusions

Electrocatalytic activities of Pt/C, Pt-Ru/C, and Pt-Ni/C for the oxidation of ethylene glycol were evaluated in basic solutions by cyclic voltammetry and quasi-steady state polarization. The catalytic activities were in the order of Pt-Ru/C > Pt-Ni/C > Pt/C. The analysis of intermediates for ethylene glycol oxidation by HPLC demonstrated that the degree of complete oxidation of ethylene glycol depended on the catalysts. As a result, the catalysts show some disadvantages such as bad fuel utilization, catalyst poisoning, etc. To solve these problems, we conducted Pt-Ni-SnO2/C catalyst and evaluated its catalytic activities and intermediates. Pt-Ni-SnO2/C showed superior catalytic activities for ethylene glycol oxidation and increased the degree of complete electro-oxidation of ethylene glycol. Therefore, we concluded that Pt is active for dehydrogenation, Ni is for cleavage of C–C bond, and SnO2 is for the suppression of catalyst poisoning.

We believe these results provide a guideline to construct active catalysts that break C–C bonds in C2 molecules and utilize ethylene glycol as DAPCs’ fuel effectively.

References
