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Short Communication

High-performance direct ethanol fuel cell using nitrate reduction reaction

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ABSTRACT

In this study, we propose a high-performance direct ethanol fuel cell (DEFC) using nitrate reduction reaction with a carbon felt electrode (DEFC-HNO₃) instead of oxygen reduction reaction (ORR) on a Pt catalyst (DEFC-O₂). The activation energy for the nitrate reduction reaction on the carbon electrode is found to be relatively low at ~14.2 kJ mol⁻¹, compared to the ORR. By using the nitrate reduction reaction at the cathode and oxidation of ethanol as a fuel at the anode, the DEFC shows a significantly high open circuit voltage of 0.85 V and two-fold maximal power density of 68 mW cm⁻² at 80 °C, compared to the DEFC-O₂, due to the significantly fast reaction rate of the nitrate reduction reaction.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have recently received attention as eco-friendly electrochemical power sources, that can simultaneously resolve environmental and energy issues, due to high energy efficiency and low emission of pollution [1–5]. Among the PEMFCs, alcohol fuel cells can be operated using liquid fuels such as formic acid, methanol, and ethanol, at low temperatures [6–10]. In particular, ethanol as a relatively nontoxic fuel can be inexpensively produced from biomass. Direct ethanol fuel cells (DEFCs) can be divided into two types: acid- and alkaline-membrane DEFCs [11,12]. However, since, in DEFCs, electrochemical reactions such as ethanol

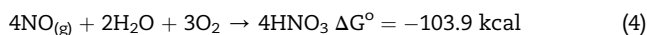
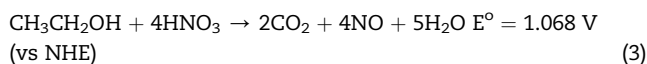
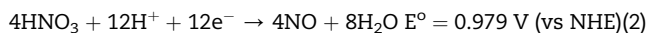
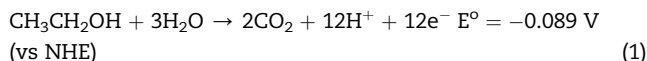
oxidation reaction (EOR) at an anode and oxygen reduction reaction (ORR) at a cathode are sluggish, Pt-based catalysts with a highly excellent electrocatalytic activity for EOR and ORR are mainly used at both electrodes [6,13–15]. In the EOR at the anode, catalysts must be able to activate C–C bond scission for complete oxidation to CO₂. However, strong C–C bond in ethanol leads to more complicated reaction intermediates and products during oxidation such as acetic acid or acetaldehyde [16–20]. Thus, various studies to alloy Pt with other transition elements such as Sn, Ru, and Au are investigated to improve the catalytic activity [21–27]. In particular, Sn can provide an active site for C–C bond scission and modify the electronic properties of Pt for an enhanced EOR activity [28–32].

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In particular, chemically regenerative redox fuel cells (CRRFCs) are electrochemical energy devices that generate electricity by the electrochemical reactions of redox couples ($\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{V}^{4+}/\text{V}^{5+}$, Br^-/Br_2) as fuels and oxidants that can be regenerated using hydrogen and oxygen at an anode and a cathode, respectively [33–38]. The electrochemical reactions of the redox couples on carbon-based electrodes as catalysts in CRRFCs are significantly faster than those in PEMFCs, which consist of catalytic reactions on Pt-based metal catalysts [39–41]. Thus, to overcome the slow reduction reaction in the PEMFCs, redox couples are proposed as an oxidant with a high solubility in an aqueous solvent instead of using oxygen or air as the typical oxidant. Herein, as a novel attempt of an all-liquid-type fuel cell designing, we proposed a high-performance DEFC using the relatively efficient reduction reaction of nitric acid (DEFC- HNO_3), which has a high energy density of 68 mAh g^{-1} and a high solubility (Fig. 1). In the DEFC- HNO_3 , the ethanol oxidation and nitrate reduction occur on the PtSn alloy catalyst at the anode (Eq. (1)) and on the carbon felt at the cathode (Eq. (2)), respectively [38,42]. The overall reaction of the DEFC- HNO_3 can be expressed as shown in Eq. (3). However, a product of the reaction is NO, an environmental pollutant and a toxic compound. The NO can be oxidized using O_2 and H_2O and regenerated to HNO_3 (Eq. (4)) [37].



Experimental

Synthesis and characterization of PtSn catalyst

To synthesize the PtSn(3:1) alloy catalyst for ethanol electro-oxidation, 93.1 mg H_2PtCl_6 (99.99%, Aldrich) and 30.1 mg $\text{Sn}(\text{acac})_4$ (99.9%, Aldrich) were dissolved in 80 mL ethanol

(95%, Aldrich) with continuous stirring. After complete dissolution, the metal salts were reduced using a borohydride reduction method. 41 mg NaBH_4 (99%, Aldrich) dissolved in 20 mL deionized (DI) water was added to the salt solution with vigorous stirring for 12 h. The precipitate was filtered and washed with ethanol, acetone, and DI water. The final product was dried in an 80°C oven for 24 h. The crystal structure and alloy formation of the catalyst were characterized using the X-ray diffraction method (XRD, Bruker, D2 Phase System). In the XRD analysis, the radiation source was $\text{Cu K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) and the applied voltage and current of the tube were 30 kV and 10 mA, respectively. The particle size and structure for the catalyst were observed using a transmission electron microscope (TEM, JEM-ARM 200F) operating at 200 kV. The specimen for TEM analysis was prepared by dropping the catalyst solution dispersed in ethanol on a carbon-free Cu grid.

Electrochemical analysis

The electrochemical properties of the catalyst were characterized using a potentiostat (Eco Chemie, AUTOLAB). Pt wire and Ag/AgCl (in 3 M KCl) were used as the counter and reference electrodes, respectively. The catalyst ink was prepared by mixing and sonicating the powder in DI water. 6.5 μL ink was dropped on a glassy carbon electrode and dried in a 50°C oven for 2 h. 5.4 μL Nafion® solution (5 wt%, Aldrich) was dropped on the electrode and dried in a 50°C oven for 30 min. The amount of catalyst deposited on the electrode was $\sim 40.8 \mu\text{g cm}^{-2}$. The ethanol oxidation of the catalyst was evaluated using cyclic voltammetry in 2 M EtOH + 0.5 M H_2SO_4 . The reduction reaction and activation energy of nitrate were characterized in 2 M HNO_3 at different reaction temperatures using linear sweep voltammetry with a scan rate of 5 mV s^{-1} .

Fabrication of membrane-electrode-assembly and unit cell measurement

The membrane-electrode-assembly (MEA) was fabricated using the decal method with a PtSn anode catalyst. The ink for the anode was prepared by mixing and sonicating the catalyst (0.1 g) in DI water (200 μL), isopropanol alcohol (4 mL), and Nafion® solution (230 μL). The catalyst ink was sprayed on teflon film using an ultrasonicator and Nafion® solution (100 μL) was then coated on the catalyst layer. The MEA without a cathode was prepared by hot-pressing the anode catalyst-coated teflon film on a pre-treated Nafion®

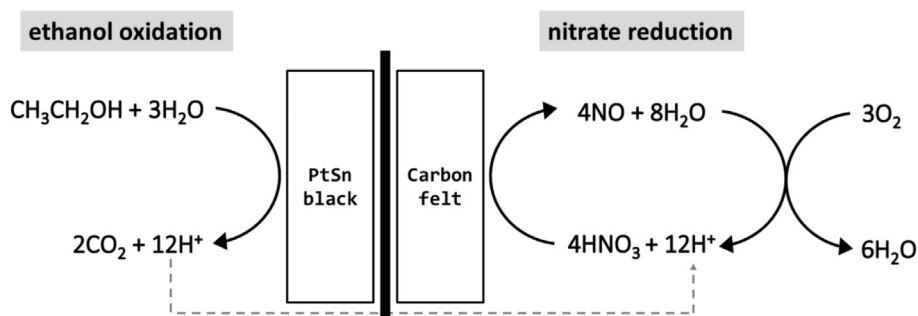


Fig. 1 – Schematic illustration of direct ethanol fuel cell using nitrate reduction reaction.

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