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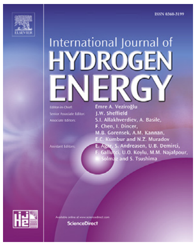

Highly dispersed and CO_{ad}-tolerant Pt_{shell}-Pd_{core} catalyst for ethanol oxidation reaction: Catalytic activity and long-term durability

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ABSTRACT

Highly dispersed Pt_{shell}-Pd_{core} catalyst is synthesized via an electroless deposition and a galvanic displacement. From electrochemical analysis, the catalyst is confirmed to be active toward an ethanol oxidation reaction for a prolonged time, and is more resistive against CO_{ad}-poisoning than a conventional Pt/C catalyst. The stable activity of Pt_{shell}-Pd_{core}/C is ascribed to the modified electronic property of Pt over-layer, which leads to a weak CO-adsorption strength with a high affinity for OH. The weakened binding property of surface Pt with CO_{ad} was experimentally confirmed by conducting a CO_{ad}-stripping and by measuring an electrochemically active surface area of the catalyst over multiple cycles. The CO_{ad} oxidation ability of as-synthesized catalyst is further proved by a computational method via density functional theory (DFT) calculation. The result presents a potential application of the catalyst for the efficient ethanol oxidation in a direct ethanol fuel cell.

Introduction

Much attention has been made to proton exchange membrane fuel cells (PEMFCs) due to its versatility as a power source for portable electronics and electric vehicles [1–5]. PEMFCs are classified into H_2-PEMFC (gaseous hydrogen) and direct alcohol-PEMFC (methanol, ethanol), based on which type of fuel is oxidized to generate electrons. Of those, direct alcohol-PEMFC is more advantageous than H_2-PEMFC, in terms of easy storage, transportation, and high volumetric-/gravimetric energy density [6–8].

For the last two decades, direct methanol fuel cell (DMFC), one of the direct alcohol-PEMFCs, has been widely investigated as a future power source. However, methanol is toxic as well as volatile, and therefore it is not an ultimate replacement for H_2. As an alternative fuel, ethanol provides more advantages; safer, more energy density compared to methanol (8.01 kWh kg^{-1} *vs.* 6.09 kWh kg^{-1}) [9,10]. Therefore,

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ethanol is more attractive source for low-temperature fuel cell than methanol. For this reason, direct ethanol fuel cell (DEFC) is being studied extensively at present times [11–17].

However, DEFC suffers from the poisoning problem, induced by the reaction intermediates of ethanol such as surface-adsorbed CO (CO_{ad}), just as DMFC does. The poisoning effect triggers the deactivation of DEFC, and hinders its long-term operation. Moreover, the electro-oxidation of ethanol is more complex than that of methanol. As it was known, the complete oxidation of ethanol requires 12 electrons per molecule (only 4 electrons for methanol activation), and more intermediates were formed during the reaction [10]. For above reasons, there is a strong need to develop more active and stable anode catalyst for DEFC.

Pure Pt has been the most active catalyst for oxidation of small molecule alcohol, such as methanol and ethanol. However, at room temperature Pt becomes readily poisoned by adsorbed intermediates. Making the catalyst more resistive to poisoning, Pt has been alloyed with other transition metals (Pt-M, M = Ru [7–9,12–14,18–20], Sn [7–9,13–15,21], Pd [7–10,22–24], W [7–9,19], and Ni [12], Rh [20,25,26]). Among them, the oxophilic Ru and Sn imposed the synergetic effect, which delivered facile oxidation of adsorbed intermediate, CO_{ad}. These metals activated water molecule at lower over-potential and provided more active site of $-OH_{ad}$ on the Pt surface [7]. It was also found that Pt-Pd alloy facilitates the oxidation of ethanol in both acidic [7–9,22–24] and basic [10] environment. CO_{ad}-poisoning can also be resolved by modifying Pt surface with foreign metal, forming Pt monolayer (ML) on metal substrate [24]. The method is the cost-effective strategy because less amount of Pt is involved in the catalysts compared to the conventional alloyed catalysts, and it tunes the catalytic properties for alcohol oxidation as a consequence of substrate-induced strain effect in Pt ML. Both theoretical prediction and experimental results for the facile oxidation of alcohol on Pt_{ML} have been reported [27].

In this study, the electro-oxidation of ethanol was attempted on carbon-supported Pt-Pd electro-catalyst with shell-core structure (Pt_{shell}-Pd_{core}/C). We applied electro-less deposition (ELD) of Cu, followed by galvanic displacement with Pt to fabricate the catalyst. By virtue of spontaneous reaction between pre-deposited Cu and Pt precursor, the amount of Pt deposit was restricted and controllable (1.3 Pt layer) [28,29]. Such controllable synthesis of nanocrystals is attractive, in that the accurate control of size, composition, and morphology provides opportunities of tailoring their catalytic properties. As-prepared Pt_{shell}-Pd_{core}/C showed an improved and stable activity for ethanol oxidation during long-term operation, exhibiting high CO_{ad}-tolerance of which rationale were supported by calculating CO oxidation capacity of the catalyst via density function theory.

Experimental methods and materials

The preparation of Pt_{shell}-Pd_{core}/C consists of two steps; synthesis of carbon-supported Pd nanoparticles (Pd/C), and formation of Pt layer on Pd nanoparticles. The latter process once again comprises the ELD of Cu on Pd (Cu_{shell}-Pd_{core}/C) and the successive displacement of Cu with Pt (Pt_{shell}-Pd_{core}/C). The detail of synthetic process was already addressed in our previous study [28].

Preparation of Pd/C

Carbon-supported Pd nanocrystal was synthesized via novel colloidal method. 44.51 mg of $PdCl_2$ (Sigma-Aldrich) was dissolved in 150 ml of de-ionized water with 0.15 M HCl. 47.3 mg of high-surface-area carbon black (VulcanXC-72, Cabot corp.) was dispersed in the mixture of de-ionized water and isopropyl alcohol (JUNSEI) by ultrasonic agitation (v/v = 1). Both solution were mixed and stirred for 2 h. 24.6 mg of Na_2WO_4 (Sigma-Aldrich) was added in the mixed solution. Then 20 ml of 0.1 M $NaBH_4$ solution was added drop-wise into the solution to finalize the synthesis of Pd/C. Pd/C was washed and filtered multiple times to remove excess precursor and reducing agent, and then dried in vacuum at 60 °C overnight.

Preparation of Pt_{shell}-Pd_{core}/C

The solution for Cu ELD was prepared with the following composition; 3.6 mM $CuSO_4 \cdot 5H_2O$, 7.7 mM ethylenediaminetetraacetic acid (EDTA), and 7 mM paraformaldehyde (HCHO) in 200 ml of de-ionized water. The pH of the solution was controlled up to 12 by adding 0.052 M KOH. 20 mg of Pd/C was ultrasonically dispersed in the mixture solution of isopropyl alcohol and de-ionized water. The suspension was added into Cu-containing electrolyte and stayed for 5 min at 75 °C to deposit Cu. The solid powder was filtered and placed in 1 mM $H_2PtCl_6 \cdot 6H_2O$ (Sigma-Aldrich) in 0.05 M H_2SO_4 for 30 min to replace Cu with Pt. The synthesized product was filtered and dried at 50 °C in vacuum, followed by heat treatment in H_2 environment (99.9%, 100 ccm) at 120 °C for 1 h.

Physicochemical analysis

X-ray diffractometer (XRD, Rigaku Corp.) was used to confirm the formation of Pd, Pt. X-ray photoelectron spectroscopy (XPS, Thermo, Al Kα) was utilized to investigate the existence of Cu and Pt with their oxidation states, after ELD and after galvanic displacement, respectively. All spectrums were referenced to C_{1s} (284.6 eV) and were fitted by XPSPEAK41 software for deconvolution. Analytical transmission electron microscope (TEM, Technai-F20) was used to image the morphology of the catalyst. Even though the accelerating voltage of F20 was 200 kV (~930 kx), it was specialized to perform atomic analysis. It was equipped with high angle annular dark field (HAADF) detector in scanning TEM mode (~230 Mx), which means that it was capable of obtaining dark field image as well as bright field image, and differentiating heavy and light elements by Z-contrast. Energy dispersive X-ray spectroscopy (EDS) line scanning could monitor the geometric distribution of Pt and Pd in Pt_{shell}-Pd_{core}/C, and prove core-shell configuration by their position. Thermogravimetric analysis (TGA) measured the amount of Pd, loaded in the carbon support after colloidal synthesis of Pd/C, and the total metal amount of Pt_{shell}-Pd_{core}/C. The weight percentage (wt%) of each metal in catalyst (Pt, Pd) was measured by inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer).

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