



Preparation and characterization of palladium-nickel on graphene oxide support as anode catalyst for alkaline direct ethanol fuel cell

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ABSTRACT

A catalyst consisting of palladium – nickel supported on exfoliated graphene oxide (PdNi/EGO) composite was synthesized. The catalytic activity was tested for ethanol oxidation reaction (EOR) in half-cell using cyclic voltammetry (CV) and subsequently it was used as an anode material in a direct ethanol fuel cell (DEFC). Transmission Electron Microscopy showed the catalyst particles are uniformly dispersed on the surface of graphene oxide with the particle size ranging from 3 to 6 nm. X-ray Photoelectron Spectroscopy analysis of catalysts revealed that the surface consisting of mostly Pd, PdO, Ni(OH)₂, and NiOOH. CV and chronoamperometry measurements demonstrated higher electrocatalytic activity and stability for PdNi/EGO in the alkaline medium than the unsupported PdNi and carbon black-supported PdNi (PdNi/C) catalysts. A single cell anion exchange membrane DEFC constructed with a PdNi/EGO anode catalyst showed a maximum power density of 16.6 mWcm⁻² at 50 °C, which is higher than the unsupported PdNi, PdNi/C, and commercial Pd/C catalyst.

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1. Introduction

Direct ethanol fuel cell (DEFC) is widely recognized as one of the alternatives and clean energy devices. The use of ethanol as a fuel is greatly preferred because of its advantages such as high availability, low cost, easy handling, storage and transport management, and fewer hazard concerns. Generally, it is a promising fuel due to its high bioavailability, low toxicity and high energy density (6.8 kW h L⁻¹) [1]. In this regard, electrocatalysts with high catalytic activities toward the ethanol oxidation reaction (EOR) are needed to maximize the fuel cell performance. Recently, several studies focused on the development of electrocatalysts for direct ethanol fuel cell applications [2–4].

Platinum (Pt) is usually used as an anode catalyst for fuel cells due to its high catalytic activity with a wide range of fuels [5]. However, its use is limited by its high cost, low availability and prevalent poisoning by adsorbed intermediate compounds of ethanol. Thus, numerous studies have highlighted the reduction [5–8] or replacement [9–11] of Pt catalysts. Palladium (Pd) based catalysts are extensively studied as an alternative to Pt-based catalysts in alcohol oxidation due to its higher availability, lower cost and higher electrocatalytic activity towards the EOR in alkaline condition [4,10,12–14]. For instance, Ma and colleagues [15] have reported that Pd/C catalyst exhibited a higher ethanol oxidation activity than Pt/C in an alkaline condition which could be attributed to the inherent ability of Pd to cleave the C–C bond needed for the effective oxidation of ethanol. Furthermore, Pd/C has higher poisoning tolerance and stability than Pt/C at low temperatures [15]. With the recent advancement in the alkaline membrane, studies on the application of Pd-based composites in alkaline conditions have increased [16]. Likewise, the addition of metal oxides such as NiO [17,18], CeO₂ [18], SnO₂ [19], and Co₃O₄ [20] on carbon black support has been reported to improve the activity of Pd towards EOR due to the bi-functional mechanism. Aside from reducing the Pd loading, it is presumed that the oxophilicity of these metals

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provide the necessary –OH group needed for the oxidation of the surface-adsorbed ethanol molecules. Specifically, Pd catalyst with nickel oxide promoter has been investigated to obtain higher electrocatalytic activity towards ethanol oxidation than the other metal oxides (Co_3O_4 , CeO_2 and Mn_3O_4) [18].

To further increase the utilization of such catalysts, metal nanoparticles are usually dispersed on high surface area support materials. Carbon-based materials, such as carbon black, and carbon nanotubes are widely used supports [21]. Graphene, a two-dimensional carbon allotrope, is a promising carbon support due to its larger surface area compared to the other carbon materials [22–26]. Pt-based catalysts deposited on graphene nanosheets have been described to exhibit higher catalytic activity towards methanol oxidation than carbon black-supported Pt [26–30]. Graphene-supported Pd-based catalysts exhibited higher electrocatalytic activity towards the ethanol oxidation compared to carbon black-supported Pd catalysts [23–25]. Ghosh et al. have reported that the Pd catalyst exhibited an improved electrocatalytic activity towards ethanol oxidation upon the addition of graphene as a support material [31]. Furthermore, PdSn/graphene composite catalyst synthesized by Awasthi et al. [32] showed higher electrocatalytic activity towards the methanol oxidation in comparison to the Pd/graphene composite catalyst. An improvement in the activity towards the oxidation of ethanol was also observed with graphene-supported bimetallic PdSn, PdRu, and PdIr in comparison with monometallic Pd on graphene support [33]. Another study showed that when PdNi nanoparticles were supported on rGO, the catalyst composite exhibited an enhanced activity towards oxidation of formic acid [34]. Meanwhile, a preliminary study reported by our group on the use of electrochemically exfoliated graphene oxide from carbon rod as a support for PdNi revealed a higher electrocatalytic activity towards the ethanol oxidation reaction [35]. The source and quality of graphene are necessary to achieve higher electrocatalytic activities. In this article, we report the detailed electrochemical and physico-chemical characterizations of PdNi catalyst supported on exfoliated graphene oxide (PdNi/EGO) and compare the electrochemical performance with the unsupported PdNi and PdNi/C composites. To the best of our knowledge, so far, the fuel cell performance of the synthesized PdNi/EGO as an anode catalyst in alkaline direct ethanol fuel cell has not been reported.

2. Experimental

2.1. Synthesis of PdNi/EGO composites

Graphite powder, purchased from Showa Chemical Co. Ltd. (Japan), was used as received. Palladium chloride (PdCl_2), nickel chloride (NiCl_2) and sodium borohydride (NaBH_4) were of analytical grade and were purchased from Sigma-Aldrich, Singapore. All solutions were prepared using Millipore system (Milli-Q SP-TOC; $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$) and sonicated to achieve homogeneity.

Graphene oxide was fabricated from natural graphite flakes using a modified Hummer's method [36]. The graphite oxide was exfoliated through ultrasonication. The dispersed exfoliated graphene oxide was separated from the unexfoliated graphite by centrifugation at 5000 rpm for 20 min and was dehydrated by lyophilization. In a typical synthesis, 60 mg of exfoliated graphene oxide (EGO) was dispersed in 50 mL ultrapure water by sonication for 30 min before the addition of equal volumes (22.1 mL) of 0.01 M PdCl_2 solution and 0.01 M NiCl_2 solution. The pH of the mixture was adjusted to pH 10 using 0.1 M NaOH solution. Excess NaBH_4 aqueous solution with a concentration of 2.0 mg mL^{-1} was added slowly and stirred for 12 h at room temperature. This mixture was filtered and washed repeatedly with ultrapure water. The resulting solid was wetted with a small amount of water and dried

by lyophilization [26]. The same procedure was used to fabricate both PdNi/C and PdNi without carbon black. The metal loading of the carbon-supported PdNi and Pd:Ni atomic ratio was confirmed using thermogravimetric analysis (TGA) and energy dispersive X-ray spectroscopy (EDX), respectively (Table 1). Both PdNi/EGO and PdNi/C gave 36.4 and 42.0% metal loading, respectively. On the other hand, the Pd to Ni ratios of the catalyst composites, i.e. PdNi, PdNi/C and PdNi/EGO, were 1:0.8, 1:0.97 and 1:0.96, respectively. Both PdNi/C and PdNi/EGO metal loading and Pd:Ni ratio were almost equal to the nominal values which are 40% PdNi and 1:1 Pd:Ni, respectively.

2.2. Characterization

The powder X-ray diffraction patterns were obtained using a MiniFlex X-ray diffractometer (Rigaku, Japan) using a $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The 2θ angle ranges from 10° to 90° and was scanned at a rate of $0.5^\circ \text{ min}^{-1}$. The surface elemental analysis was performed using ESCALAB 250 XPS system (Thermo Fisher, Theta Probe System, USA), with a monochromatic $\text{Al K}\alpha$ radiation at 150W, in the pass energy (PE) mode ($\text{PE} = 20 \text{ eV}$). All of the spectra were obtained under identical conditions. Surface topography and morphology of EGO were investigated with NX-10 atomic force microscopy system (Park System, South Korea). The morphology and particle size of PdNi nanoparticles on different carbon supports were studied using HF-3300 transmission electron microscope system (Hitachi, Japan) at 200 kV.

Electrochemical measurements were conducted using a three electrode cell connected to a potentiostat (EDAQ, Australia). Pt wire, saturated silver/silver chloride (ALS Inc., Japan) and glassy carbon electrode (GCE, ALS Inc., Japan, ID: 3 mm, 0.0707 cm^2) were used as a counter, reference, and working electrode, respectively. Catalyst powder with a mass of 5 mg was dispersed in $4 \mu\text{L}$ of 60% PTFE and $496 \mu\text{L}$ of *N,N*-dimethylformamide solution and sonicated until homogenized. A small volume ($\sim 2.9 \mu\text{L}$) of the ink was drop-casted onto the surface of the glassy carbon electrode with a loading of $100 \mu\text{g}_{\text{Pd}} \text{ cm}^{-2}$. For cyclic voltammetry (CV) measurements, the working electrode was immersed in 1.0 M ethanol in 0.1 M NaOH solution saturated with high purity nitrogen (99.999%, Linde. Co, Philippines) with a potential window between -0.9 V and 0.4 V versus Ag/AgCl.

2.3. Membrane electrode assembly and fuel cell testing

The catalyst performance was evaluated using a single fuel cell assembly. The selected catalysts were incorporated in the membrane electrode assembly (MEA) as an anode catalyst along with a commercially available Pt/C (40% Pt, Premetek, U.S.A.) as the cathode catalyst. The catalyst layers were prepared by coating the gas diffusion layer with the dispersion of the catalyst. Briefly, the catalyst ink was prepared by adding a few drops of deionized water to sufficient amount of the catalyst for a loading of $1 \text{ mg}_{\text{Pd}} \text{ cm}^{-2}$. Then, 100 mg of the ionomer, AS4 (Tokuyama, Japan), and 2 mL of isopropyl alcohol was added to the catalyst and sonicated for 40 min or more until it was homogeneous. The resulting catalyst ink was repeatedly hand-brushed onto a 5.0 cm^2 gas diffusion layer (Anode: Nickel Foam and Cathode: GDL 25 BC, SGL Carbon Ltd., Germany) until a uniform catalyst surface was achieved. This was done for both anode and cathode catalysts to produce the corresponding catalyst layers.

The MEA was prepared by thermal pressing the anode and cathode catalyst layer to the PTFE re-enforced Tokuyama AHA membrane (Eurodia, France) in a sandwich fashion. The thermally pressed MEA was fixed in a cell fixture (Fuel Cell Technologies, USA).

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