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Improved performance using tungsten carbide/carbon nanofiber based anode catalysts for alkaline direct ethanol fuel cells

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ABSTRACT

Tungsten carbides (WC) nanoparticles on platelet type-carbon nanofibers (p-CNFs) catalysts have been synthesized for alkaline direct ethanol fuel cells (ADEFC). Physical properties of WC/CNFs samples with various WC contents are analyzed by transmission electron microscope (TEM), thermal gravimetric analysis (TGA) and nitrogen isotherm (BET). The WC/CNFs catalysts showed an improved kinetics for the ethanol oxidation than p-CNFs did. It indicates that the significant increase in the catalytic activity for ethanol oxidation on WC/CNFs than p-CNFs did due to the synergistic structural effect between WC nanoparticles and the p-CNFs supports. WC/CNFs also showed good performances in ADEFC single cells. The maximum current density of P4W3 and P4W4 was 9.0 and 4.4 mA cm⁻², respectively. These catalysts can be used as the ethanol oxidation in direct ethanol fuel cells in alkaline media.

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Introduction

The arising interest of direct alcohol fuel cells (DAFCs) is highlighted as the alternative power sources [1,2]. DAFCs have lots of advantages such as easy handling, their high efficiency, high energy density, the capacity of some of them to be renewable and low toxicity compare to polymer electrolyte membrane fuel cells (PEMFCs) [3]. The applications of DAFCs are automobiles and portable consumer electronics like laptop

computer, cellular phones and etc. In this group, methanol, ethanol and ethylene glycol are included [4]. Both alcohols, however has the problem that the overall efficiency of Platinum (Pt) based electro-catalysts suffer the consequences of effective catalyst poisoning by CO that is an intermediate of the oxidation of any alcohol [5]. Improved alcohol oxidation kinetics can be also facilitated in the basic media electrolyte than in the acid media. It can help to overcome the kinetic constraints in the alcohol oxidation for operating the DAFCs. An advantage of using alkaline direct alcohol fuel cells

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(ADAFCs) is the potential use of non-Pt catalysts that could prevent a CO poisoning on the catalyst surfaces. With the wide range of choices for support and catalyst, better performances for ADAFCs are researched.

Tungsten carbide (WC) is recognized as promising catalyst, having a resemble activity of platinum among interstitial carbides. It was investigated as a potential electro catalyst for hydrogen [6,7], methanol [8–10] and ethanol [11,12]. Electrochemical stability of tungsten and tungsten mono carbide has been studied over potential ranges and a wide pH and they were promising as anode materials [13,14]. Tungsten carbide could be prepared by various methods, the catalytic activity of it can be improved by the methods but the important thing of the synthesis is to produce tungsten carbide with high surface area, which is affected by the sintering temperature [15]. The hexagonal tungsten carbide based on Palladium (Pd-WC/C) showed the significant in the catalytic activity compared to that of Pd/C because of the higher electrochemical active surface areas (ECSAs) [16,17].

In order to improve the activity of tungsten carbides as the catalyst and platelet carbon nanofibers (p-CNFs) were used as the catalyst support. Carbon nanofibers have chemical stability, high strength, and high surface areas and are also suitable for electrode materials, catalyst supports [18]. There are three types of CNFs; platelet-type CNFs (p-CNFs), tubular-types (t-CNFs), and fishbone-type CNFs (f-CNFs) [19]. The surfaces of p-CNFs and f-CNFs were composited of the perpendicular and graphitic edges to the fibers, respectively while the t-CNFs were consisted of rounded basal planes. Among them, p-CNFs were applied due to their high surface areas and more edge atoms than other CNFs.

In this research, Tungsten carbide/platelet type-carbon nanofibers (WC/CNFs) composite catalysts were synthesized for anode materials of ADAFCs using non-Pt catalysts. To understand the electrochemical characterization of the WC/CNFs, their uses for the ethanol oxidation were investigated by cyclic voltammetry (CV) measurement. Single cell performances with WC/CNFs which showed the better catalytic activity were applied for alkaline direct ethanol fuel cells (ADEFCs).

Experimental

Catalyst preparation

Platelet type-Carbon fibers (p-CNFs, SUNTEL Co., South Korea) were used in this study. Tungsten hexa-carbonyl ($W(CO)_6$) and Toluene was purchase from Sigma Aldrich chemistry. $W(CO)_6$ (1 g, 2 g, 3 g, 4 g) was dissolved in the toluene at 80 °C for 2 h and p-CNFs (4 g) were added in the solution. The mixtures were stirring at room temperature for 24 h and then the solvent was removed, using a rotary evaporator under reduced pressure at 70 °C. The powders annealed in the vacuum oven at 70 °C for 2 h and then treated under N_2 flow at 200 °C. The each powder was named by P4W1, P4W2, P4W3 and P4W4, respectively.

Catalyst characterization

The pore parameters and specific surface areas were evaluated by performing the nitrogen adsorption–desorption isotherms measured at 77 K using a Brunauer–Emmett–Teller (BELSORP-mini, BEL Japan INC.). Prior to the measurement, the samples were dehydrated at 200 °C for 3 h. The pore size and distributions were analyzed from the desorption isotherm using the Barrett–Joyner–Halenda (BJH) method.

To analysis the amount of WC in the synthesized WC/CNFs, the catalysts were examined to thermal gravimetric analysis (TGA), using STA409PC (NETZSCH). The temperature range was from 30 °C to 900 °C with a constant heating rate of 5 °C/min under oxygen flow to burn out C-support. The residues correspond to pure WC.

The morphology observations of the samples were performed on transmission electron microscope (TEM, TECNAI G2 T-20S, FEI, Nederland). Prior to the measurement, the TEM samples were prepared by dissolving in ethanol using ultrasonication and then were dropped onto copper grids. The TEM was operated at 145 kV.

Cyclic voltammetry measurement

Cyclic voltammetry (CV) measurements were carried out using Galvanostat/Potentiostat in a standard three-electrode cell. The reference electrode, Ag/AgCl and the platinum counter electrode was applied in a Pyrex cylinder. The glassy carbon (0.2826 cm²), covered by the catalyst was serving as working electrode. 10 mg of the catalyst was dispersed in 20 μL of deionized water, 1600 μL of iso propanol and 57.2 μL of 5% Nafion solution (ion-exchange resin in alcohol solution, Sigma–Aldrich). This suspension was treated in ultrasonic bath for 5 min. Afterward, 10 μL of the suspension was dropped onto working electrode and dried for 15 min at 70 °C. Cyclic voltammograms were recorded in 1 M ethanol and 1 M KOH (SAMCHUN chemicals) with Ar bubbling at 35 °C, with a potential range from –0.8 V to 0.4 V, at scan rate of 10 mV/s. All potential data are referred to the reversible hydrogen electrode (RHE).

Single cell performance of ADAFC

Preparation of membrane electrode assemblies (MEA)

The P4W3 (0.8 mg/cm² loading), P4W4 (0.8 mg/cm² loading) catalysts were prepared as the anode. Hispec 13100 (2 mg/cm² loading, Johnson Matthey, UK) had a Pt:C composition of 72:28 and was selected for the cathode. A 10% Nafion dispersion solution (Dupont Fluoro products, USA), 1-propanol and 2-propanol were purchased to make the catalyst slurry. TGP-H-060 (Toray, Japan, PTFE 5%, treated in house) was used for the gas diffusion layer (GDL) on the anode after hydrophobic treatment with poly tetra fluoro ethylene (PTFE) emulsion. SGL-25BC (SGL Carbon Group, Germany) was used for the GDL on the cathode which was treated with PTFE. The slurry was brushed repeatedly onto 9 cm² of the GDL on the anode and the cathode until the WC loading was 0.8 mg/cm² and Pt loading was 2 mg/cm². The anode, A-301 (Tokuyama Corp.) and the cathode were then pressed to fabricate the MEA for the DMFC.

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