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Lignin-derived electrospun carbon nanofiber mats with supercritically deposited Ag nanoparticles for oxygen reduction reaction in alkaline fuel cells

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ABSTRACT

Ag nanoparticles (AgNPs) (11, 15, and 25 wt.%) were deposited on the surface of the freestanding and mechanically flexible mats consisting of lignin-derived electrospun carbon nanofibers (ECNFs) by the supercritical CO_2 method followed by the thermal treated at 180 °C. The electrochemical activity of Ag/ECNFs electrocatalyst systems towards oxygen reduction reaction (ORR) was studied in 0.1 M KOH aqueous solution using the rotating disk/rotating ring disk electrode (RDE/RRDE) technique. The SEM, TEM, and XRD results indicated that, the spherical AgNPs were uniformly distributed on the ECNF surface with sizes in the range of 2-10 nm. The electrocatalytic results revealed that, all of the Ag/ECNFs systems exhibited high activity in ORR and demonstrated close-to-theoretical four-electron pathway. In particular, the mass activity of 15 wt.% Ag/ECNFs system was the highest (119 mA mg^{-1}), exceeding that of HiSPEC 4100^{TM} commercial Pt/C catalyst (98 mA mg^{-1}). This study suggested that the lignin-derived ECNF mats surface-deposited with AgNPs would be promising as cost-effective and highly efficient electrocatalyst for ORR in alkaline fuel cells.

1. Introduction

Nowadays, fossil fuels are the primary source to meet energy demands of the present and future generations to come; however, inefficient consumption of fossil fuels is not sustainable and has led to growing concerns regarding environmental pollution. In consequence, alternative energy resources (*e.g.*, wind energy and solar energy) have been extensively investigated in terms of energy storage using fuel cells and batteries producing green electric power with high efficiency and minimal impact for the environment [1–5]. Fuel cells and in particular, alkaline fuel cells (AFCs) [6–8] have attracted significant attentions due to their advantages such as faster kinetic rates for oxygen reduction reaction (ORR) than proton exchange membrane fuel cells (PEMFCs); furthermore, Pt-free electrocatalytic systems can be adopted in AFCs [9]. Currently, Pt-based electrocatalytic systems are predominantly used in AFCs; and such a situation hinders the large-scale commercial applications of AFCs [10,11]. According to a study carried out by the U.S. Department of Energy in 2007, the cost of Pt-based electrocatalytic systems typically accounts for ~56% of the total cost for large-scale production of fuel cells.

Numerous studies have been focused on the developments of various catalysts based on metals with lower cost than Pt (*e.g.*, Pd, Ni, Fe, and Ag) as well as metal-free catalysts [4,12–19]. Among metal catalysts, Ag is particularly attractive due to its high ORR activity and excellent corrosion resistance in alkaline electrolytes [20,21]. In addition to metal catalysts, support materials are also important for the development of highly efficient electrocatalysts and are known to appreciably improve the electrocatalytic efficiency in AFCs [22]. Many carbon-based materials such as carbon black [23], activated carbon fibers [24], carbon nanotubes [17,19], and graphene [25] have been investigated as support materials. Ideally, the support materials ought to possess large surface area and porosity, high electrical conductivity, and superior resistance against corrosive electrolyte in fuel cell environment.

The materials-processing technique of electrospinning provides a convenient approach to produce fibers with diameters typically ranging from tens to hundreds of nanometers (commonly known as electrospun nanofibers) [26,27]. Recently, electrospun carbon nanofibers (ECNFs) in the form of overlaid nanofiber mats

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demonstrated the potential application as novel support for electrocatalysts due to high surface-to-mass ratio, desired nanofiber mat structure, excellent electrical conductivity, and high resistance against corrosive electrolytes [28,29]. Our previous study [30] indicated that the freestanding and mechanically flexible ECNF mats with large Brunauer-Emmett-Teller (BET) specific surface areas could be prepared from a natural product of lignin by the technique of electrospinning followed by the thermal treatments of stabilization (in air) and carbonization (in inert atmosphere). Compared with other carbon-based supports, the lignin-derived ECNF mats possess a number of advantages such as abundance of lignin as a by-product of cellulose processing; and thus the utilization of lignin as carbon source is cost-effective and environmentally friendly. Furthermore, the BET specific surface area of lignin-derived ECNF mats is ~583 $m^2 g^{-1}$ without any additional physical/chemical activation which is several orders of magnitude larger than those of conventional carbon fibers or polyacrylonitrile-derived ECNF mats without activation. We assume that the large surface area combined with suitable pore size (~3.5 nm) would facilitate the surface deposition of ECNFs with catalyst nanoparticles in supercritical CO_2 ($scCO_2$) environment. Another advantage is that the lignin-derived ECNF mats are highly graphitic, and thus their resistance against corrosive electrolyte is excellent. Additionally, since these ECNF mats are freestanding and mechanically flexible, they can be directly used as support for electrocatalysts without using any binding agents.

In this study, the lignin-derived ECNF mats were first prepared; subsequently, these mats were surface-deposited with Ag nanoparticles (AgNPs) by the $scCO_2$ approach followed by the thermal treatment at 180 °C. The $scCO_2$ approach is well-known for deposition of metal-based nanoparticles at close to ambient critical temperature and has several advantages including the controllable solubility of organometallic precursor in $scCO_2$ and the negligible mass transport limitation due to high diffusivity of the precursor; hence, small and uniform metal nanoparticles are likely to be formed on the surface of support materials [31–33]. The goal of this study was to investigate the $scCO_2$ deposition of AgNPs, and the electrocatalytic activity of the prepared Ag/ECNFs systems towards ORR in alkaline aqueous solution was also investigated in terms of silver loading, limiting current density, and mass activity.

2. Experimental

2.1. Materials

Alkali lignin (Mw ~ 10,000 g/mol, containing 4 wt.% sulfur), polyvinyl alcohol (PVA, Mw ~85,000 – 124,000 g/mol, degree of hydrolysis ~87 – 89%), 2-propanol, (1,5-cyclooctadiene) (hexafluoroacetylacetonato) silver(I) (Ag(hfa)(COD)), and KOH were purchased from Sigma-Aldrich. Commercial Pt/C electrocatalyst HiSPEC 4100^{TM} (~40 wt.% Pt on advanced carbon support with high surface area) was purchased from Alfa Aesar. All of the chemicals and materials were used as received without further purification.

2.2. 2.2. Preparation of lignin-derived Ag/ECNFs mats via the $scCO_2$ method

Lignin-derived ECNF mats (with specific surface area of ~583 $cm^2 g^{-1}$ and average pore size of ~3.5 nm) were prepared according to the method as described in our previous publication [30]. Prior to the $scCO_2$ deposition of AgNPs, the ECNF mats were pre-treated with O_2 plasma for 10 min by using a PE-50 plasma generator (Plasma Etch Inc., USA). For each batch, a certain amount of Ag(hfa)(COD) and a certain amount of ECNF mats were placed in a high-pressure vessel with the volume of 50 mL and the length of 20 cm. For the control of Ag loading amounts, three different mass ratios of Ag(hfa)(COD) *versus* ECNF mats were adopted (*i.e.*, 1:1, 2:1, and 3:1). In the $scCO_2$ process, the sealed stainless steel was first pressurized to 2500 psi with CO_2 at room temperature by using a Teledyne Isco 2600 syringe pump and then heated to 36 °C and maintaining it for 24 hrs using a heating belt wrapped around the vessel. The entire process of supercritical deposition was performed under the stirring condition, during which Ag(hfa)(COD) was first dissolved in the $scCO_2$ and then adsorbed on the surface of ECNF mats. Thereafter, the vessel was cooled down to room temperature and slowly depressurized with the depressurization rate of ~10 psi/min. To obtain AgNPs *via* the decomposition of Ag(hfa)(COD), the acquired Ag(hfa)(COD)/ECNF mats were first placed in a Carbolite 301 tube furnace at 180 °C for 2 hrs with the flow of 10% N_2/H_2 mixture gas at 100 cc/min [34]. After thermal treatment, the system was cooled down to room temperature.

2.3. Morphological and structural characterizations

A Zeiss Supra 40VP field-emission scanning electron microscope (SEM) was employed to examine morphologies of ECNF, Ag(hfa)(COD)/ECNF, and Ag/ECNF mats. The average diameters/sizes of ECNFs and AgNPs were measured by using the Images J software. The microstructures of ECNF and Ag/ECNF mats were characterized with a JEOL JEM-2100 transmission electron microscope (TEM). X-ray diffraction (XRD) patterns were acquired from a Rigaku Ultima Plus X-ray diffractometer operated at 40 kV and 90 mA with CuKα radiation (wavelength $\lambda = 1.54$ Å). The XRD profiles were recorded from 10° to 90° with the scanning speed of 2° min^{-1}.

2.4. Electrochemical evaluations

The catalytic activity of Ag/ECNFs catalysts was tested with an electrochemical setup consisting of a computer-controlled Pine bypotentiostat (Pine Instrument Company, USA) and an AFMSRCE speed control unit with rotating ring disk electrode (RRDE) from Pine Instruments, USA. The preparation of electrocatalyst inks was performed by sonication of 1.0 mL of the solution containing 0.4 mL 5% 1100 Nafion^{TM} solution, 20 mL 2-propanol, and 79.6 mL deionized water with 6.0 mg of Ag/ECNFs catalyst. After that, 10 μL of each electrocatalyst ink was placed on the surface of glassy carbon electrode and dried to form a thin film. The electrochemical properties were measured in N_2- and O_2-purged 0.1 M KOH solution by using a conventional three-electrode cell with a Pt wire as the counter electrode and an Ag/AgCl, Cl^- (0.1 M KCl solution) as the reference electrode. The cyclic voltammograms (CVs) were recorded at the potential scan rate of 20 mV s^{-1}. The production of H_2O_2 in O_2-saturated 0.1 M KOH solution was monitored in a RRDE configuration using a Pt ring biased at 0.5 V *versus* Ag/AgCl, Cl^- reference electrode.

3. Results and discussion

The lignin-derived ECNFs have the cylindrical morphology with fiber diameters of ~120 nm (Fig. 1a). The inset in Fig. 1a depicts a representative ECNF mat, which is freestanding and mechanically flexible. After the $scCO_2$ deposition of Ag(hfa)(COD) while before the thermal treatment at 180 °C, the morphologies of three Ag(hfa)(COD)/ECNF samples did not exhibit identifiable difference (Fig. 1b, 1c, and 1d); however, the EDS results (insets in Fig. 1b, 1c, and 1d) indicate that Ag(hfa)(COD) have been successfully deposited on the surface of ECNFs. As described in the experimental section, three different mats with Ag(hfa)(COD)/ECNFs mass ratios of 1:1, 2:1, and 3:1 were prepared. After the thermal treatment at 180 °C to convert Ag(hfa)(COD) into (elemental) Ag, the corresponding loading amounts of AgNPs calculated from the weight