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# Oxygen reduction reaction over nitrogen-doped graphene oxide cathodes in acid and alkaline fuel cells at intermediate temperatures

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## ARTICLE INFO

## ABSTRACT

Graphene oxides with various nitrogen contents were prepared by annealing them in an $NH_3$ flow between 350 and 850 °C, and their electrocatalytic properties toward the oxygen reduction reaction (ORR) in acid and alkaline fuel cells at intermediate temperatures were investigated. In both acid and alkaline fuel cells, graphene oxide treated with $NH_3$ at 700 °C for 1 h was the most active cathode at operating temperatures between 75 and 200 °C, where the ORR activity was enhanced by an increase in the operating temperature. This cathode also exhibited high chemical and thermal stability toward the ORR. X-ray photoelectron and Raman spectroscopic measurements of the nitrogen-doped graphene oxides indicated that the pyridinic nitrogen introduced disordered edge planes into the graphene structure. BET analysis also revealed that the surface area of graphene oxide was increased by the exposure of such edge planes. These observations lead to the assumption that the defects introduced by pyridinic nitrogen act as active sites for the ORR. Considering the similarity in ORR activity between the acid and alkaline fuel cells, dissociative adsorption of $O_2$ at the active site is a rate-determining step.

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## 1. Introduction

Proton and alkaline anion exchange membrane fuel cells (PEM-FCs and AAEMFCs) have been aggressively studied with the goal of commercialization [1,2]. A recent trend in developing fuel cells is to increase the operating temperature up to 120 °C or higher, as recommended by the U.S. Department of Energy (DOE) [3]. Operating fuel cells at such high temperatures offers many advantages over conventional fuel cells that run at ~80 °C [4,5]. In particular, the electrode reaction kinetics are enhanced, facilitating the replacement of Pt with inexpensive catalysts. Among alternatives to Pt-based cathodes, graphene and related materials have recently attracted great interest because of their unique electrocatalytic properties, large surface area, and high chemical stability [6–9]. Since these characteristics are closely related to the nanostructure of graphene, various attempts have been made to control the structural parameters of graphene, which include the preparation of graphene sheets with different dimensions, thickness, crystallinity, and defects [10–13].

Chemical doping with foreign atoms, such as nitrogen, is regarded as an effective method to modify the nanostructure of various carbon materials at the atomic level, as reviewed for

example by Shao et al. [14]. In this case, nitrogen works as an n-type dopant, so that the basal plane of carbon could contain extra electrons, and donate such electrons to $O_2$ [15]. Alternatively, pyridinic nitrogen species formed by doping nitrogen could be an intermediate for the oxygen reduction reaction (ORR) [16]. Although the nature of active sites for ORR still remains unclear, some recent studies have proved that nitrogen-doped graphene has higher activity for the ORR than graphene [17–19]. Also, a similar performance was reported for a cathode in Li-air batteries [20]. However, all of the above experimental results were obtained at room temperature. Furthermore, these series of studies, especially for graphene, were conducted in only one of either acid or alkaline solutions. There are two questions that arise: How much is the ORR promoted over nitrogen-doped graphene at elevated temperatures, and is this reaction more effectively promoted in acid or alkaline fuel cells? Therefore, it is interesting and worthwhile to investigate the ORR activity of nitrogen-doped graphene in both acid and alkaline media at intermediate temperatures. Here, we report the results of experiments designed to address these questions.

In this study, we used acceptor-doped $SnP_2O_7$ as an electrolyte for PEMFCs and AAEMFCs, because these compounds possess high proton or hydroxide ion conductivity above $10^{-2}$ S cm$^{-1}$ in the temperature range from 50 to 300 °C [21,22]. The $SnP_2O_7$ structure can be described as a network of $MO_6$ octahedra sharing corners with $P_2O_7$ units, characterized by the presence of intersecting

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zigzag tunnels delimited by pentagonal windows [23]. Proton and hydroxide ion exchange capabilities are typically introduced into bulk $SnP_2O_7$ by the partial substitution of $Sn^{4+}$ cations with low valency $In^{3+}$ and high valency $Sb^{5+}$ cations, due to charge compensation for the dopant cations. We also prepared graphene with different nitrogen contents by annealing graphene oxide under an $NH_3$ flow in the temperature range of 350–850 °C. The ORR activity of the obtained cathodes was evaluated using electrochemical measurements, including current interruption and impedance methods. Moreover, the nano- or microstructure of the cathode materials was characterized using various techniques, including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy, and BET analysis.

## 2. Experimental

### 2.1. Materials

The graphene oxides used in this study were three xGNP materials (grades H-5, M-5, and C-750) obtained from XG Science, USA. The xGNP (C-750) sample was treated with $NH_3$ as follows. 1.0 g of the sample powder was packed homogeneously into a silica tube with an outer and inner diameter of 30 and 26 mm, respectively, where the thickness of the sample layer was approximately 8 mm. After purging with 10% $NH_3$ diluted with Ar for 10 min at room temperature, the sample powder was heated to the desired temperature at a heating rate of 3 °C min$^{-1}$, and held at this temperature for 1 h, unless otherwise stated. Finally, the sample powder was cooled to room temperature at a cooling rate of 3 °C min$^{-1}$ in the $NH_3$ flow. The electrolyte membranes were synthesized according to a procedure reported previously [21,22], where the optimal compositions of these compounds were determined to be $Sn_{0.9}In_{0.1}H_{0.1}P_2O_7$ and $Sn_{0.92}Sb_{0.08}(OH)_{0.08}P_2O_7$. Briefly, $SnO_2$ and $In_2O_3$ or $Sb_2O_5$ were mixed with 85% $H_3PO_4$ and deionized water. The mixture was stirred at 300 °C until it formed a high viscosity paste. The paste was calcined in an alumina pot at 650 °C for 2.5 h and then ground into a powder with a mortar and pestle. 0.04 g polytetrafluoroethylene (PTFE) powder was added to 1.00 g of $Sn_{0.9}In_{0.1}H_{0.1}P_2O_7$ or $Sn_{0.92}Sb_{0.08}(OH)_{0.08}P_2O_7$ powder, kneaded using a mortar and pestle, and finally cold-rolled to a thickness of 150 μm using a laboratory rolling mill.

### 2.2. Characterization

The untreated and $NH_3$-treated graphene samples were characterized using TEM, XPS, Raman spectroscopy, and BET analysis. The morphological structure of the samples was examined using a JEOL JEM2100F TEM instrument at an accelerating voltage of 200 kV with a beam current of 92 μA. Specimens for the TEM measurements were prepared by ultrasonic dispersion in $n$-butanol, and a drop of the resultant suspension was evaporated on a Mo grid. The chemical charge states of N 1s and O 1s were analyzed using a VG Escallab220i-XL XPS with an Al Kα (1486.6 eV) X-ray source. The photoemission angle was set at 45° to the sample surface, allowing for a reduction in the escape depth to a few namometers. The crystallinity of the samples was quantified using a JASCO NRS-1000 Raman spectrophotometer with visible (532 nm) laser excitation. Specimens for the Raman measurements were placed on a glass plate under ambient conditions, and data for two scans were accumulated. The BET specific surface area of the samples was measured through $N_2$ adsorption at liquid $N_2$ temperature using a conventional flow-type adsorption apparatus. Specimens for the BET measurements were pre-treated at 250 °C in a He flow for 30 min.

### 2.3. Electrochemical studies

The ORR activity of the cathode was investigated using an electrochemical cell, $H_2$, Pt/C | electrolyte | N-doped graphene, air. The graphene-based cathodes were prepared using the following procedure. A mixture of the graphene powder (0.255 g), PTFE dispersion (0.425 g), 2-propanol (1.00 mL), and deionized water (1.75 mL) was dispersed using a Thinky AR-100 mixer. This slurry was deposited on the surface of a gas diffusion layer (Toray TGPH-090) using a screen-printing technique and dried at 80 °C in air to remove the solvent. The loading of graphene was adjusted to *ca.* 25 mg cm$^{-2}$. A commercially available Pt/C electrode (0.5 cm$^2$, Electrochem Inc.) with a Pt loading of 1 mg cm$^{-2}$ was employed as an anode. The electrolyte membrane (12 mm diameter, 150 μm thickness) was sandwiched between the two electrodes and then pressed at room temperature and 2 MPa for 2 min. Two gas chambers were set by placing the membrane electrode assembly (MEA) between two alumina tubes and sealing with an inorganic adhesive. Electrochemical measurements were performed by supplying $H_2$ saturated with $H_2O$ vapor at room temperature (50 mL min$^{-1}$) and air saturated with $H_2O$ vapor at 70 °C (50 mL min$^{-1}$) to the anode and cathode, respectively. The IR-corrected electrode potential was recorded using the current interruption method, where a sharp change in voltage corresponds to IR loss, and a slow voltage change corresponds to polarization losses. The polarization resistance was analyzed using a Solartron SI 1260 impedance analyzer and a Solartron 1287 electrochemical interface. The frequency range for the measurements was 0.1–10$^6$ Hz and the AC amplitude was 10 mV. To monitor the cathode potential and impedance in the electrochemical cell, a Pt reference electrode was attached to the surface of the side of the electrolyte, which was exposed to a $H_2$ atmosphere.

## 3. Results and discussion

### 3.1. ORR over three types of graphene oxides

Three types of graphene oxides were examined as cathode samples for acid and alkaline fuel cells. TEM observations revealed that all the samples were transparent with a two-dimensional structure (for example, C-750 in Fig. 1(a)). In contrast, these samples showed different stacked layers: 25–35 (H-5), 12–15 (M-5), and 5–10 (C-750) layers (Fig. 1(b)–(d)). The interlayer distances were estimated to be 0.2–0.4 nm for all the tested samples, although the stacked layers were slightly wavy. This variation in thickness was reflected considerably in the BET specific surface area values of these samples: 80.9 m$^2$ g$^{-1}$ (H-5), 140.5 m$^2$ g$^{-1}$ (M-5), and 734.0 m$^2$ g$^{-1}$ (C-750), which are very close to the database of XG Science data [24].

The degree of structural deformation of the three graphene oxide samples was evaluated from their Raman spectra (Fig. 2). Two distinct peaks were observed in the 1200–1700 cm$^{-1}$ region: a G-band at ~1580 cm$^{-1}$ and a D-band at ~1340 cm$^{-1}$. The G-band is attributable to the Raman-active $E_{2g}$ vibrational mode on the sp$^2$ bonded graphitic basal planes, while the D-band is associated with structural defects mainly present in the graphitic edge planes [25]. The intensity ratio of the D-band to the G-band, $I_D/I_G$, gives information about the amount of disordered edge planes relative to the ordered basal planes. The $I_D/I_G$ ratios obtained from each area of the D- and G-bands were 0.19 (H-5), 0.24 (M-5), and 0.93 (C-750). In particular, the first two ratios are smaller than those reported earlier for other graphenes [26,27]. These results may also be consistent with the BET specific surface area values of these samples.

The IR-corrected potentials of the three cathode samples in acid and alkaline fuel cells were recorded during cell discharge at 150 °C