



S-doped carbon aerogels/GO composites as oxygen reduction catalysts

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ABSTRACT

Composites of carbon aerogel and graphite oxide (GO) were synthesized using a self-assembly method based on dispersive forces. Their surface was modified by treatment in hydrogen sulfide at 650 and 800 °C. The samples obtained were characterized by adsorption of nitrogen, TA-MS, XPS, potentiometric titration, and HRTEM and tested as catalysts for oxygen reduction reactions (ORR) in an alkaline medium. The synergistic effect of the composite (electrical conductivity, porosity and surface chemistry) leads to a good ORR catalytic activity. The onset potential for the composite of carbon aerogel heated at 800 °C is shifted to a more positive value and the number of electron transfer was $2e^-$ at the potential 0.68 V versus RHE and it increased to $4e^-$ with an increase in the negative values of the potential. An excellent tolerance to methanol crossover was also recorded.

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1. Introduction

Platinum/carbon (Pt/C) based cathodes, which are used for the oxygen reduction reaction (ORR) [1,2], are expensive and show a low tolerance to fuel crossover. This caused an extensive search for effective non-noble metal catalysts [3–12] or even better, for non-metal based catalysts [13–19]. An example of the latter are heteroatom-doped carbonaceous materials including graphene oxide, graphene and nanoporous carbons [10,13–19] or graphitic-carbon nitride together with its composites with carbons [20,21]. Extensive research in this field indicated that heteroatoms such as nitrogen [5,19,20–22], sulfur [14–16,22], phosphorus [17,18], or boron [17,23,24] provide catalytic sites on which oxygen reduction is enhanced [15,16,23]. Among all heteroatom doped carbonaceous materials, the three-dimensional flowerlike nitrogen-doped carbon showed the highest number of electron transfer (n) and the kinetic-current density (J_k) [25] reaching $3.96e^-$ and 4.02 mA/cm^2 at -0.50 V versus SCE (0.51 V versus RHE), respectively. On the other hand, for the nitrogen-modified graphene at the potential -0.50 V versus Ag/AgCl (0.48 V versus RHE) the number of electron transfer was close to $3.3e^-$ and the kinetic current density -7.8 mA/cm^2 [22]. Dual S and N doped mesoporous graphene showed $n = 3.3e^-$ and $J_k = 24.5 \text{ mA/cm}^2$ at -0.50 V versus Ag/AgCl (0.48 V versus RHE) and a high tolerance to methanol crossover [15].

Even though doping with nitrogen was the first modification path to explore in order to increase the catalytic activity of carbon based materials [5,19,20–22], an introduction of sulfur along with nitrogen, as indicated above, resulted in even more promising properties based on a synergistic effect of these two heteroatoms [15]. Recent results have also shown that doping only with sulfur might result in efficient oxygen reduction catalysts [14–16,22]. On sulfur-doped graphene the number of electron transfer was found to be $3.82e^-$ and the kinetic current density reached 9.34 mA/cm^2 at -0.30 V versus Ag/AgCl (0.68 V versus RHE) [14]. The catalytic activity for oxygen reduction was linked to change in electronic properties of the carbon matrix [14–16], change in the spin and in charge density [14,15], and defects related to the polarity and larger size of sulfur [16,26].

Recently we have shown that hydrophobicity introduced by sulfur in thiophenic compounds is important for withdrawing oxygen from the electrolyte and its physical adsorption on the surface [26,27]. Moreover, location of these groups in small pores seemed to have a marked effect on the physical adsorption process. There was also an indication that other bulky sulfur surface groups in configurations with oxygen (sulfoxide, sulfones and sulfonic acids) located in larger pores (mesopores), owing to their sizes, attracted an electrolyte with dissolved oxygen to the pore system. Not without importance is the electrical conductivity of a catalyst, which promotes the electron transfer to oxygen.

As a continuation of the previous research where carbon aerogels doped with sulfur were addressed as efficient ORR catalysts [26], the research presented in this paper focuses on evaluation of the ORR capability of the carbon aerogel/GO composites obtained

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using a self-assembly methods [28]. This method, even though it employs the physical/dispersive forces, has been shown as resulting in composites of synergistic properties owing to chemical reactivity of both phases. The new materials obtained are extensively characterized and their activity is linked to surface features including both chemistry and porosity. The ORR performance of the composites was compared to that of a commercial Pt/C catalyst.

2. Experimental

2.1. Materials

The new synthesized composites consisted of 50:50 wt% graphite oxide:carbon aerogel or S-doped carbon aerogel. The former was obtained using Hummers method [29] and the latter was addressed in details elsewhere [26]. Carbon aerogel was obtained from resorcinol-formaldehyde polymer aerogel [30]. First, GO was well dispersed in water by sonication, and then finely ground carbon aerogel (CA) was added to the GO suspension. The mixture was sonicated for 1 h more and then stirred overnight. Afterward, the suspension was filtrated without washing and dried at 120 °C. The composite obtained is referred to as CA-GO.

The S-doped composites, referred to as CA1-GO and CA2-GO, are built with sulfur-doped carbon aerogel, CA1 and CA2 addressed elsewhere, and GO [26]. Sulfur was doped by heating the initial aerogel, CA, at 650 °C (CA1) or 800 °C (CA2), respectively, in H₂S for 3 h (1000 ppm of H₂S balanced in nitrogen, flow rate 150 mL/min).

2.2. Methods

2.2.1. Electrochemical characterization

The performance of our materials for electrochemical ORR was investigated in 0.1 M KOH using a three-electrode cell with Ag/AgCl/KCl (3 M) as a reference electrode. The measurements of chronoamperometry and long-term stability by applying 1300 potential cycles were carried out on VersaSTAT MC (AMETEK, Princeton Applied Research) with a scanning rate of 5 mV/s (cyclic voltammetry). The working electrode was prepared by mixing the active material with polyvinylidene fluoride (PVDF) and commercial carbon black (carbon black, acetylene, 50% compressed, Alfa Aesar) (8:1:1) in *N*-methyl-2-pyrrolidone (NMP) until a homogeneous slurry. The slurry was coated on a Ti foil (current collector) with the total surface area of 1 cm² of an active material. Linear sweep voltammograms (LSVs) were obtained in 0.1 KOH using 757 VA Computrace (Metrohm) at various rotation rates (from 0 to 2000 rpm) with Ag/AgCl (3 M KCl) and Pt wire as a reference and a counter electrode, respectively. The measurements of cyclic voltammetry were carried out under O₂ or N₂ saturation in the electrolyte in the potential range of 0.19 to −0.8 V versus Ag/AgCl (1.17 V–0.18 V versus RHE) at a scan rate of 5 mV/s. The working electrode was prepared by dispersing 5 mg of the catalyst in 1 mL of deionized water and 0.5 mL of 1 wt% Nafion aqueous solution. About 5 μL of the prepared slurry were dropped (three times) on a polished glassy carbon electrode (Metrohm, Switzerland, diameter 2 mm) and dried at 50 °C in air. The potential was swept from 0.19 to −0.8 V versus Ag/AgCl (1.17 V–0.18 V versus RHE) at a scan rate of 5 mV/s. After each scan, the electrolyte was saturated with air (the source of O₂) for 20 min. All the experiments were carried out at room temperature.

RHE conversion:

The measured potentials versus the Ag/AgCl (3 M KCl) reference electrode were converted to the reversible hydrogen electrode

(RHE) scale using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}}$$

where E_{RHE} is the converted potential versus RHE, $E_{\text{Ag/AgCl}}$ is the experimental potential measured against the Ag/AgCl reference electrode, and $E^{\circ}_{\text{Ag/AgCl}}$ is the standard potential of Ag/AgCl (3 M KCl) at 25 °C (0.210 V). The electrochemical measurements were carried out in 0.1 M KOH (pH = 13) at room temperature; therefore, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.977$ V.

2.2.2. Evaluation of porosity

Sorption of nitrogen at −196 °C was carried out using an ASAP 2020 (Micromeritics, Surface Area and Porosity Analyzer). Before the experiments, samples were out-gassed at 120 °C to constant vacuum (10^{−4} Torr). The BET surface area, total pore volumes, V_t , (from the last point of isotherm at relative pressure equal to 0.99), micropore volume, volume of pores less than 0.7 nm and 1 nm, $V_{<0.7\text{ nm}}$ and $V_{<1\text{ nm}}$, mesopore volumes along with pore size distributions were calculated from the isotherms. The volume of mesopores, V_{meso} , represents the difference between total pore and micropore volume. The volume of pores and pore size distributions were calculated using 2D-NLDFT (www.NLDFT.com) assuming a heterogeneous surface of pore walls [31].

2.2.3. DC conductivity measurements

The DC conductivity was measured using a 4-probe method on the pellets with the composition consisting of 90 wt% carbon materials and 10 wt% polytetrafluoroethylene as a binder. The prepared composition was pressed by a Carver Press machine applying 2 tons pressure and disk-shaped well-packed pellets with diameter 8 mm were formed. The pellets were dried in an oven for 12 h. The thickness of the pellets was measured by a spring micrometer. The measurement of conductivity was carried out using a Keithley 2400 Multimeter.

2.2.4. Thermal analysis-mass spectroscopy (TA-MS)

Thermogravimetric (TG) curves were obtained using a TA Instrument thermal analyzer (SDT Q 600), which was connected to a gas analysis system (OMNI StarTM) mass spectrometer. The samples were heated up to 1000 °C (10 °C/min) under a constant helium flow (100 mL/min). From the TG curves, differential TG (DTG) curves were derived. The composition of gases was measured by MS and m/z evolution profiles as a function of temperature were evaluated.

2.2.5. X-ray photoelectron spectroscopy (XPS)

XPS analysis was collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K_{α} radiation (300 W, 15 kV, 1253.6 eV) for the analysis of the core level signals of C 1s, O 1s, S 2p and with a multichannel detector. Spectra of powdered samples were recorded with the constant pass energy values at 29.35 eV, using a 720 μm diameter analysis area. Under these conditions, the Au 4f_{7/2} line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. The PHI ACCESS ESCA-V6.F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in BE was estimated to be ca. 0.1 eV.

2.2.6. Potentiometric titration

Potentiometric titration measurements were performed with an 888 Titrando automatic titrator (Metrohm) set at the mode to collect the equilibrium pH. The samples (0.05 g) were dispersed in

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