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The value of mixed conduction for oxygen electroreduction on graphene–chitosan composites

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ABSTRACT

Graphene-based electrocatalysts have been widely investigated for their excellent performance in electrocatalytic oxygen reduction. The surface chemistry of graphene-based electrocatalysts is important for developing more efficient fuel cells and metal-air batteries. In addition, the nanostructured gas-diffusion electrode (GDE) on which the electrocatalysts are loaded needs to be carefully tailored to facilitate mass transport (reactants and products). A polymer binder is often used to fabricate the GDE which means there is a need to optimize the ratio of binder to electrocatalyst. Herein we demonstrate the impacts of graphene-based GDE nanostructures on the efficiency of oxygen electroreduction by comparing a series of graphene/chitosan composites with varying compositions. In these nanostructured GDEs graphene acts as the electrocatalyst and chitosan as the binder. Our results illustrate a critical ratio of graphene to chitosan for enhanced electrocatalytic surface area and facilitated mass transport, while a continuous network for electron conduction is effectively established. We believe this work is an important piece of the puzzle to better understanding the electrode behavior of electrocatalysts consisting of graphene-like two-dimensional materials in oxygen reduction reaction.

1. Introduction

The oxygen reduction reaction (ORR) is an important topic in research on fuel cells and metal-air batteries [1,2]. These energy conversion devices are capable of delivering a much higher specific energy that potentially outperforms conventional energy storage devices, such as lithium-ion batteries and supercapacitors [3,4]. Unfortunately the anticipated performance is largely limited by the sluggish ORR kinetics at the cathode, which degrades the energy efficiency. Significant research effort has thus been devoted to developing low-cost and robust ORR electrocatalysts to tackle this problem. Two vital bottlenecks being intensively investigated are the large onset reaction overpotential and the low reaction current density [4–6]. Both limitations are the combined consequences of poor intrinsic electrocatalytic activity, limited electron conductivity, slow mass transfer for reactant and product molecules and low electrocatalytic surface area [7–9]. Clearly, ORR electrocatalysis can only become efficient if all the influential structural factors are optimized.

Intensive research has focused on the (i) heteroatom functionalization/doping [10–16] and (ii) hybrid modification [17] of graphene nanosheets. Nitrogen-containing functional groups or dopants were observed to be very active towards

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direct 4-electron reduction of dioxygen [11–13]. Other heteroatoms, such as O [10], S [15,16] and B [14], also demonstrate superior ORR activity compared to an unmodified graphene electrocatalyst. Covalently bonded metal oxides even exhibit a synergy with a graphene matrix for oxygen reduction, typically when N heteroatoms are introduced [17]. The robust surface chemistry of graphene and of its derivatives is clearly of significance for understanding and developing advanced ORR electrocatalysts. In spite of this, however, the nanostructures of gas-diffusion electrodes (GDE) consisting of graphene-based electrocatalysts and a binder can affect the processes of electron conduction and mass transfer and can change the accessible electrocatalytic surface area. These effects will eventually impact on the overall ORR efficiency, but they have often been overlooked in studies of graphene-based ORR electrocatalysts.

GDEs usually take the form of a composite which incorporates an active electrocatalyst and a polymer binder at certain mass ratios. The morphology and physical properties of the GDE composite can affect the mass transfer and electron conduction which in turn alters the catalytic properties of the electrocatalyst. For example, the electron conduction network may not develop effectively if the active electrocatalyst particles (which are usually conducting) are isolated by the polymer binder. This may in turn suppress the reaction by generating resistance to charge transport. It is therefore important to understand how the structure of a composite electrocatalyst influences ORR behavior.

We have fabricated a nanostructured GDE consisting of chemically-derived graphene nanosheets as the electrocatalyst and chitosan as the binder to demonstrate the significance of optimization of GDE nanostructures for ORR. The graphene nanosheet is used as a two-dimensional (2D) electrocatalytic platform with high surface area and excellent electron conductivity, while chitosan is a polysaccharide which exhibits satisfactory ion conductivity and stability as a binder in alkaline electrolytes [18]. Compared to the widely-used Nafion, chitosan is a much cheaper natural product derivative which is highly hydrophilic and facilitates hydroxide ion conduction in an alkaline electrolyte [18]. While graphene nanosheets are 2D anisotropic materials, they are known to exhibit enormous surface area and can self-assemble into versatile structures. With the goal of investigating the structure–performance relationship, graphene and chitosan were blended in various ratios to tune the GDE nanostructures. We have employed several techniques to provide a relatively complete picture of the composite structure and the electrocatalytic ORR performance.

2. Experimental section

2.1. Materials

Graphene nanosheets were prepared by thermal exfoliation and reduction of graphite oxide through a short insertion into a 1000 °C Ar-filled furnace. The graphite oxide was synthesized by a modified Hummer's method from expandable graphite (see Supporting Information). Chitosan powder (>75% deacetylated, from shrimp shell) was purchased from Sigma–Aldrich and used as received.

2.2. Preparation graphene/chitosan composite electrode

A saturated chitosan solution was prepared by dissolving excessive chitosan in a given volume of purified water at 50 °C and stirring overnight. This solution was allowed to settle and maintained under ambient conditions for more than a day before extracting the chitosan-saturated supernatant. Since this supernatant is chitosan saturated, we have used the solution volume to represent the chitosan content in the composite. In a typical preparation of graphene/chitosan (G/Chit) suspension, a quantity of graphene nanosheets was dispersed in the supernatant at a certain weight-to-volume ratio with the help of ultrasonic probe treatment for at least 2 h to achieve a uniform suspension; the same treatment was applied for graphene nanosheets in 1% Nafion solution and purified water for comparison purposes.

A circular glassy carbon (GC) working electrode (ALS Co., Ltd.) with a diameter of 3.0 mm was adopted for electrochemical measurements. The vigorously shaken aqueous G/Chit suspension was loaded onto the electrode by drop-casting. 12 μL of each suspension was applied onto the GC electrode which was then dried in an oven at 60 °C. A platinum reference (Pt/C) using 20 wt% platinum on carbon was used directly as purchased (Sigma–Aldrich). The Pt/C electrode was prepared in a similar way to G/Chit composite at 1.0 mg/mL in a chitosan-saturated supernatant.

2.3. Characterizations and measurements

Scanning electron microscopy (SEM, JEOL6610) was employed for imaging the composite morphology at a working distance of 12 mm. The acceleration voltage was 4.0 kV and no conductive coating was applied to the samples. Transmission electron microscopy (TEM) was operated on a FEI Tecnai G2 F20 microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra spectrometer using Al Kα radiation (15 kV, 150 W). The survey spectra were recorded from 0 to 1200 eV at an energy interval of 1 eV/step. The high resolution C 1s spectra were collected at an interval of 0.05 eV/step. Raman spectroscopy (Renishaw Raman spectrometer) was performed with a red laser of 785 nm wavelength. Fourier-transform infra-red (FTIR, Perkin Elmer Spectrum 2000) spectra were collected from 4000 cm^{-1} to 650 cm^{-1} by an attenuated total reflection (ATR) technique, at a resolution of 4.0 cm^{-1}.

All electrochemical measurements were performed on a CHI-440B potentiostat–galvanostat instrument in a 0.1 M KOH electrolyte, saturated with oxygen (O_2) bubbling for at least 30 min. A three-electrode system consisting of a working electrode, a Pt wire counter electrode and an HgO/Hg reference electrode (0.1 M KOH) was used. The as-described setup was employed for cyclic voltammetry (CV) and linear sweep voltammetry on a rotating disk electrode (LSV–RDE).