Electrocatalysis of Oxygen Reduction Reaction on Nitrogen-Doped Graphene in Alkaline Media

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A great deal of work has been made to develop new electrocatalysts for oxygen reduction reaction (ORR) in alkaline and acidic media. In order to replace expensive and scarce Pt-based catalysts that have been primarily employed as cathode catalysts in low-temperature fuel cells, different carbon-based materials that possess lower price, better availability and improved chemical stability have been studied.

Previously, we have investigated the reduction of oxygen on CVD grown nitrogen-doped carbon nanotubes[1] and on CNTs heat-treated in the presence of urea.[2]

In current work, glassy carbon (GC) electrodes modified with annealed graphene oxide (GO) and nitrogen-doped graphene (NG) catalysts were studied. The purpose of this research was to test the electrocatalytic properties of these materials toward the ORR. Electrochemical experiments were carried out in 0.1 M KOH solution using the rotating disk electrode (RDE) method. GC electrodes were modified using GO and NG suspension in water in the presence of ionomer AS-04 (Tokuyama).

The GO was synthesized by modified Hummers' method. Nitrogen doping was achieved by pyrolysis of GO in the presence of melamine, urea or dicyandiamide (DCDA) at 800 °C. To compare different materials, GO/melamine, GO/urea and GO/DCDA with ratio 1/20 were prepared. These materials are designated as 1-NG, 2-NG and 3-NG, respectively. The surface morphology and composition of NG materials was examined with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The SEM images showed typical graphene structure (crumpled sheet-like morphology and porous architecture) revealing a high exfoliation degree of this material (Fig. 1). In the XPS spectra the N1s peaks were present, which shows successful doping of graphene with nitrogen. Different types of nitrogen were identified.

Electrochemical experiments revealed a higher ORR activity of all the NG materials studied compared with annealed GO, whereas 3-NG catalyst showed the best results. Fig. 2 presents the RDE results of O_2 reduction obtained with 3-NG/GC electrode. The Koutecky-Levich (K-L) analysis showed that the process of O_2 reduction on 3-NG/GC proceeded by a 4-electron pathway in a wide range of potentials (Fig. 3). Comparison of the RDE results at a single rotation rate is shown in Fig. 4. The onset potential and half-wave potential of O_2 reduction for all the NG materials shift positive compared with that of annealed GO. The high electrocatalytic activity of 3-NG catalyst toward O_2 reduction might be caused by the pyridine-type nitrogen incorporated into the graphene. NG materials are promising catalysts for alkaline membrane fuel cells. Work is in progress to test these in a fuel cell.

References

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2. M. Vikkisk, I. Kruusenberg, U. Joost, E. Shulga, K. Tammeveski, Electrochim. Acta **87**, 709 (2013).

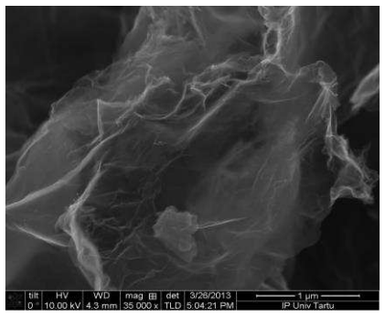

Fig. 1. SEM image of N-doped graphene modified GC.

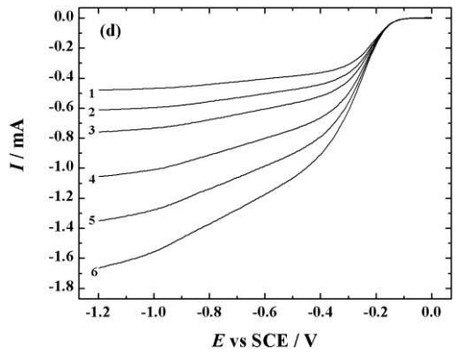

Fig. 2. RDE voltammetry curves for oxygen reduction on 3-NG modified GC electrodes in O_2-saturated 0.1 M KOH. v = 10 mV s^{-1}, ω = (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm.

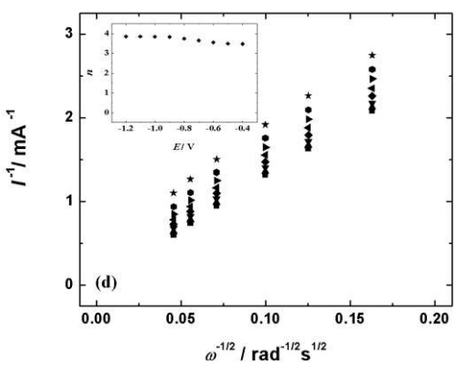

Fig. 3. K-L plots for oxygen reduction on 3-NG/GC electrodes in 0.1 M KOH solution. E = (★) -0.4, (⬢) -0.5, (►) -0.6, (◄) -0.7, (♦) -0.8, (▼) -0.9, (▲) -1.0, (●) -1.1 and (■) -1.2 V. Inset shows the potential dependence of n

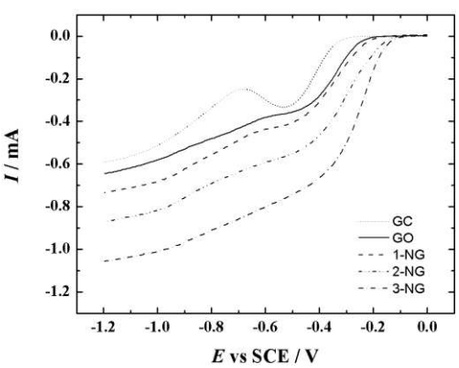

Fig. 4. Comparison of RDE results of oxygen reduction on bare GC, GO/GC and NG/GC electrodes in O_2-saturated 0.1 M KOH. v = 10 mV s^{-1}, ω = 1900 rpm.