Modified Graphene as Electrocatalyst towards Oxygen Reduction Reaction for Fuel Cells

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Abstract. This paper reports modified graphene-based materials as metal-free electrocatalysts for oxygen reduction reaction (ORR) with outstanding electrocatalytic activity in alkaline conditions. Nitrogen-doped graphene samples are synthesized by a novel procedure. The defect density in the structure of the prepared materials is investigated by Raman spectroscopy. Further structural characterization by X-ray photoelectron spectroscopy reveals the successful nitrogen doping of graphene. The electrochemical characterization of graphene and nitrogen-doped graphene in 0.1 M KOH solution demonstrates the material’s electrocatalytic activity towards ORR. For graphene an onset potential of -0.175 V vs. Ag/AgCl reference electrode is determined, while for nitrogen-doped graphene the determined onset potential is -0.160 V. Thus, the electrocatalytic activity of nitrogen-doped graphene towards ORR is enhanced which can be ascribed to the effect of nitrogen doping.

1. Introduction

Fuel cells generate electric power through the conversion of the chemical energy contained in a fuel into electrical energy. Within the framework of an electrochemical process the fuel such as hydrogen or methanol oxidizes at the anode and the oxidizing agent, usually oxygen is reduced to water at the cathode. In general catalysts at the respective electrode are used to increase the fuel cell’s efficiency.

Due to the sluggish oxygen reduction reaction kinetics platinum-based catalyst materials are widely used as cathodes in fuel cell applications to catalyse the oxygen reduction reaction. [1] A fundamental drawback for the development of commercial fuel cells containing platinum-based electrodes is derived from high costs as well as limited reserves of platinum in nature. [2] Further problems arise from the vulnerability of platinum-based materials to time-dependent drift and poisoning effects such as CO “poisoning” leading to the catalyst deactivation. Therefore the development of novel metal-free materials has become the focus of research to substitute platinum-based catalysts. [2] [3]

Regarding to the excellent properties of carbon-based materials, different modifications of graphene are of particular interest due to easy processability, low costs, high surface and porosity, high electrical, thermal conductivity and mechanical strength. [3] The electronic and optical properties of graphene can be modified by doping with heteroatoms such as nitrogen or boron. [4] [5] In particular, nitrogen-doped carbon materials represent promising metal-free catalysts due to their enhanced...
electrocatalytic activity, long-term stability and environmental sustainability. [6] Compared with Pt and commercial PtC catalysts nitrogen-doped graphene is characterized by better stability. [7] [8] Besides, it is also demonstrated that the activity of nitrogen-doped graphene is not influenced by adding carbon monoxide or methanol. [4] [8]

Here, we report graphene and nitrogen-doped graphene as metal-free electrocatalysts for oxygen reduction reaction. The graphene-based materials were synthesized by a novel procedure. A detailed report about the synthesis procedure is under preparation and will be published soon. The structure of the prepared materials was characterized by Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS). Furthermore graphene and nitrogen-doped graphene were electrochemically characterized by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The electrocatalytic activity of the prepared materials towards ORR is demonstrated and compared to that of commercial 20% PtC catalyst.

2. Structural characterization

Raman spectroscopy was used to investigate the defect level in carbon lattice of the prepared materials. Figure 1 displays the Raman spectra of nitrogen-doped graphene compared with graphene and graphite. The Raman spectrum of graphite mainly shows a typical G peak at 1576 cm$^{-1}$ corresponding to ideal single-crystal graphite. [9] The Raman spectra of graphene and nitrogen-doped graphene display G bands shifted to 1595 cm$^{-1}$ and 1588 cm$^{-1}$, respectively. In addition, clearly rised D bands appear at 1344 cm$^{-1}$ for graphene and 1365 cm$^{-1}$ for nitrogen-doped graphene relating to the disorder-induced feature which can be attributed to a modest defective structure of the graphene-based materials. [10]

Besides the I$_D$/I$_G$ ratio is taken into account to investigate the density of defects in the samples. For graphite the I$_D$/I$_G$ ratio is approximately 0.15, it increases to 1 for graphene and 1.11 for nitrogen-doped graphene. The increase of I$_D$/I$_G$ can be ascribed to the presence of a substantial amount of defects in the prepared materials.

![Figure 1. Raman spectra of graphite, graphene (TRGO) and nitrogen-doped graphene (CN).](image1)

![Figure 2. XPS spectra of graphene (TRGO) and nitrogen-doped graphene (CN).](image2)

X-ray Photoelectron Spectroscopy (XPS) was further used to characterize the chemical composition of the prepared samples, thus to verify the nitrogen doping. The XPS spectra of graphene and nitrogen-doped graphene are depicted in Figure 2. In the survey spectrum of nitrogen-doped graphene the peaks occurring at approximately 400 eV correspond to nitrogen and clearly confirm the successful incorporation of nitrogen atoms into carbon lattice, wherein the content of nitrogen atoms
Furthermore oxygen functionalities are present in both graphene and nitrogen-doped graphene. The nitrogen spectrum additionally can be deconvoluted to individual peaks corresponding to different nitrogen types in carbon lattice, usually pyridinic-, pyrrolic- and tertiary-type nitrogen functionalities. This is necessary to study the ORR mechanism in nitrogen-doped graphene and will be further investigated in future reports.

3. Electrochemical characterization

The electrochemical properties of graphene and nitrogen-doped graphene are characterized via cyclic voltammetry and linear sweep voltammetry. The electrochemical measurements are carried out at a scan rate of 5 mV/s in 0.1 M KOH solution. Each sample was dispersed in isopropanol. The working electrode, a glassy carbon (GC) electrode of 3 mm in diameter, was coated with 20 µl of the respective sample. A platinum electrode was used as counter electrode and Ag/AgCl as reference electrode.

The cyclic voltammetry was first performed in nitrogen-saturated 0.1 M KOH solution. As shown in Figure 3a, clear capacitive current background was seen within the CV. Afterwards oxygen was introduced to the solution. The measured CV curves are presented in Figure 3b featuring significant cathodic current peaks, thus showing the ORR performance of all samples in oxygen-saturated KOH solution. The highest value of current density is obtained for nitrogen-doped graphene, followed by graphene and glassy carbon, still lower than that of PtC. Compared with glassy carbon, the onset potentials of graphene and nitrogen-doped graphene shift positively confirming better electrocatalytic activity towards ORR. The highest value of current density is obtained for nitrogen-doped graphene, followed by graphene and glassy carbon, still lower than that of PtC.

![Figure 3](image-url)

**Figure 3.** CV-measurement of GC, TRGO, CN, PtC in 0.1 M KOH solution in N$_2$-saturated ambience (a), and in O$_2$-saturated ambience (b) demonstrating electrocatalytic activity towards ORR.

In addition, LSV-measurements were performed on a rotating-disk electrode (RDE) in oxygen-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. The recorded LSV-curves, displayed in Figure 4, show that nitrogen-doped graphene has the most positive onset potential and highest current density among the carbon-based materials. The LSV observations accord with the CV results and demonstrate that the electrocatalytic activity of graphene towards ORR is enhanced by doping with nitrogen. Onset potentials and reduction’s current densities of glassy carbon, graphene, nitrogen-doped graphene and PtC are calculated and listed in Table 1.
Table 1. Onset potentials and reduction’s current densities of glassy carbon (GC), graphene (TRGO), nitrogen-doped graphene (CN) and commercial 20% PtC derived from CV-measurements.

| Material   | $E_{ONSET,\text{Red}}$ vs Ag/AgCl (mV) | $J_p$ (mA cm$^{-2}$) |
|------------|-----------------------------------------|----------------------|
| GC         | - 250                                   | - 0.175              |
| TRGO       | - 175                                   | - 0.150              |
| CN         | - 160                                   | - 0.256              |
| PtC        | - 20                                    | - 0.285              |

Figure 4. LSV measurements of glassy carbon (GC), graphene (TRGO), nitrogen-doped graphene (CN) and commercial 20% PtC in O$_2$-saturated 0.1 M KOH solution at rotation speed of 1600 rpm.

4. Conclusions

As determined by Raman spectroscopy, nitrogen-doped graphene possesses a similar defect density to that of graphene. It can therefore be concluded that the incorporation of nitrogen into graphene apparently enhances the performance towards ORR.

The successful doping process of nitrogen in carbon lattice is evidenced by X-ray Photoelectron spectroscopy. Considered together with the experimental results, we estimate a significant importance of nitrogen doping for enhancing the ORR performance. In this context, it is necessary to investigate the individual nitrogen functionalities in carbon lattice and their impact on the ORR performance which will be addressed in future reports.

In summary, prepared graphene and nitrogen-doped graphene have proven their electrocatalytic activity towards oxygen reduction reaction. The electrocatalytic activity is enhanced by nitrogen doping. First stability tests have been performed delivering good results and will be continued in more detail. With regard to further modification, nitrogen-doped graphene represent a promising metal-free electrocatalyst as cathode in fuel cell applications.

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