
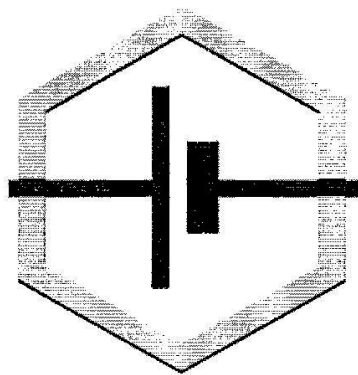
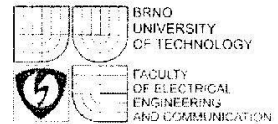


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13th ABAF

BRNO 2012

Advanced Batteries, Accumulators
and Fuel Cells

Book of Proceedings

August 26th - August 30th 2012

Organised by:

Department of Electrical and Electronic Technology,
Faculty of Electrical Engineering and Communication,
Brno University of Technology

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ELECTROCATALYTIC PROPERTIES OF REDUCED GRAPHENE OXIDE IN OXYGEN ELECTRODE

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Abstract

Reduced graphene oxide obtained by oxidation of multiwalled carbon nanotubes followed by reduction with sodium hypophosphite and sodium sulfite. X-ray diffraction and electron microscopy showed that the resulting product is reduced graphene oxide. Reduced graphene oxide has been investigated as an electrode material for oxygen electrodes of fuel cells. It has been shown that reduced graphene oxide obtained by the oxidation of multiwalled carbon nanotubes with subsequent reduction with sodium hypophosphite is a promising material for fuel cell oxygen electrodes and does not require the use of highly toxic reagents.

Key words: graphene, electrocatalysis, oxygen electrode, electrochemical power sources.

Introduction

The use of air or oxygen electrode in devices generating electrical energy is very promising since it does not give rise to environmental problems and makes it possible to save natural resources, such as oil and gas. Air and oxygen electrodes in current sources are a three-phase electrode-electrolyte-gas system, where the electric current generation processes are localized at the interface between these phases. The current magnitude generated at such a gas-diffusion electrode depends on the size of the zone of the triple contact of these three phases. The electrode consists of a catalyst and a support. Platinum is at present the most efficient oxygen reduction catalyst, but it has a considerable demerit, high price. There are a large number of papers dealing with the investigation of other efficient catalysts. Another important problem is catalytically active and stable support. References (1-4) showed the advantage of carbon nanotubes as catalyst support. At the present time, in view of the advent of a new carbon nanomaterial such as graphene, a number of papers have appeared which deal with its investigation as an electrode material for lithium ion batteries (5) and as a support for catalysts in fuel cells (6,7). Graphene is an atom thick carbon layer, which consists of condensed six-membered rings.

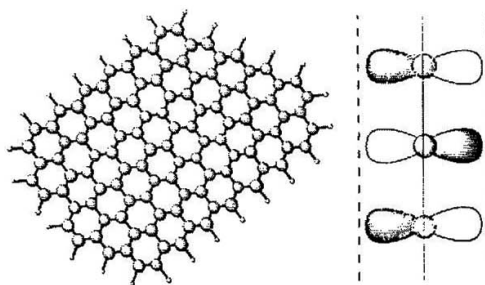


Fig. 1: The schematic structure of graphene: (a) top view, (b) side view.

The carbon atoms in graphene are bonded by sp^2 bonds into a hexagonal two-dimensional (2 D) lattice. Ideal graphene consists solely of six-membered rings; the appearance of defects leads to the formation of a number of five- or seven-membered rings in the graphene structure and hence to the curving of flat surface. At the same time, the extended π -system of conjugated aromatic rings makes graphene fairly stable in comparison with other nanosized objects. The structure peculiarities of graphene sheet are such that the charge carriers, having unlimited freedom to move in plane, are confined in a narrow space between "walls" (Fig. 1), which are the shortest atomic distance of ~ 0.3 nm apart, which gives rise to unique electrophysical characteristics and other extraordinary properties of graphene. In view of this, the study of the dependence of electrochemical properties on the method for the preparation of reduced graphene oxide (RGO), which is used as a catalyst support for fuel cell oxygen electrodes, is of great interest.

Experimental

Multiwalled carbon nanotubes (MWCNTs) were chosen as a precursor, for they resemble in structure several graphene layers rolled into a tube; therefore, using a strong oxidant, one can "break" nanotubes to form oxidized graphene nanostrips (8). To this end, a procedure for the oxidation of MWCNTs with heptavalent manganese (8) with subsequent reduction was chosen. We used alkaline solutions of sodium hypophosphite and sodium sulfite as oxidized- graphene reductants. MWCNTs with a bulk density of $25\text{-}30$ g/dm³, purified of catalyst impurities by treatment in a hydrofluoric acid solution, were used for the synthesis. The outside diameter of nanotubes was about $10\text{-}30$ nm, the specific surface area was 230 m²/g.

Two-layer oxygen electrodes were prepared by pressing. The hydrophobic layer contained 0.07 g/cm² acetylene black with 25% polytetrafluoroethylene, and the active layer contained 0.02 g/cm² graphene oxide, reduced with different reductants, with 5% polytetrafluoroethylene. The investigations were carried out on a fuel cell mockup, a zinc electrode being used as the anode. The mockup for the testing of gas-diffusion electrodes is shown in Fig 2.

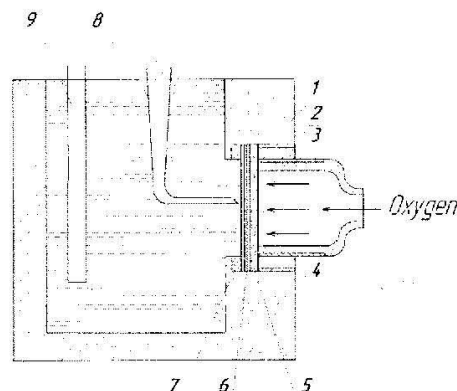


Fig. 2: Scheme of the cell: (1) cell body, (2) clamping coupling, (3) metallic current tap and oxygen supply tube, (4) metallic net of the oxygen electrode, (5) hydrophobic layer of the oxygen electrode, (6) active layer of the oxygen electrode, (7) polytetrafluoroethylene gasket, (8) reference electrode, (9) zinc anode.

The electrolyte was a solution of 5 M KOH with 1 M LiOH. A silver-chloride electrode connected through a salt bridge was used as a reference electrode. The electrochemical characteristics were recorded under galvanostatic conditions. The oxygen source was a U-shaped electrolyzer with alkaline electrolyte. Oxygen was supplied to the gas electrodes under an excess pressure of 0.01 MPa. Before measurements, the oxygen electrode was blown through with oxygen for an hour. The electron micrographs have been obtained with the aid of a JEM-100 CXII electron microscope. The X-ray phase analysis was performed with the aid of a DRON-4 X-ray diffractometer with CuK α radiation.

Results and discussion

One gram of MWCNTs was dispersed in 300 mL of concentrated sulfuric acid under stirring for an hour. Then 5 g of KMnO₄ was added, and the mixture was stirred on an oil bath for an hour at a temperature that was not over 17 °C. After that, the mixture was heated on an oil bath to 55 °C within 30 min. Then the solution was brought up to 65 °C, held for 20 min and cooled to room temperature. To remove possible by-product (manganese dioxide), the resulting mixture was poured into 400 mL of bidistilled water with ice, which contained 5 mL of H₂O₂. Then filtration was performed using a dense, fine-pored paper filter. The filtered off precipitate was transferred into a colloidal solution in bidistilled water. To reduce the product, two samples were prepared by the above procedure. One sample of oxidized product was reduced with an alkaline solution of sodium hypophosphite (pH = 11) and the other with an alkaline solution of sodium sulfite (pH = 11). The reduced substance was filtered off using a dense, fine-pored paper filter; after this, it was separated from the filter and dried in a desiccator at 140 °C for three hours. The product obtained was investigated by electron microscopy and X-ray phase analysis. Figure 3 shows X-ray diagrams of products obtained by reduction with sodium hypophosphite (Fig. 3 (b)) and sodium sulfite (Fig. 3 (a)). In the XRD pattern of RGO (which is exfoliated into individual platelets and then agglomerated into a powder form), the major peak is observed at about 23 – 24°. This gives an interlayer spacing of approximately 3.7 – 3.8 Å (8-11).

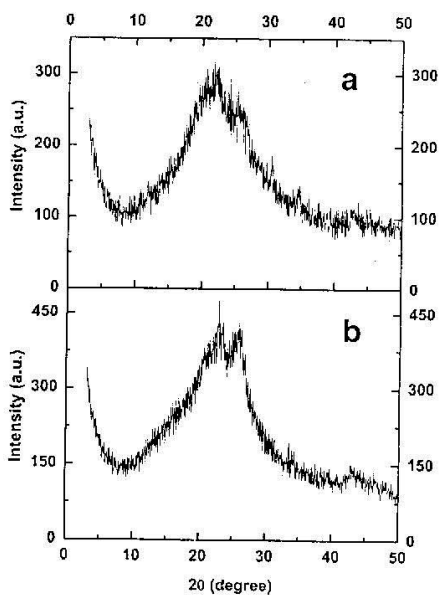


Fig. 3: X ray phase analysis of samples based on RGO obtained by reduction with sodium hypophosphite (b), RGO obtained by reduction with sodium sulfite (a).

Figures 4 and 5 show micrographs of RGO, which was obtained using different reductants. Thus, it can be concluded from the analysis of electron micrographs and comparison of the peaks in the X-ray diagrams with literature data that the above procedure gives nanosized FGO strips.

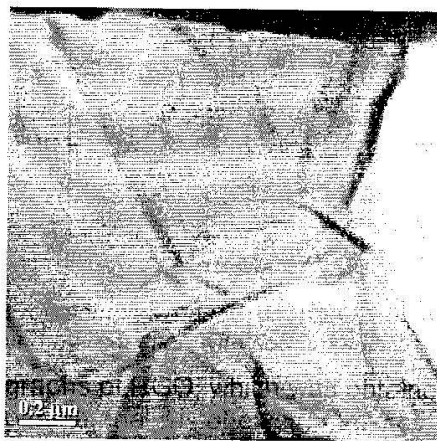


Fig. 4: Micrograph of RGO obtained with the use of sodium hypophosphite as a reductant.

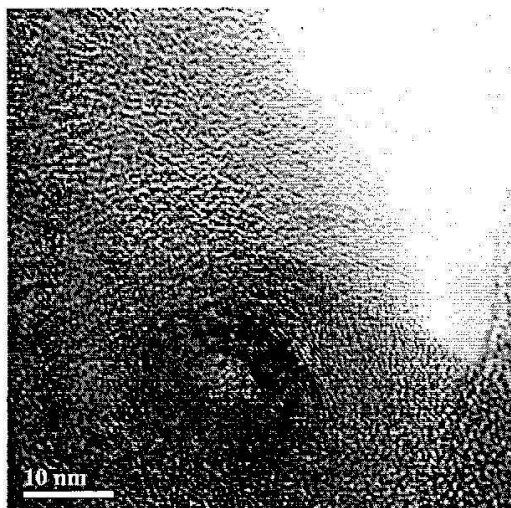


Fig. 5: Micrograph of RGO obtained with the use of sodium sulfite as a reductant.

Oxygen electrodes have been made by pressing, RGO being used as an active layer. The electrodes obtained were investigated on a mockup of oxygen fuel cell with alkaline electrolyte. Electrodes with active layer of starting MWCNTs have been made for comparison.

Electrocatalytic characteristics were investigated on the oxygen electrodes obtained. Figure 6 shows plots of potential against current density for oxygen electrodes based on graphene oxide reduced with sodium hypophosphite (curve 1, Fig 6) and RGO obtained by reduction with sodium sulfite (curve 2, Fig 6). This figure (curve 3) shows for comparison the characteristics of electrodes with starting MWCNTs, from which RGO samples have been synthesized.

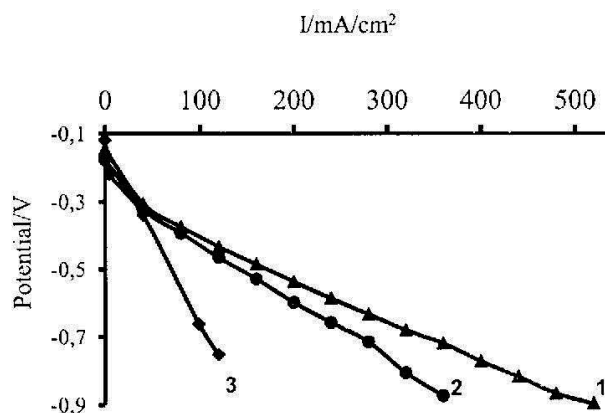


Fig. 6: Dependence of potential on current density for oxygen electrodes with active layer (0.02 g/cm²) based on RGO obtained with the use of sodium hypophosphite as a reductant (1), RGO obtained with the use of sodium sulfite as a reductant (2), initial multiwalled carbon nanotubes (3).

As is seen from Fig 6, the oxygen electrodes containing graphene oxide reduced with sodium hypophosphite have the best electrocatalytic characteristics. The electrodes containing graphene oxide reduced with sodium sulfite are inferior in characteristics to the electrodes containing graphene oxide reduced with sodium hypophosphite. The results obtained may be attributed to the fact that the active mass contains unreacted or not completely "broken" carbon nanotubes as impurities. It has been found that electrode made of graphene oxide reduced with sodium hypophosphate is greatly superior to that made of starting carbon nanotubes in electrochemical characteristics in oxygen reduction reaction. RGO has better characteristics than nanocomposite based on manganese dioxide deposited on multiwalled carbon nanotubes, which follows from comparison with the data presented in Ref (2). The results of an investigation of the characteristics of RGO-based electrodes in time showed their values to remain invariable during six-month tests.

Conclusions

Thus, it can be concluded that reduced graphene oxide obtained by the oxidation of multilayer carbon nanotubes with subsequent reduction with sodium hypophosphite is a promising material for fuel cell oxygen electrodes and does not require the use of highly toxic reagents.

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