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Electroreduction of oxygen on multi-walled carbon nanotubes modified highly oriented pyrolytic graphite electrodes in alkaline solution

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Abstract

The electrochemical reduction of oxygen has been studied on multi-walled carbon nanotubes (MWCNTs) modified highly oriented pyrolytic graphite (HOPG) electrodes in 0.1 M KOH solution using the rotating disk electrode (RDE) technique. The oxygen reduction behaviour of MWCNTs/HOPG electrodes of various modifications was compared. Electrochemical studies indicate that the MWCNTs/HOPG electrodes show a remarkable electrocatalytic activity towards O_2 reduction in alkaline media. The number of electrons transferred per O_2 molecule was a function of potential and it increased up to four at high negative potentials. The O_2 reduction behaviour of MWCNTs/HOPG electrodes using oxidatively treated MWCNTs was also studied. The oxidative pre-treatment of MWCNTs did not change their electrocatalytic properties for oxygen reduction in alkaline solution to a noticeable degree.

Keywords: Oxygen reduction; Electrocatalysis; Carbon nanotubes; Highly oriented pyrolytic graphite; Rotating disk electrode

1. Introduction

There has been much interest in the research of carbon nanotubes (CNTs) since their discovery [1]. CNTs have led to many new technical developments and applications due to their unique properties – high chemical stability, unique electronic properties, high mechanical strength and high surface area. Recent electrochemical studies have demonstrated that CNTs have the ability to promote electron-transfer reactions. It has been shown by Banks et al. that carbon nanotubes were no more electrocatalytic than the edge-planes of pyrolytic graphite [2]. They confirmed that the sidewalls of CNTs could be compared to the basal plane and the open ends with the edge planes of pyrolytic graphite. These authors also provided that the end group functionalities are responsible for the electrocatalytic properties of CNTs.

CNTs have two distinct types of structures: the single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Compared with MWCNTs, the SWCNT is a well-defined system in terms of electronic properties and individual SWCNTs can be regarded as quantum wires [3,4]. Since CNTs are insoluble in most solvents, attaching them to the support in a controlled manner is still a problem. Although carbon nanotubes have been solubilized by functionalising their sidewalls, this approach often damages their tubular structure. The controlled modification of the electrode surfaces is quite difficult to achieve due to the poor wetting properties (insolubility) of carbon nanotubes. While the ends of carbon nanotubes are quite hydrophilic and the walls are highly hydrophobic, the tubes have a tendency to rapidly agglomerate in aqueous solution or in polar solvents [5]. As a consequence, the nanotubes are usually dispersed in non-polar organic solvents [3,6].

Carbon nanotubes were easily dispersed into water in the presence of dihexadecyl hydrogen phosphate (DHP) [7–9]. The hydrophobic chains of the surfactant can wrap around the CNTs and the hydrophilic group can interact

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with water and finally CNTs were dispersed homogeneously into water with the aid of DHP [9,10]. It has also been noted that surfactants have the ability to separate individual nanotubes from the bundles [11]. The reduction of O_2 has been studied on stable and uniform SWCNT–DHP films in alkaline solution suggesting two $2e^-$ reduction steps of O_2 [7,8].

Also in the presence of Nafion, carbon nanotubes can be solubilized and uniformly deposited onto electrode surfaces. Nafion acts as a polymer back bone to give stable and homogeneous cast thin film, which has very interesting properties and a wide range of applications [12–14]. The reduction of oxygen on Nafion bounded CNTs is not so widely investigated, especially in alkaline solution. Hu et al. showed that O_2 reduction on SWCNTs with metal additive (Ag–MnO_2/SWCNT) proceeds via four electron reduction in alkaline solution [15].

To achieve homogeneous and stable multilayer films of the CNTs on solid surfaces the layer-by-layer (LBL) method has attracted increasing interest. This is a simple way to produce multilayer structures with unique mechanical properties and precise control over film composition and thickness. Poly(diallyldimethylammonium chloride) (PDDA), as a widely used polyelectrolyte, has been often used for this purpose [16–18]. Experimental results have revealed that the LBL assembled MWCNTs films possess remarkable electrocatalytic activity towards O_2 reduction in alkaline media [16].

Abrasive immobilisation is probably the simplest method in the modification of surfaces with CNTs. However, the disadvantage is that it is impossible to control the exact loading of the material attached. This method was used for immobilising chemically or electrochemically modified MWCNTs to pyrolytic graphite electrodes [19,20]. It was shown that the quinone moieties covalently attached to MWCNTs act as effective mediators for O_2 reduction [20].

Various properties of CNTs, for instance their electronic properties and solubility, are largely influenced by surface functional groups. It has been ascertained that the treatment of CNTs with oxidising agents results in the formation of oxygen-containing groups preferably at the ends of nanotubes [21–24]. This makes CNTs more hydrophilic and leads to an increase in the electron transfer rate for various redox couples. In an attempt to shorten the nanotubes and to remove graphitic nanoparticles, amorphous carbon and catalyst impurities the electrochemical, chemical, physical and sonochemical oxidative pre-treatments have been used [22–26].

In most of the previous studies glassy carbon (GC) and ordinary pyrolytic graphite were used as electrode substrates for CNTs attachment. The purpose of the present work is to describe and compare the electrochemical behaviour of untreated and oxidatively treated MWCNTs modified HOPG electrodes of various modifications. The electrocatalytic reduction of O_2 was explored in 0.1 M KOH using the rotating disk electrode (RDE) technique.

2. Experimental

2.1. Apparatus and reagents

Multi-walled carbon nanotubes (MWCNTs, purity ≈95%, diam. 30 ± 10 nm, length 5–20 μm) purchased from NanoLab, Inc. (Brighton, MA, USA) were used in this work. In some experiments the nanotubes treated by the following oxidation procedure were employed: MWCNTs were refluxed slightly in a mixture of concentrated sulfuric and nitric acids (1:1, v/v) at 80 °C for 5 h. Afterwards, the nanotubes were washed with Milli-Q water by centrifugation (3000 rpm, 10 min) repeating it for several times and the CNTs were resuspended in Milli-Q water. Finally, the MWCNTs were dried under vacuum for 15 h.

Dihexadecyl hydrogen phosphate (DHP) was a product of Fluka. Poly(diallyldimethylammonium chloride) (PDDA) ($M_w = 200\,000$–$350\,000$) was purchased from Aldrich and was used as received. A 0.5% Nafion solution used in this work was prepared by diluting the 5% Nafion solution (Aldrich) into ethanol. All other chemicals were analytical grade reagents and all the solutions were prepared with Milli-Q water (Millipore, Inc.).

The rotating disk electrode (RDE) technique was employed. An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were used. The electrode rotation rate (ω) was varied from 360 to 4600 rpm. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT10 (Eco Chemie BV, The Netherlands) and the experiments were controlled with the general purpose electrochemical system (GPES) software. A Pt foil served as the counter electrode and a saturated calomel electrode (SCE) was used as a reference. All the potentials are referred to this electrode. The working electrode was a highly oriented pyrolytic graphite (HOPG) disk of 0.2 cm^2 surface area (NII Graphite, Russia), which was mounted in a special holder for the RDE experiments.

The electrodes were electrochemically characterized by cyclic voltammetry (CV) and oxygen reduction was studied in 0.1 M KOH (BDH, AristaR) solution. The solutions were saturated with Ar (99.999%, AGA) or O_2 (99.95%, AGA). In some experiments, the electrochemical reduction of peroxide was studied in Ar-saturated 0.1 M KOH containing 1 mM HO_2^-. A continuous flow of gases was maintained over the solution during the electrochemical measurements. All measurements were conducted at room temperature.

2.2. Preparation of the MWCNTs-modified HOPG electrodes

Four methods of MWCNTs attachment were used in the present work. These are given in brief. Prior to the preparation of modified electrodes the fresh surface of HOPG was achieved by removing the top layers with adhesive tape.

As the first method of modification, the MWCNTs–DHP suspension was prepared by dispersing 1 mg of