Nitrogen-doped carbon nanotubes as metal-free catalysts for the oxygen reduction in alkaline and acidic media

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Abstract

The electrochemical reduction of oxygen was investigated on carbon nanotube (CNT) electrodes in alkaline aqueous solution. The CNT-based electrodes were produced by means of chemical vapor deposition (CVD) technique with decomposition of acetonitrile (ACN) and benzene (BZ) carbon source materials in the presence of catalyst. Namely, upon decomposition of ACN and BZ, nitrogen-doped and pristine CNTs, respectively, were produced. The electrochemistry experiments were performed by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in Ar-protected and O2-saturated aqueous solution of KOH and H2SO4. For comparison reasons, the electrochemical experiments were also performed on epitaxial graphene deposited on SiC as well as on conventional Pt, Au, and glassy carbon electrodes. The obtained results demonstrate that the strong doping with nitrogen of low-dimensional carbons is the best strategy to obtain an efficient metal-free catalyst for the oxygen reduction.
Keywords: Carbon nanotubes; Chemical vapor deposition; Cyclic voltammetry; Electrochemical impedance spectroscopy; Oxygen reduction

1. Introduction

The electrochemical performance of fuel cells is strongly affected by the construction of counter cathode that should promote the oxygen reduction. The kinetics of oxygen reduction in the absence of catalysts seems to be very slow and therefore for the improvement of the kinetics of redox process, cathode catalysts are typically used. The most commonly used catalysts for oxygen reduction are Pt-based materials [1,3]. However, the high cost of Pt-based catalysts seems to be the greatest disadvantage of using these materials in fuel cell technology, and thus, there is growing demand to rapidly find new catalysts for the reduction of oxygen [4,5]. It has been found that graphenes and carbon nanotubes (CNTs) could act as effective metal-free electro-catalysts [6,7]. Their improved electro-catalytic activity arises from the creation of positively charged carbon atom nets [8,9].

Calculations show that nitrogen doping of carbon nanotubes forms an electron rich structure which can hinder their adsorption properties [10,11]. Results of studies through density functional theory computations including single N atom substitution, pyridine and pyrrole-like structures suggest that in nanotubes with high content of nitrogen (N-CNTs) for the observed donor states are responsible N atoms substituting for C atoms [12]. Three electrons of the nitrogen dopant form $\sigma$ bond. The left two electrons are used to form a $\pi$ and $\pi^*$ electronic states. It has been demonstrated that the electron transfer kinetics through electrolyte CNT interface is controlled by the $\pi$-electron band of individual tubules [13].

There are two approaches to inducing positively charged carbon sites in the graphene tubules that lead to the enhanced ORR electro-activity. The first one is the modification of as-prepared pristine CNTs. It has been shown that CNTs covalently functionalized with sulphonic and phosphonic acids catalyze the ORR [14]. The enhanced catalytic activity has been also demonstrated in CNT-PDDA composites, where ammonium functional groups along the PDDA backbone induce the net of positive charge in the nanotubes [15]. Pristine CNTs coated with polyaniline and carbonized are also an effective electrocatalysts [16].
The second approach relies on the introducing of donor dopants during the synthesis, which induce positive charge net in CNTs. Several attempts have been made to synthesize N-CNTs. ORR catalytic activity tests in alkaline and acidic media were performed on the N-CNT films immobilized on glassy carbon (GC) electrode. N-CNTs where produced by pyrolysis of iron (II) phtalocyanine and then electrochemically examined in the form of CNT-polystyrene [17]. As precursor in the synthesis of N-CNTs has been also used acetonitrile [18, 19], mixture of CH$_4$ and NH$_3$ [20], ethylene with melamine [21], ethylenediamine [22], and imidazole [23].

In each of the experiments mentioned above, electrochemical ORR tests were carried out on the CNTs which are scrapped from the original substrate and spread on the (GC) electrode. Thus, the electrochemical response was resulting from the interference of the catalytic activity of the CNT film and GC electrode.

We propose to examine the electrocatalytic activity towards ORR of the vertically aligned N-CNTs on the oxidized silicon wafers. To attain the electrochemical data only from the N-CNTs, the as-grown tubules on their original isolating substrate were used as a working electrode in the electrochemical cell. ORR efficiency has been assessed by cyclic voltammetry (CV) technique accompanied by electrochemical impedance spectroscopy (EIS) in alkaline and acidic media. To the best of our knowledge, this is the first experiment, in which the intrinsic electro-activity of N-CNT towards ORR was characterized.

In the present work we compare the ORR efficiency of the N-CNTs with other carbon electrodes such as pristine CNTs, GC and epitaxial graphene (Institute of Electronic Materials Technology in Warsaw). The results were referred to the metallic electrodes (Pt and Au).

2. Experimental

2.1. Materials

CNTs were grown on oxidized silicon wafers using the spray pyrolysis CVD method [24,25,26]. Argon was used as a carrier gas, whereas ACN containing 2% w/w ferrocene was applied as feedstock material. The reaction mixture was sprayed into quartz tube(internal diameter: 30mm; length: 1000mm) with a flow rate of 10 cm$^3$·h$^{-1}$.The quartz tube was heated
by cylindrical furnace equipped with a very precise temperature control of ±1°C. During CVD process the temperature was maintained at 900°C. Pristine CNTs were also grown on oxidized silicon substrate using the same conditions and BZ as carbon feedstock.

Pure epitaxial graphene was grown on SiC substrates using propane as carbon feedstock at the temperature of 1600°C. The experimental conditions for the growth procedure were the same as reported previously [27].

The morphology of CNTs grown on Si/SiO$_2$ substrate was examined by scanning electron microscope FEI/Philips (model XL30 ESEM) equipped with an energy dispersive X-ray spectrometer (EDX) and Philips TECNAI transmission electron microscope.

2.2. Apparatus and procedures

The electrochemical response of the fabricated electrodes towards the reduction of oxygen was examined by means of CV and EIS techniques in KOH (0.1 mol·L$^{-1}$) and H$_2$SO$_4$ (0.5 mol·L$^{-1}$) aqueous solutions. The same electrolytes are used in alkaline fuel cell. To investigate the activities of the N-carbon materials for oxygen reduction, the measurements were performed both in O$_2$-saturated and Ar-protected electrolyte. The CVs and EIS spectra were recorded using a computer-controlled system Zahner/IM6/6EX. The measurements were carried out using a three electrode cell configuration. The working electrode was either, CNT-based electrodes, Pt, Au, glassy carbon or graphene grown on SiC, the counter electrode was Pt plate, while the reference electrode was Ag/AgCl (sat. KCl). All measurements were carried out at the room temperature (25°C). The EIS spectra were measured by applying small amplitude of alternate voltage (10mV) in the frequency range from 0.1 Hz to 100 kHz at the room temperature (25°C). The EIS spectra were analyzed using the software Thales (version 4.15).

3. Results and Discussion

The differences in morphology between pristine and nitrogen doped CNTs can be clearly seen in the micrographs shown in Figure 1. The CNTs grown with decomposition of BZ (further referred as pristine CNTs) in carpet are rather muddled, whereas the CNTs grown with decay of ACN (further referred as N-CNTs) are rather smooth and possess characteristic
flat tips. The estimation of percentage (atomic) nitrogen content in the nanotubes by means of EDS reveals that N-CNTs (N: 7% at.) contain grated amount of nitrogen compared to pristine CNTs (1% at.). The structure of individual tubes is visible in HR TEM images. The pristine CNTs are composed of concentric graphene cylinders (inset of Figure 1a). The N-CNTs show bamboo-like morphology (inset of Figure 1b).

The Raman spectra recorded from pristine CNTs and N-CNTs are displayed in Figure 2. For both cases, features which are typical for sp² carbon systems are present. Namely, the G-band attributed to the oscillation mode of E_{2g} symmetry, the D and D* bands which are due to the one- and two-phonon second order Raman scattering process. The main Raman features are accompanied by the weaker M band, which is an overtone produced by the IR-active out-of-plane transverse optic phonons. The iTOLA band is attributed to the second order Raman scattering of the combined in-plane transverse optic and longitudinal acoustic phonons. The positions of the Raman active bands in N-CNTs are up-shifted in regard to the positions obtained in the pristine CNTs. The increase of the D band intensity is considered as consequence of incorporation of nitrogen atoms into carbon atom sites. As the D* band is free from defect effects, its relative intensity decreases in N-CNTs.

CVs recorded at Pt, Au, glassy carbon, pristine CNTs, N-CNTs, and epitaxial graphene in aqueous KOH solution (0.1 mol·L⁻¹) at the scan rate of 0.05 V·s⁻¹ are shown in Figure 3. Peaks due to oxygen reduction can be observed in CVs recorded on both metallic Pt and Au electrodes in O₂-saturated, but not in Ar-saturated KOH solution (Figures 3a-b). The O₂ reduction reaction reveals higher exchange current density on Pt electrode (~300µA·cm⁻²) compared to that of Au electrode (~150µA·cm⁻²). On Pt electrode the reduction potential of oxygen lies at about -0.22 V (vs. Ag/AgCl) while on Au electrode the reduction process is slightly shifted to more cathodic potential (-0.31 V vs. Ag/AgCl).

As it can be seen in CVs shown in Figures 3(c-f), the catalytic capability of carbon-containing electrodes towards oxygen reduction depends strongly on the structure of electrode’s material. Consequently, cathodic peaks due to the oxygen reduction can be observed in CVs recorded on glassy carbon (-0.42 V vs. Ag/AgCl) pristine CNTs (-0.45 V vs. Ag/AgCl) and N-CNTs (-0.39 V vs. Ag/AgCl) electrodes but no reduction peaks can be observed in graphene electrodes. The observed overpotentials for the reduction of oxygen are higher on carbon electrodes than on metallic ones, what is a bottleneck to use the carbon catalysts in fuel cells. For the overpotential in ORR are responsible such factors as slow electron transfer, blocking of the O₂ adsorption sites, and very stable adsorbed hydroxyl
intermediate [28,29]. The lowest overpotential among carbon electrodes was observed on the N-CNTs which possess the best electron transfer kinetics [25].

The current density for reduction of oxygen obtained on carbon-based electrodes seems to be significantly greater compared to that measured on conventional electrodes. Specifically, on glassy carbon, pristine CNTs and N-CNTs the current densities of about 930, 390 and 870 µA·cm\(^{-2}\) were determined, respectively, that appear to be greater to those measured on metallic electrodes. However, within the carbon-based electrodes studied, better electro-catalytic activity towards reduction of oxygen exhibits the N-CNTs due to the strong electronic affinity of the nitrogen atoms that are incorporated in nanotubes [30]. The comparison of CVs recorded on glassy carbon, pristine CNT, and N-CNT electrode (Figures 3c-e) shows that donor doping cause the broadening of the electrochemical windows. The most apparent ORR peak is visible on the N-CNT electrode.

The capability of carbon electrodes to catalyze the ORR was also tested in aqueous H\(_2\)SO\(_4\) solution. CVs recorded in argon protected and oxygen saturated media are presented in Figure 4. Background currents due to the large capacitance in forward and backward scans are observed on CNT electrodes. Surface specific capacitance in the H\(_2\)SO\(_4\) solution was estimated to \(\sim 1\ \text{mF} \cdot \text{cm}^{-2}\) and \(\sim 6\ \text{mF} \cdot \text{cm}^{-2}\), for the pristine CNT and N-CNT electrode, respectively. As a result of dissolution of remains of metallic catalyst by acid, redox peaks of Fe\(^{2+}\)/Fe\(^{3+}\) are present in CVs recorded on CNT electrodes with the half potential at 0.44 V and separation of oxidation and reduction peak of 0.18 V.

The apparent ORR occurs only on the N-CNT electrode at potential of +0.12 V vs. Ag/AgCl. The corresponding exchange current density of 280 µA·cm\(^{-2}\) was estimated by subtraction of the background current. Its value is three times lower than in alkaline medium, what confirms results obtained for N-CNTs immobilized on glassy carbon electrode [22]. Weak ORR peak appeared also on the glassy carbon electrode at the edge of its electrochemical windows.

To gain further insight into oxygen reduction process occurring on novel electrodes, EIS measurements in Ar-protected and O\(_2\)-saturated alkaline solutions were performed. Figure 5 shows the Nyquist plots for metallic and CNT-based electrodes. The Nyquist plots exhibit a trend for the formation of two semicircles of “capacitive type”. The higher frequency semicircle is attributed to the charge transfer process taking place at the surface of the working electrode and illustrates the charge-transfer resistance of the system, while the
A semicircle occurring at lower frequencies arises due to oxygen diffusion [31]. The equivalent circuit \((R_1+(C_1/R_2)+(C_2/R_3))\) has been used for the analysis of the recorded EIS spectra. The EIS results confirm further the obtained CVs data. The highest charge transfer resistances were obtained for Au (\(~25 \, \text{k}\Omega\)) and GC (\(~23 \, \text{k}\Omega\)) electrodes. The Pt electrode that exhibits much better exchange current has a charge transfer resistance of about \(~2.0 \, \text{k}\Omega\). As revealed by the EIS data, the CNTs are the most efficient catalysts among the electrode materials investigated. The charge transfer resistance in the CNT-based electrodes is lower by approximately one order of magnitude than those obtained for the other investigated electrodes (Pt, Au, and GC). As was expected, the smallest charge transfer resistance was obtained for the N-CNTs electrode (\(~0.06 \, \text{k}\Omega\)). The pristine CNTs with comparatively low content of the N dopant have a charge transfer resistance of about \(~0.1 \, \text{k}\Omega\).

4. Conclusions

The CV and EIS data for oxygen reduction in alkaline (KOH) and acidic (H_2SO_4) solution demonstrate that nitrogen doping is an essential factor for the catalytic efficiency of carbon-based catalysts. The epitaxial graphene shows no catalytic capability towards reduction of oxygen. Within the two metallic electrodes tested the poorest exchange current density and greater charge transfer resistance (slower electron transfer kinetics) was estimated for Au confirming that Pt is more capable to catalyze reduction of oxygen. It is interesting that within the different CNT-based electrodes tested the best electrochemical performance, namely smaller charge transfer resistance (fast electron transfer kinetics) and higher exchange current density, exhibits the N-CNTs based electrode. The findings demonstrate the strong effect of the nitrogen doping of CNTs on the electrochemical performance of electrodes. Better activity of the N-CNT electrodes in alkaline medium is also confirmed.

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Figure 1. Forest of (a) pristine and (b) N-CNTs grown directly on Si/SiO$_2$ substrate. Inset: HR TEM images of individual tubules.
Figure 2. Raman spectra of pristine and N-CNTs.
Figure 3. CVs for oxygen reduction at Pt (a), Au (b), glassy carbon (c), pristine CNTs (d), N-CNTs (e), and epitaxial graphite on SiC substrate (f) recorded in Ar-protected (black dotted line) and O$_2$-saturated (red solid line) KOH solution (0.1 mol·L$^{-1}$) at $v=0.05$ V·s$^{-1}$.
**Figure 4.** CVs for oxygen reduction at glassy carbon (a), pristine CNTs (b), and N-CNTs (c) recorded in Ar-protected (black dotted line) and O$_2$-saturated (red solid line) H$_2$SO$_4$ solution (0.5 mol·L$^{-1}$) at $\nu=0.05$ V·s$^{-1}$.

**Figure 5.** Nyquist plots for oxygen reduction at Pt (a), Au (b), pristine CNT (c), and N-CNT (d) recorded in Ar-protected (solid black triangles) and O$_2$-saturated (open red circles) KOH solution (0.1 mol·L$^{-1}$). Inset: Zoom of EIS spectra in high frequency region.
References