

Oxygen Reduction on Multiwalled Carbon Nanotube Modified Glassy Carbon Electrodes

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Carbon nanotubes (CNTs) are novel materials, that reveal unique electronic, mechanical and chemical properties. The electronic behavior of CNTs reveals that they have the ability to promote electron-transfer reactions, therefore they can be used as a support material for various catalysts and for this reason their electrocatalytic properties towards O_2 reduction are of great fundamental and practical importance. The aim of this work was to compare the differences of the oxidatively pre-treated and untreated multiwalled carbon nanotubes (MWCNTs) and also to study the pH-dependence of O_2 electroreduction on MWCNTs modified electrodes.

The electrocatalytic reduction of oxygen has been studied on MWCNT modified glassy carbon (GC) electrodes in 0.5 M H_2SO_4 solution using the rotating disk electrode (RDE) technique (1). The oxygen reduction behavior of acid-treated and untreated MWCNTs modified GC electrodes was compared. MWCNTs were treated in a mixture of acids (H_2SO_4 - HNO_3 ; 1:1) at 80 °C. The results obtained indicate that the electrocatalytic properties of untreated MWCNTs toward O_2 reduction in acid media are noticeably better than that of pre-treated MWCNTs. This effect is caused by catalyst impurities, which remain in the nanotubes prepared by chemical vapor deposition and can be largely removed by treatment in acids. The RDE results show that oxidative pre-treatment of MWCNTs has a strong effect on the electrocatalytic activity for O_2 reduction in acid solution (Figure 1). The half-wave potential shifted more than 250 mV in the negative direction upon MWCNTs treatment in acids. According to CV results it was evident that chemical oxidation of MWCNTs increases the amount of oxygenated species on the surface of nanotubes, but these groups do not enhance the oxygen reduction reaction in acid solution. The results obtained in this work clearly demonstrate the effect of impurities containing in MWCNTs on the kinetics of O_2 reduction.

The pH-dependence of O_2 electroreduction has been investigated on MWCNT modified GC electrodes (2). Electrochemical experiments were carried out in 0.5 M H_2SO_4 solution, acetate buffer (pH 5), phosphate buffers (pH 6, 7 and 8), borate buffer (pH 10), 0.01 M KOH, 0.1 M KOH and in 1 M KOH solution, using the RDE method. GC electrodes were modified with nanotubes using aqueous suspensions (1 mg/ml) in the presence of various surfactants: 0.3% cetyltrimethylammonium bromide (CTAB), 1% sodium dodecyl sulfate (SDS), 0.1% dihexadecyl hydrogen phosphate (DHP) and 0.3% Triton X-100. Carbon nanotubes were physically attached to the surface of GC electrodes. Experiments carried out with nanotube-modified electrodes demonstrated a strong electrocatalytic effect of carbon nanotubes on O_2 reduction. Oxygen reduction studies at different pHs indicated the following: 1) at pH values 6, 7 and 10 the number of electrons transferred per oxygen molecule (n) was close to 2 showing that in these solutions the reduction of oxygen yields hydrogen peroxide, but peroxide would not reduce further, 2) at higher pHs the value of n is close to 2 at low overpotentials, whereas at more negative potentials the peroxide formed reduces further ($n > 2$). In 0.5 M H_2SO_4 solution (pH 0.3) n is about 2 and oxygen reduces to H_2O_2 within the entire

range of potentials studied. The RDE results revealed that the half-wave potential ($E_{1/2}$) of oxygen reduction was higher in solutions of high pH. At lower pHs (pH < 10) the value of $E_{1/2}$ did not essentially depend on solution pH (Figure 2). The results obtained in this work were compared with those of bare glassy carbon (3) and carbon nanotube modified electrodes (1,4). The pH dependence of the half-wave potential of oxygen reduction on carbon nanotube-modified GC electrodes follows a similar trend that has been observed for bare GC (3).

References

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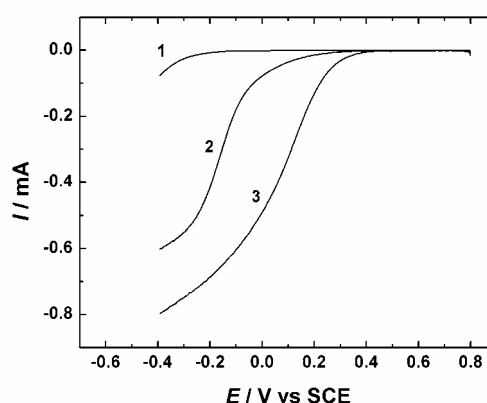


Figure 1. RDE voltammetry curves for O_2 reduction on: (1) Nafion-coated GC, (2) oxidatively pre-treated MWCNTs modified GC and (3) untreated MWCNTs modified GC electrodes in O_2 saturated 0.5 M H_2SO_4 at 1900 rpm. $v = 10 \text{ mV s}^{-1}$.

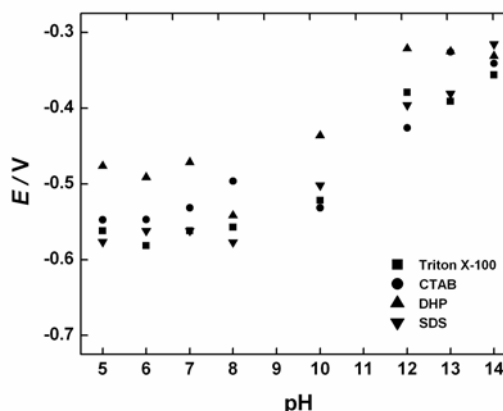


Figure 2. The pH dependence of $E_{1/2}$ for O_2 reduction on MWCNT/GC electrodes at $\omega = 960 \text{ rpm}$.