Oxygen Electroreduction on Nitrogen-Doped Carbon Nanotube Modified Glassy Carbon Electrodes

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In recent years there has been an increased research activity to find cheaper alternatives to Pt-based cathode catalysts for low-temperature fuel cells. In this regard a great deal of attention has been paid to the study of electrocatalytic activity of various non-precious metal catalysts toward the oxygen reduction reaction (ORR). An attractive approach is to employ nitrogen-containing carbon nanomaterials as electrocatalysts for ORR.[1]
In this work glassy carbon (GC) electrodes modified with undoped and nitrogen-doped carbon nanotubes (NCNTs) were studied.[2] The purpose was to test the electrocatalytic activity of these materials toward oxygen reduction. The electrochemical experiments were carried out in 0.1 M KOH and 0.5 M H_2SO_4 solutions using the rotating disk electrode (RDE) method. GC electrodes were modified using carbon nanotube suspension in isopropanol in the presence of ionomer AS-04 or Nafion.[2]
The undoped MWCNT materials were synthesized using the chemical vapor deposition method. In this work a pyrolytic approach was used for nitrogen doping of MWCNTs. Pure MWCNTs and materials with different urea and nanotube ratio (before pyrolysis) were used. The following nitrogen-doped carbon materials were tested: 5(urea):1(CNT); 2.5(urea):1(CNT) and 1(urea):2(CNT). These are designated as 1-NCNT, 2-NCNT, and 3-NCNT. The surface morphology and composition of NCNTs was investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The SEM images revealed a rather uniform distribution of NCNTs on the GC electrode substrate. The XPS analysis showed a successful doping of MWCNTs with N species (Fig. 1). It was demonstrated that the electrocatalytic activity for ORR depended on the solution in which the experiments were carried out and on the amount of nitrogen doped in MWCNTs. Fig. 2 presents a set of RDE polarization curves for O_2 reduction on 1-NCNT catalysts. The onset potential of the ORR is more positive by ca. 100 mV compared to the MWCNT/GC electrode. The Koutecky-Levich analysis showed that the number of electrons transferred per O_2 molecule (*n)* for MWCNTs was 2, but for N-doped material it was considerably higher than two (Fig. 3). Fig. 4 compares the RDE results obtained with the NCNT catalysts of different N content. It was evident that the larger the amount of nitrogen doped in MWCNTs, the better electrocatalytic properties the material has.
In acid solution the NCNT materials showed a modest O_2 reduction activity, but in alkaline solution the N-doped nanotube materials possessed remarkable electrocatalytic activity for ORR. Therefore these NCNT materials show a great promise for the application as cathode catalysts in alkaline membrane fuel cells.

References

1. N. Alexeyeva, E. Shulga, V. Kisand, I. Kink, and K. Tammeveski, *J. Electroanal. Chem.* **169**, 648 (2010).
2. M. Vikkisk, I. Kruusenberg, U. Joost, E. Shulga, and K. Tammeveski, *Electrochim. Acta* (in press).

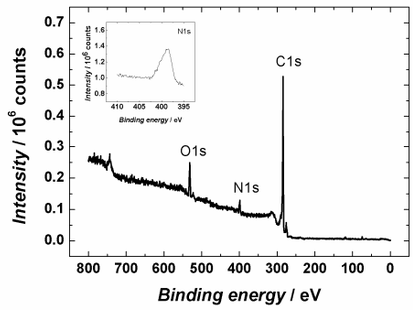

Fig. 1. XPS survey spectrum of 1-NCNT material. Inset shows the high-resolution scan in the N1s region.

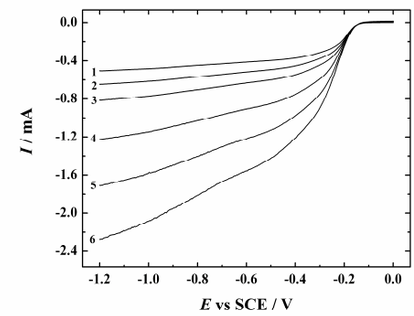

Fig. 2. RDE voltammetry curves for O_2 reduction on a 1-NCNT/GC electrode in O_2-saturated 0.1 M KOH. ω = (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100, (6) 4600 rpm.

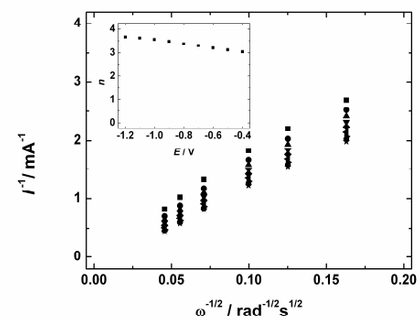

Fig. 3. K-L plots for oxygen reduction on a 1-NCNT/GC electrode in 0.1 M KOH solution. E = (■) -0.4, (●) -0.5, (▲) -0.6, (▼) -0.7, (♦) -0.8, (◀) -0.9, (▶) -1.0, (⬢) -1.1 and (★) -1.2 V. Inset shows the potential dependence of *n*.

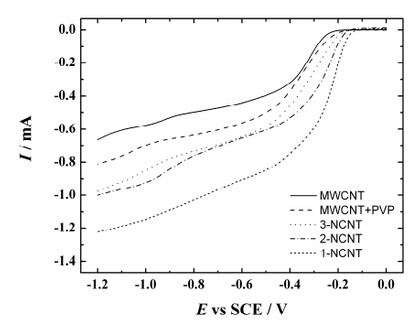

Fig. 4. Comparison of RDE results on oxygen reduction on MWCNT/GC and NCNT/GC electrodes in O_2-saturated 0.1 M KOH. v = 10 mV s^{-1}, ω = 1900 rpm.