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Electrochemical Reduction of Oxygen on Multi-walled Carbon Nanotubes Electrode in Alkaline Solution

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Abstract: The multi-walled carbon nanotubes (MWNTs) electrode was constructed using polytetrafluoroethylene as binder, and the electrochemical reductive behavior of oxygen in alkaline solution was first examined on this electrode. Compared with other carbon materials, MWNTs show higher electrocatalytic activity, and the reversibility of O_2 reduction reaction is greatly improved. The experiments reveal that the electrochemical reduction of O_2 to HO_2^- is controlled by adsorption. The preliminary results illustrate the potential application of MWNTs in fuel cells.

Keywords: Electrochemical reduction, oxygen, multi-walled carbon nanotubes.

The reduction of oxygen on carbon-based electrodes has been a major topic of research both recently and in the past. The well-known importance of oxygen reduction reaction (ORR) in fuel cells, organic electrosynthetic processes and electrochemical devices for decontamination of wastewaters has provided the economic driving force for decreasing the ORR overpotential. Except that the great efforts have been made on the modification of the carbon electrode, ORR on various carbon materials are also widely investigated. Although the mechanisms of ORR on carbon remain incomplete, it is found that the state of carbon surface structure has great effect on ORR kinetics. Carbon nanotubes as a novel carbon material have been proved to have high catalytic activity for ORR as catalyst or support[1~3]. However, all of these studies are conducted in acidic and neutral media, and no reports have been made in alkaline solution up to now. Therefore, the electrocatalytic characteristics of multi-walled carbon nanotubes (MWNTs) for ORR in KOH solution were investigated in this paper.

The MWNTs were purchased from Nanotech Port Co. with purity over than 95% and diameters of 10-30 nm. The MWNTs electrode was prepared as follows: a MWNTs film with surface density of 6.8 mg/cm^2 and thickness of 0.2 mm was made from 85 wt% MWNTs and 15 wt% polytetrafluoroethylene, then the film was pressed onto one side of a graphite paper at 10 MPa for 1 min. The opposite side of the graphite paper was insulated by epoxy resin. For comparison, a graphite electrode was made with the same procedure except that spectral grade graphite powders replaced MWNTs. The surface density and thickness of graphite film were 26.0 mg/cm^2 and 0.2 mm, respectively.

The experiments were performed with a CHI660 electrochemical workstation (CHI,

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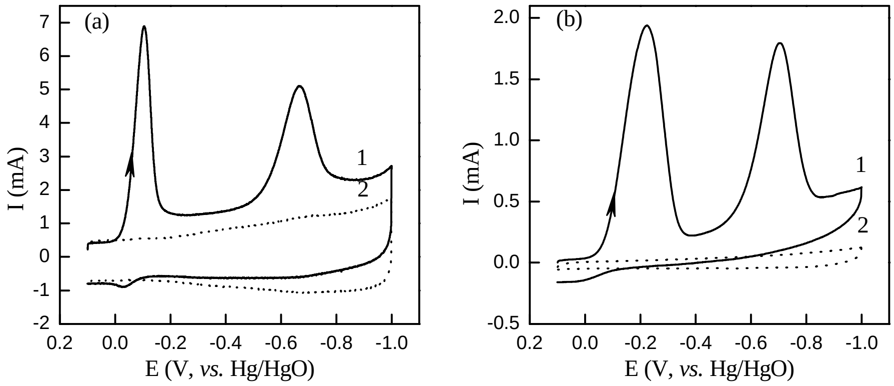
USA) in a conventional three-electrode cell at 20±1°C. The counter and working compartments were separated by a glass frit. The MWNTs electrode and graphite electrode were used as working electrodes with geometric area of 1 cm^2. A platinum foil and a Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. The electrolyte was 40% KOH solution made from deionized water and analytical grade KOH. In each measurement, the fresh electrolyte was used and previously saturated with O_2 or Ar by bubbling high purity O_2 or Ar through it for 30 min. During data acquisition, the purging gas was passed over the solution. The electrolyte resistance was compensated by positive feedback technique.

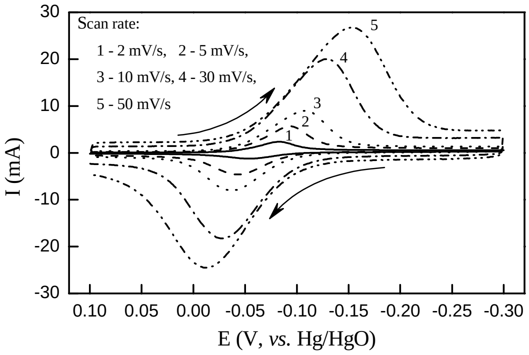
Figure 1 Cyclic voltammograms on MWNTs electrode (a) and graphite electrode (b)



Electrolyte: 1 - O_2 saturated 40% KOH solution; 2 - Ar saturated 40% KOH solution.
Scan rate: 10 mV/s.

Figure 1 shows the cyclic voltammograms (CVs) on MWNTs electrode and graphite electrode in O_2 saturated 40% KOH solution, along with the background curves in Ar saturated electrolyte. In Ar saturated solution, no cyclic voltammetric peaks are observed on both electrodes. The background current on MWNTs electrode is much bigger than that on graphite electrode, indicating that MWNTs electrode has larger electrochemical active area due to the unique structure of MWNTs. However, two well- defined cathodic peaks appear at -0.105 V and -0.665 V on MWNTs electrode in the O_2 saturated electrolyte. The corresponding peaks on graphite electrode shift negatively to -0.224 V and -0.703 V, respectively, while the peak currents are only about one third of those on MWNTs electrode. When the loads of MWNTs and graphite powders are taken into account, the peak currents of the first reduction of O_2 on MWNTs electrode and graphite electrode are 1.11 mA/mg and 0.084 mA/mg, respectively. These indicate the catalytic activity of MWNTs is higher than that of graphite for ORR. According to the previous conclusions[4,5], the first cathodic peak relates to the two-electron reduction of O_2 to HO_2^-, and the second one is the consecutive reduction of HO_2^-, presumably to H_2O and OH^-. However, the second cathodic peak is less important due to its negative potential and is usually bypassed by catalyzing HO_2^- decomposition.

Figure 2 Cyclic voltammograms on MWNTs electrode at different scan rate



When the cyclic voltammetric experiments were performed in the potential range of 0.1–-0.3 V, a couple of redox peaks with good symmetry appear, as shown in **Figure 2**. The potential difference (ΔE_p) of the redox peaks at 2 mV/s is 0.029 V, which confirms that the first cathodic peak corresponds to the two-electron reduction of O_2 to HO_2^-. ΔE_p increases with the scan rate to 0.140 V at 50 mV/s. These indicate that the reduction of O_2 to HO_2^- is a quasi-reversible process on MWNTs electrode. But the first reduction of O_2 on graphite is irreversible even at low scan rate, and the anodic peak is ill-defined. These also reveal that MWNTs have higher electrocatalytic activity for ORR than graphite. The cathodic peak currents increase linearly with the scan rate in the range of 5–100 mV/s with a correlation coefficient of 0.99664. This indicates that the reduction of O_2 to HO_2^- is controlled by the adsorption[6]. In addition, the continuous CV experiments show that the peak current decreases with the number of cycles, which also confirms that the adsorptive process controls the reduction of O_2 to HO_2^- on MWNTs electrode in alkaline solution.

The preliminary results obtained from the above experiments show that compared with other carbon materials, MWNTs have much higher electrocatalytic activity for ORR in alkaline solution, and the reversibility of ORR is greatly improved on MWNTs. These suggest that MWNTs could be a kind of promising novel electrode material in fuel cells.

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