Electrochemical oxidation of sulfites by DWCNTs, MWCNTs, higher fullerenes and manganese

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Abstract. Different electrocatalysts were tested for oxidation of sulfites to sulfates, namely, manganese thin films deposited on fullerenes and carbon nanotubes. The results presented clearly show that electrodes containing HF’s (higher fullerenes), DWCNTs (double-wall carbon nanotubes) and manganese acetate are effective catalysts in S/O₂ fuel cells. HF’s and DWCNTs have high catalytic activity and can be employed as standalone catalysts. Manganese was deposited on DWCNTs, HF’s and fullerenes C₆₀/C₇₀ by a thermal process. The electrocatalysts were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical testing was carried out by plotting the E/V polarization curve. The polarization curves of the electrodes composed of pristine DWCNTs showed the lowest overpotentials.

1. Introduction

The present work considers the possibility of utilizing electrocatalysts, such as fullerenes and carbon nanotubes. The use of fullerenes and nanohorns as catalysts in fuel cells has been discussed in the past [1]. In this study we used ‘higher fullerenes’ (also termed ‘small-bandgap fullerenes’) as prepared by Diener and Alford by applying the carbon-arc method [2]. These were purchased together with manganese acetate from the Sigma Aldrich company. The fullerenes C₆₀/C₇₀, DWCNTs (double-wall carbon nanotubes) and MWCNTs (multiwall carbon nanotubes) were bought from SES Research, Huston, Texas. Vulcan XC-72 has been utilized as an electrocatalyst support in the past; this was acquired from the Cabot Corporation [3]. The first application of nanotubes in electrochemistry was reported by Britto [4], who, using bromoform as a binder, packed a paste of nanotubes into a glass tube in order to study the redox reaction of dopamine. The process was found to occur at a much faster rate than that observed using other catalytic surfaces. Later, Britto [5] and co-authors were the first to show that MWCNTs can be used for the electrocatalysis of oxygen. In the work reported here, our studies on DWCNTs found that they have superior electrochemical properties as compared to other fullerene-type materials. The role of carbon in fuel cells was studied in the past by Dicks [6] and recently reported in [7].

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Our aim was to develop a fuel cell for simultaneous purification of sulfates and nitrites. We studied novel catalysts incorporated in the electrode material and used half cells to oxidize SO$_3$ to SO$_4$.

The current work is part of a project entitled “New fuel cells based on chemical and microbial processes”, whose objective is exploring the possibility to decontaminate compounds containing sulfur and nitrogen.

2. Experimental

2.1. Experimental Setup

The catalytic properties of a set of anode electrodes were determined with the aid of a three-electrode cell (figure 1) while studying the process of oxidation of sulfites to sulfates in solution

$$\text{SO}_3^{2-} + 0.5\text{O}_2 \leftrightarrow \text{SO}_4^{2-}.$$ 

The solution was 1 M Na$_2$SO$_3$ + 18 g l$^{-1}$ NaCl as an additive electrolyte. The cell volume was 50 ml. The counter electrode was platinum foil and the reference electrode, a “Gaskatel” hydrogen electrode.

2.2. Measurements

2.2.1. XRD Measurements. The X-ray diffraction (XRD) patterns were recorded by a Philips diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.54178 \text{ Å}$, 40 kV, 30 mA) at a scanning rate of 2° min$^{-1}$. The intense diffraction peaks at 36.92°, 42.42 and 55.96° were referred to the characteristic peaks of $\gamma$-MnO$_2$, while the peaks at 17.94°, 28.78°, 49.0° and 60.44° were ascribed to $\alpha$-MnO$_2$ [8]. The XRD of manganese acetate as purchased from Sigma Aldrich and scanned in our lab is presented in figure 2. The XRD of the sample of manganese acetate with added polypyrrole is presented in figure 3. The XRD of MWCNTs as purchased from SES Research and scanned in our lab is presented in figure 4. The XRD of DWCNTs as purchased from SES Research and scanned in our lab is presented in figure 5. Shown in figure 6 is the XRD of higher fullerenes, DWCNTs and manganese acetate. Shown in figure 7 is the XRD of HFs and manganese acetate. Presented in figure 8 is the XRD of the d space for the sample comprised of HFs. Shown in figure 9 is the XRD of pristine HFs.

![Figure 1. A drawing of the three-electrode cell used in the experiments.](image)

![Figure 2. XRD of manganese acetate.](image)

![Figure 3. XRD of manganese acetate and polypyrrole.](image)
2.2.2. Catalyst synthesis. Small quantities of MWCNTs and of DWCNTs were each dispersed in 6 ml of distilled water in a sonic bath for 15 min. Next, 40 mg of manganese acetate and 60 mg of polypyrrole were slowly added to the aqueous suspensions. These ternary components were then baked at 180 °C for 12 h in a Teflon autoclave. Thus, MnO₂ particles were deposited on the carbon nanotube lattice structures with polypyrrole binding. The DWCNTs used clearly maximize the electroactive surface area of the catalyst. The porous structure of the catalyst consisting of DWCNTs and manganese was observed by SEM and is shown in figure 10. The catalyst consisting of MWCNTs and manganese was observed by a SEM and is shown in figure 11.
Several partial polarization curve measurements were performed to characterize the DWCNTs, MWCNTs and higher fullerenes with deposited MnO$_2$ particles and polypyrrole binder in different ratios.

**Figure 10.** SEM images of the catalyst consisting of DWCNTs and manganese acetate.

**Figure 11.** SEM images of the catalyst consisting of MWCNTs and manganese acetate.

### 2.2.3 Electrode preparation

Several sample electrodes with geometrical area of 1 cm$^2$ were prepared by depositing the sample catalyst on both sides of the electrode followed by pressing and heating. All electrodes were made from a mixture of the catalyst and teflonized carbon black [60 mg cm$^{-2}$ Vulcan XC-72 (35% Teflon)] [9]. The mixture was pressed at 300 kg cm$^{-2}$ on both sides of a stainless steel current collector at 150 °C. The catalysts studied were as follows: a NORIT & manganese oxide catalyst; HFs, DWCNTs and manganese oxide; HFs and manganese oxide. We used higher fullerenes and DWCNTs to maximize the electro-active surface area of the catalyst.

In the course of the experiment, several electrodes from each catalytic mass were prepared. The volt/ampere characteristic of each electrode was measured several times and the average values calculated.

The electrodes contained the following catalysts: 1 – 100 mg DWCNTs; 2 – 60 mg manganese acetate; 3 – 100 mg higher fullerenes; 4 – 100 mg MWCNTs; 5 – 120 mg fullerenes C$_{60}$/C$_{70}$; 6 – 20 mg C$_{60}$/C$_{70}$ + 60 mg manganese acetate + 40 mg polypyrrole; 7 – 3 mg MWCNTs + 37 mg manganese acetate + 57 mg polypyrrole; 8 – 3 mg DWCNTs + 37 mg manganese acetate + 57 mg polypyrrole.
2.2.4. Polarization curves. As it is seen, the polarization curves of the pristine DWCNTs samples as presented in figures 12 and 13 are the most advantageous, yielding the lowest overpotentials at the respective current densities. The DWCNTs electrode as compared to the MWCNTs electrode shows a 300-mV decrease in overpotential at $i = 10$ mA cm$^{-2}$.

3. Results and discussions

The multiwall carbon nanotubes (MWCNTs) comprise many graphene layers decreasing in diameter for each successive layer. The double-wall carbon nano tubes (DWCNTs), on the other hand, consist of only a few layers that are hollow and larger in diameter. It was argued in the past that the inner tube formation of the DWCNTs structure could be very defective, containing pentagons, heptagons and octagons [10]. In catalysis, a large number of active sites are sought in order to optimize the process. The rolled-up carbon networks of DWCNTs clearly would play a major role in the synthesis of more effective catalysts. We found that the electrode catalyst sample composed of DWCNTs was the most effective, yielding the lowest overpotentials at the respective current densities for the polarization curves. Therefore, it can be expected that this catalyst will exhibit the highest mass activity in the process of oxidation of sulfites to sulfates. Our recent study [11] showed that it is possible to implement electrochemically reduction of nitrates and oxidation of sulfite by means of electrodes containing DWCNTs and HFs.

4. Conclusions

The results presented show that higher fullerenes and DWCNTs have high catalytic activity on their own, i.e. without any deposited traditional catalysts such as manganese, and can be employed as stand-alone catalysts. Due to their large cation exchange capacity, strong adsorption ability, huge surface area and suitable electronic properties, DWCNTs exhibit high catalytic activity, as clearly evidenced by the polarization curve plots.

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