

Electrocatalysts for sulphur ions oxidation based on DWCNTs, MWCNTs, higher fullerenes and manganese

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The possibility of utilizing electrocatalysts such as manganese deposited on fullerenes and carbon nanotubes is considered. These have been studied for oxidation of SO₃ to SO₄ and reduction of NO₃ to NO₂ and N₂, thus creating a SO_x/NO_x fuel cell suitable for cleaning the environment while generating electrical energy. Mn has been deposited on Double Wall Carbon Nanotubes (DWCNTs) and Higher Fullerenes (HFs) from manganese acetate by thermal treatment and/or freeze drying. The electrocatalysts were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrochemical testing has been done by cyclic voltammetry and E/V polarization curve plotting. The freeze dried electrodes comprised of Mn/HFs are found to yield the lowest overpotentials at sulfite oxidation, while the electrodes comprised of Mn/HFs/DWCNTs yield the highest activity at nitrite reduction. The results presented clearly show, that electrodes containing HFs, DWCNTs and manganese oxides are effective catalysts in SO_x/NO_x fuel cells.

Key words: electrocatalyst, DWCNTs, MWCNTs, C₆₀/C₇₀, higher fullerenes, manganese acetate.

INTRODUCTION

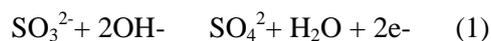
The current work considers the possibility of utilizing electrocatalysts such as fullerenes and carbon nanotubes. The possibility of utilizing fullerenes as catalysts in fuel cells has been discussed in the past [1]. Multiwall Carbon Nanotubes (MWCNTs) are comprised of many graphene layers decreasing in diameter while curved in successive layers. Double Wall Carbon Nano Tubes (DWCNTs) on the other hand are comprised of only a few layers, but larger in diameter. It has been argued in the past that the inner tube formation of the structure of open end DWCNTs can be very defective, containing pentagons, heptagons and octagons [2].

Higher fullerenes include the fairly stable species C₇₄, C₇₈, C₈₀, C₈₂, C₈₄, C₈₆, C₈₈, C₉₀, C₉₂, C₉₄, C₉₆, C₉₈, C₁₀₀. The electro catalytic properties of higher fullerenes have been studied and were deemed more promising than C₆₀ as catalysts, though their catalytic rate constants were found to be smaller [3]. An interesting new development characteristic for fullerenes and nanotubes is their ability to reversibly modify specific chemical

reactions [4]. Applied in this study is a method to fabricate the electro-catalyst for the electrodes using a lyophilization process [5]. Via the process of lyophilization nitrogen atoms are introduced into the catalyst and these appear to play a key role as active sites in oxygen reduction [6]. Fuel cells driven by sulfides that oxidize sulfides to sulfates removing the toxic pollutant, while recovering the energy stored, have been fabricated in the past [7].

In our work we make use of the electro-catalytic reduction capability of fullerenes to aid the oxidation process in the conversion of sulfites to sulfates as described in [8]. The aim of the current study is to develop a fuel cell for the simultaneous purification of sulfates and nitrites. We study novel catalysts incorporated in the electrode material and use half cells to oxidize SO₃ to SO₄.

In an oxygen saturated water suspension, SO₃²⁻ ions, in the presence of TiO₂, ZnO and Fe₂O₃ together with hydrogen peroxide, have been shown to convert to SO₄²⁻ ions [9, 10]:



The desulfurization reaction via Mn is:



An intermediate reaction of sulfites to sulphates is:



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The current work is part of a project entitled "New fuel cells based on chemical and microbial processes" that considers the possibility to decontaminate compounds containing sulphur and nitrogen.

EXPERIMENTAL

Catalyst synthesis

In this study we have used 'Higher Fullerenes' as fabricated by Diener & Alford by applying the carbon arc method, also termed 'Small-bandgap fullerenes' [11]. These were purchased together with manganese acetate from the Sigma Aldrich company. The fullerenes C_{60}/C_{70} , DWCNTs and Multi Wall Carbon Nanotubes (MWCNTs) 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 [12].

Manganese has been deposited on fullerenes C_{60}/C_{70} , HFs, DWCNTs and MWCNTs by two methods, by thermal treatment and by lyophilization. The catalyst fabricated via thermal treatment was prepared as follows: A small quantity of DWCNTs, then MWCNTs, C_{60}/C_{70} and HFs were dispersed in 6 ml of distilled water in a sonic bath for 15 minutes. Next, 40 mg of manganese acetate and 60 mg of polypyrrole were slowly added to the aqueous suspension. These ternary components were then baked at 180°C for 12h in a Teflon autoclave. Thus, MnO_2 is deposited on the carbon nanotube lattice structures with polypyrrole binding.

The process of lyophilization was applied in order to overcome catalyst agglomeration, but also helps bond nitrogen atoms to the fullerenes and nanotubes. A small quantity of HFs was dispersed in 6 ml of distilled water in a sonic bath for 15 minutes. Next, (20-40) mg of manganese acetate and (20-100) mg of polypyrrole were slowly added to the aqueous suspension. These ternary components were then baked at 180°C for 12h in a Teflon autoclave. Thus, MnO_2 was deposited on the higher fullerene lattice structures with polypyrrole binding. The suspension was finally dehydrated by freeze-drying in a lyophilizer yielding a complex structure. Lyophilization works by freezing the processed material, in this case by pouring liquid nitrogen on the sample thinly spread out on aluminum bowls, specially made for this purpose. Then, after reducing the pressure in the work chamber of the lyophilizer and heating the frozen water, the material sublimates and hence the samples are freeze-dried. Material cooling below its triple point ensures that sublimation occurs, thus

preserving the physical characteristics of the processed material.

The catalyst building up electrode No. 1 was synthesized as follows: 3 mg of higher fullerenes were added to 6 ml of distilled water and processed in an ultrasonic bath for 15 minutes. Between 20 and 40 mg of manganese acetate and 20 to 100 mg of polypyrrole were then slowly added to the water suspension. The catalyst was then processed by lyophilization. The catalyst building up electrode 2 was synthesized as follows: 8 mg of C_{60}/C_{70} fullerenes were dispersed in distilled water and processed in an ultrasonic bath for 30 minutes. 40mg of manganese acetate and 60 mg of polypyrrole were then slowly added to the suspension. In consequence the mixture was baked at 180°C for 23 hours in a Teflon autoclave. The catalyst was then processed by lyophilization.

Electrode preparation

Different electrodes were prepared with the aid of the immersed type method by deposition of the sample catalyst on both sides of the electrode followed by pressing and heating. The electrodes studied have a geometrical area of 1 cm². All the electrodes were prepared from a mixture of the catalyst and teflonized carbon blacks [60 mg/cm² Vulcan XC-72 (35% Teflon)] as a binder [13]. The mixture was pressed on to both sides of a stainless steel current collector at 150°C and pressed at 300kg/cm². Different catalysts were studied: NORIT & manganese oxide; HFs, DWCNTs & manganese oxide; HFs & manganese oxide. We used HFs and DWCNTs to maximize the electroactive 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 multiple times and the average values evaluated.

The electrodes incorporate the following catalysts:

- 1 (lyophilized) [content: 7 mg of (37 mg of manganese acetate, 57 mg of polypyrrole, 1.7 mg of HFs), pressed at 150 atm.);
- 2 (lyophilized) [content: 7 mg of (40 mg of manganese acetate, 60mg of polypyrrole, 8 mg of fullerenes C_{60}/C_{70}), pressed at 150 atm.];
- 3 (lyophilized) [content: 7 mg of (40 mg of manganese acetate, 60 mg of polypyrrole, 8 mg of NORIT), pressed at 150 atm.];
- 4 (non-lyophilized) [content: 100 mg of DWCNTs, pressed at 300°C and 300 kg/cm²];
- 5 (non-lyophilized) [content: 100 mg of MWCNTs, pressed at 300°C and 300 kg/cm²];

- 6 (non-lyophilized) [content: 120 mg of fullerenes C₆₀/C₇₀, pressed at 300 kg/cm²];
- 7 (non-lyophilized) [content: 100 mg of higher fullerenes, pressed at 300 kg/cm²];
- 8 (non-lyophilized) [content: 3 mg DWCNTs + 37 mg manganese acetate + 57 mg polypyrrole];
- 9 (non-lyophilized) [content: 3 mg MWCNTs + 37 mg manganese acetate + 57 mg polypyrrole];
- 10 (non-lyophilized): [20 mg][content: C₆₀/C₇₀ [3 mg] + 37 mg manganese acetate + 57 mg polypyrrole];
- 11 (non-lyophilized): [15 mg][content: C₆₀/C₇₀ [3 mg] + 37 mg manganese acetate + 57 mg polypyrrole];
- 12 (lyophilized) [content: 7 mg of (40 mg of manganese acetate, 60 mg of polypyrrole, 11 mg of HFs, 11 mg of DWCNTs), pressed at 150°C and 300 atm., for 5 minutes].

Electrochemical experimental set up

The catalytic properties of anode electrodes were determined with the aid of a three electrode cell Fig. 1. The process of oxidation of sulfites to sulfates in solution was studied. The solution was 1M Na₂SO₃ + 18g/l NaCl. The NaCl is an additive electrolyte. The cell volume was 50 ml. The counter electrode was platinum foil. The reference electrode was a "Gaskatel" hydrogen electrode.

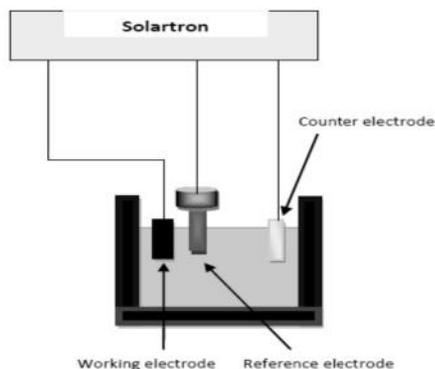


Fig. 1. Drawing of the three electrode cell used in the experiments.

The electrochemical testing methods used were cyclic voltammetry and E/V curve plotting.

RESULTS AND DISCUSSION

Physical measurements

X-ray diffraction (XRD) patterns were recorded utilizing a Philips diffractometer using CuK radiation (λ = 1.54178 Å, 40 kV and 30 mA) with a scanning rate of 2 min⁻¹. The intensive diffraction peaks at 36.92, 42.42 and 55.96 should

be assigned to the characteristic peaks for -MnO₂, while the peaks at 17.94, 28.78, 49.0 and 60.44, respectively, should be ascribed to the peaks for -MnO [14]. The XRD of manganese acetate as purchased from Sigma Aldrich and scanned in our lab is presented in Fig. 2. The XRD of the sample of manganese acetate with added polypyrrole and scanned in our lab is presented in Fig. 3.

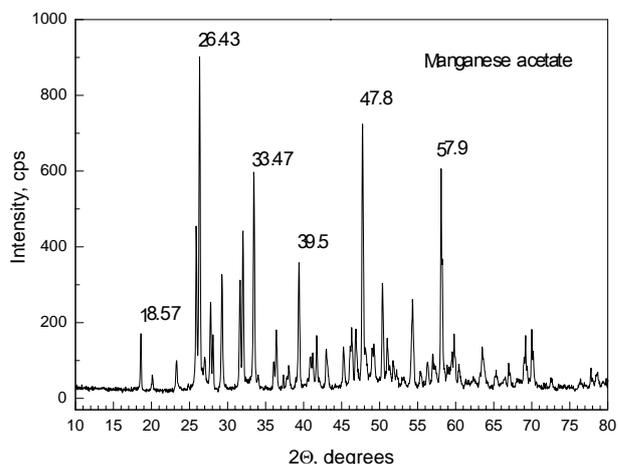


Fig. 2. XRD of manganese acetate.

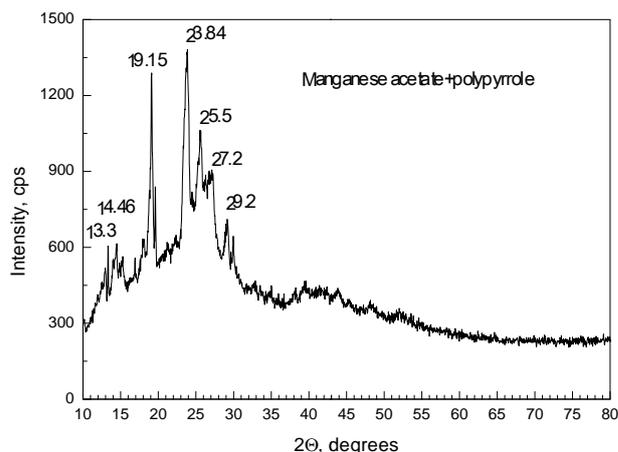


Fig. 3. XRD of Manganese acetate and polypyrrole.

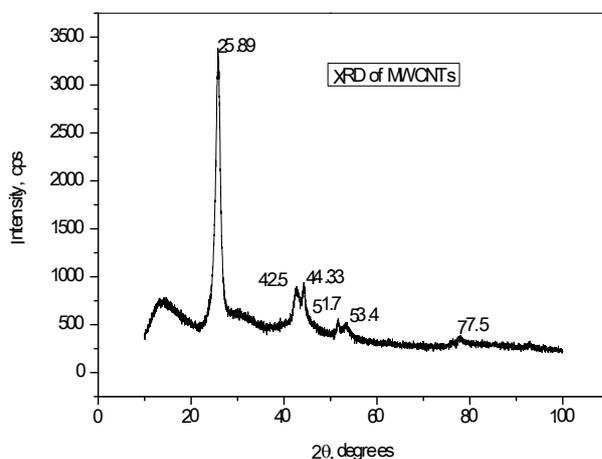


Fig. 4. XRD of MWCNTs.

The XRD of MWCNTs as purchased from SES Research and scanned in our lab is presented in Fig. 4. The XRD of DWCNTs as purchased from SES Research and scanned in our lab is presented in Fig. 5. Shown in Fig. 6 is the XRD of HF, DWCNTs and manganese acetate. Shown in Fig. 7 is the XRD of HF and manganese acetate. Presented in Fig. 8 is the XRD of the d space for the sample comprised of HF and manganese acetate.

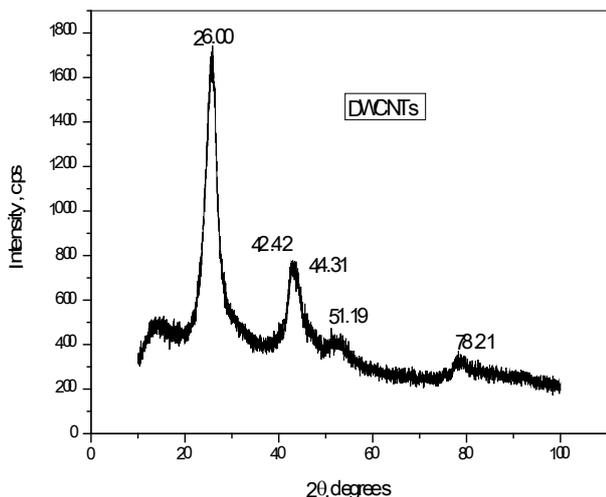


Fig. 5. XRD of DWCNTs.

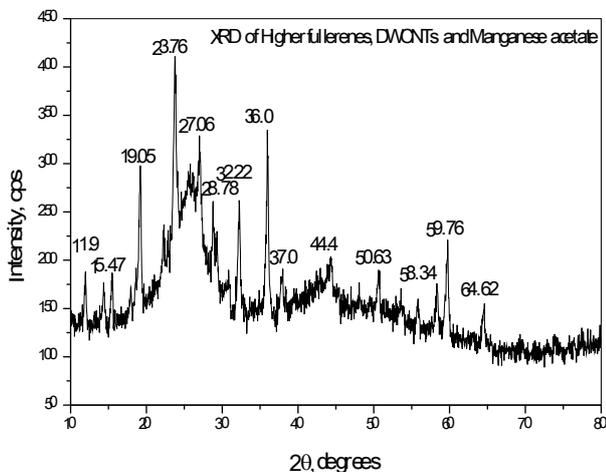


Fig. 6. XRD of HF, DWCNTs and manganese acetate.

Presented in Fig. 9 is the XRD of the HF purchased from Sigma Aldrich and scanned in our lab, numerous broad peaks can be observed characteristic of a wide range of higher fullerene species. The diffraction peak at around 19 degrees on Fig. 3, Fig. 6, Fig. 7 and Fig. 9 is clearly due to carbon especially as it is most intense on Fig. 9 when characterizing HF.

In the photographs made with a SEM presented in Fig. 10 we can observe the freeze dried catalyst containing HF, fullerenes C₆₀/C₇₀ and manganese

oxide, respectively. It is clear that the catalyst with manganese oxide on HF has a higher surface area.

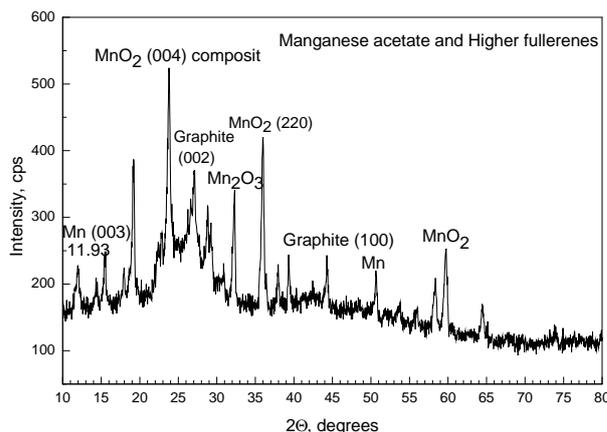


Fig. 7. XRD of HF and manganese acetate.

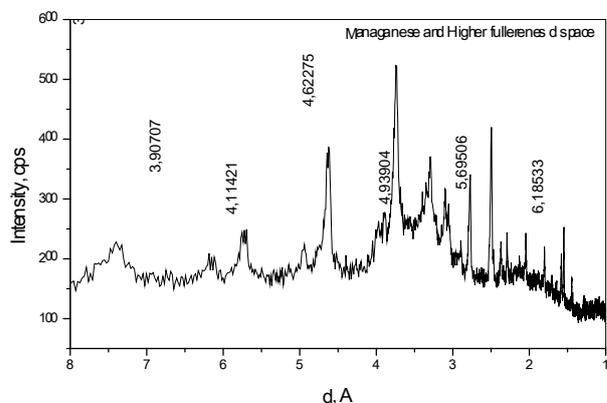


Fig. 8. XRD study of the d space for the sample comprised of HF and manganese acetate.

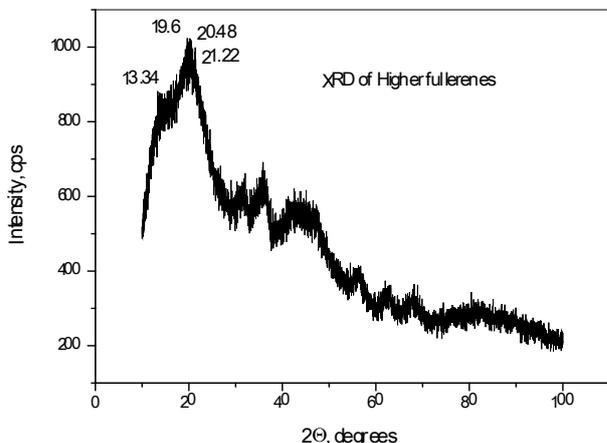


Fig. 9. XRD of HF.

In the photographs made with a SEM presented in Fig. 11 we can observe the thermally treated catalyst containing DWCNTs, MWCNTs and manganese oxide, respectively. The closed cap ends of both MWCNTs and DWCNTs are comprised of numerous pentagons and hence can be termed as macro fullerenes. At the same time as can be observed from the photographs shown in Fig. 11 the DWCNTs are larger in diameter in comparison with the MWCNTs. Some DWCNTs are also open-

ended which allows for the oxidation of sulphite to sulphate to take place within the nanotube structures.

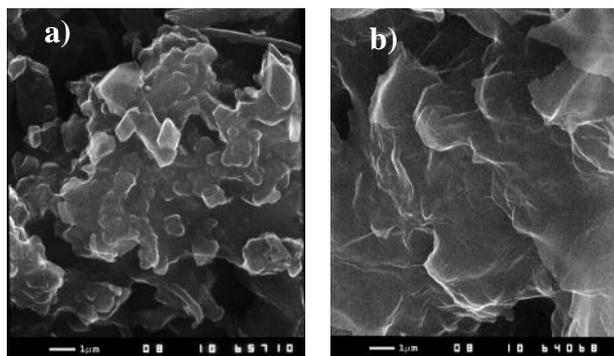


Fig. 10. SEM photographs of the catalyst comprised of lyophilized catalyst, poly pyrrol and manganese oxide; a) containing HF's and b) containing fullerenes C₆₀/C₇₀.

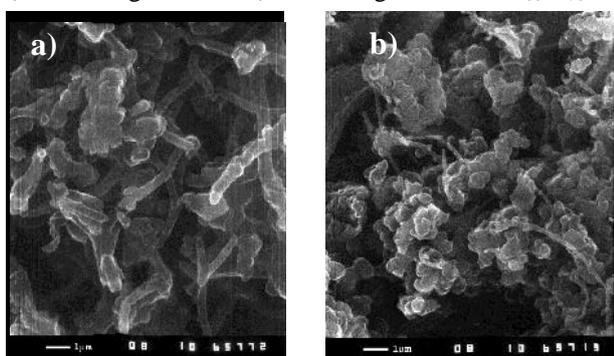
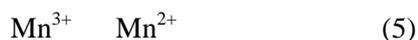
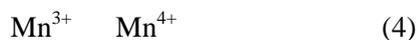


Fig. 11. Photographs made with a SEM of non-lyophilized catalyst and manganese acetate comprised of: a) DWCNTs and b) MWCNTs.

Electrochemical results

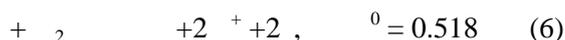
Cyclic voltammetry: Cyclic voltammetry plots were made of lyophilized and non-lyophilized catalysts. All the electrodes had a surface area of 1 cm² and were fabricated by covering both sides of a stainless steel mesh used as a current collector. The electrodes are compressed at T=300 °C and 300kg/cm².

This curve has been recorded for comparison only. The probable reaction as shown in Fig. 12 is:



with peaks 1 and 2 for the oxidation/reduction of Mn equation (4) at around 500 – 800 mV and potential plateaus for reduction of Mn compounds reaction (5) at 190 mV that correspond (peak 3) to the data as cited in the literature [15].

The fabricated electrodes correspond to number 7 from the catalysts list. A process of carbon oxidation is clearly evident at E=500 mV in Fig. 13 as follows from [16]. These researchers observe that the oxidation of carbons takes place in accordance with equation 6.



The fabricated electrodes correspond to number 1 from the catalysts list. In Fig. 14 we can observe the possible reactions 4 and 5 that are due to manganese.

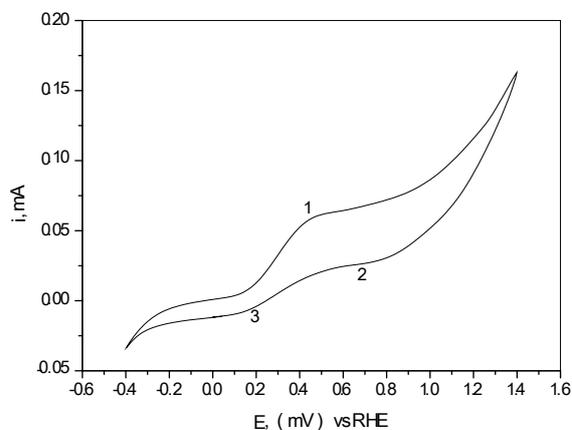


Fig. 12. Cyclic voltammogram of the electrode with MnO₂ obtained chemically; 100 mg of MnO₂ onto 35 % teflonized Vulcan XC-72, pressed at 300kg/cm². Electrolyte: 1 Na₂SO₃ + 18g.l⁻¹ NaCl, t = 20°. Scan rate 20 mV/s.

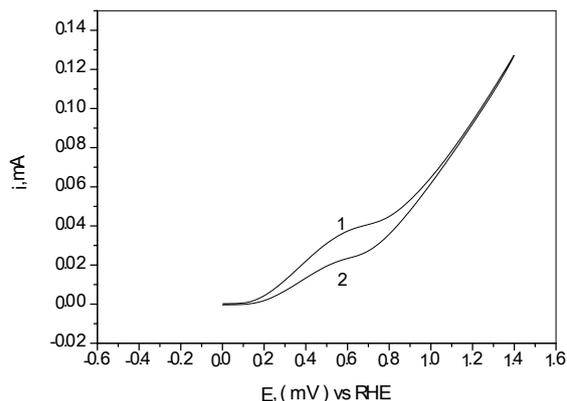


Fig. 13. Cyclic voltammogram of the electrode with non-lyophilized catalytic mass content: 100mg HF's onto 35 % teflonized Vulcan XC-72. Pressed at 300kg/cm². Electrolyte: 1 Na₂SO₃ + 18g.l⁻¹ NaCl, t = 20°C. Scan speed 20mV/s.

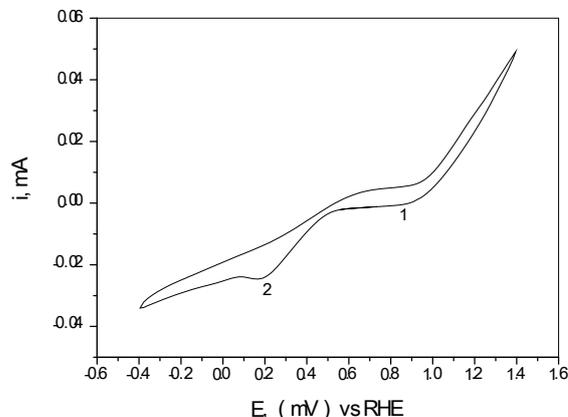


Fig. 14. The cyclic voltammogram of the lyophilized catalytic mass content: 7 mg of (37 mg - manganese acetate, 57 mg polypyrrol, 1.7 mg higher fullerenes). Scan rate 50 mV/s at room temperature in 1 M Na₂SO₃.

The electrodes fabricated correspond to number 2 from the catalysts list. In Fig. 15 we observe the peaks that correspond to reaction 4 due to the oxidation and reduction of manganese.

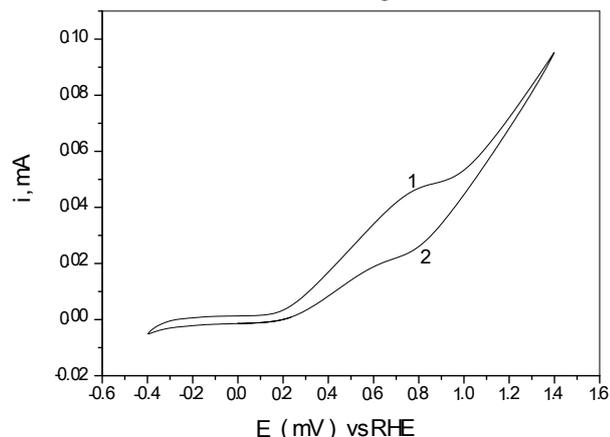


Fig. 15. The cyclic voltammogram of the lyophilized catalytic mass content: 7 mg of (40 mg - manganese acetate, 60 mg polypyrrole, 8 mg fullerenes C_{60}/C_{70} + (60 mg Vulcan 72 + 35% Teflon), pressed at 150 atm.]. Scan rate 20 mV/s at room temperature in 1 M Na_2SO_3 .

Polarization curves analysis: A number of partial polarization curve measurements were made characterizing the incorporated HFs, deposited MnO_2 and polypyrrole binder in different ratios. As observed in Fig. 16 the electrodes 7 with incorporated pristine HFs exhibit better characteristics than electrodes 6, incorporating pristine C_{60}/C_{70} . One likely reason for the better characteristics observed for the electrodes incorporating HFs is probably the fact that these have a higher surface area (see, Fig. 10) and a greater number of pentagons within their structure.

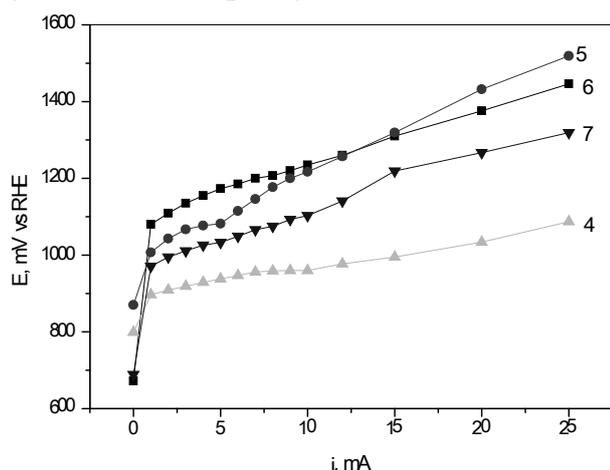


Fig. 16. Comparison of the polarization curves of electrodes incorporating non-lyophilized catalysts: 4 - DWCNTs, 7 - HFs, 5 - MWCNTs, 6 - C_{60}/C_{70} .

When comparing the polarization curves of electrodes 4, incorporating pristine DWCNTs and electrodes 5, incorporating MWCNTs it is obvious

that DWCNTs exhibit better characteristics. Judging from the photographs in Fig. 11 it is clear that the DWCNTs are greater in diameter and have a larger surface area.

Straight line Tafel plots were taken of the polarization curves presented in Fig. 16 for the electrodes incorporating DWCNTs and C_{60}/C_{70} . For C_{60}/C_{70} fullerenes the value of b was 81mV/dec. for DWCNTs $b = 37$ mV/dec., this confirmed it's higher catalytic activity (Fig.17).

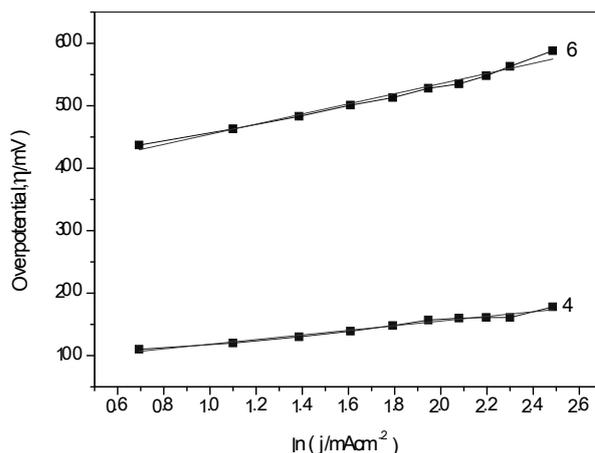


Fig. 17. Tafel plots for the electrodes comprised of: 6 - fullerenes C_{60}/C_{70} - 81mV/dec and 4 - DWCNTs - 37 mV/dec.

Shown in Fig. 18 are the polarization curves of the electrodes prepared from lyophilized and non-lyophilized catalysts. The lowest overpotential is observed for the electrodes containing a lyophilized catalyst sample + HFs (electrodes 1). With slightly higher overpotentials and therefore with inferior characteristics are the electrodes containing the most common fullerenes C_{60}/C_{70} (electrodes 2). Electrodes (electrodes 3) with a traditional carbon based catalyst, NORIT, were also fabricated using the lyophilization process and manganese acetate included. As shown in Fig. 18 these have inferior characteristics to both electrodes 1 and electrodes 2 incorporating HFs and C_{60}/C_{70} , respectively. The quantity of manganese acetate used to fabricate all three electrodes was the same, therefore, the superior performance of electrodes 1 can only be due to the differences in nature of the respective carbon structures. From the lyophilized catalysts the electrodes incorporating HFs and manganese oxide were found to be the most advantageous, yielding the lowest overpotentials at the respective current densities for the polarization curves (electrodes 1 in Fig. 18).

As shown in Fig. 19 electrodes 8 and 9 with incorporated DWCNTs, MWCNTs and manganese acetate have inferior behavior as compared to

electrodes 4, the electrodes incorporating pristine DWCNTs.

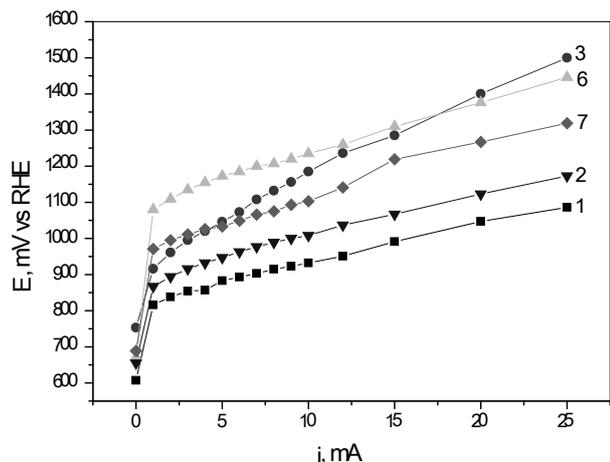


Fig. 18. Polarization curves of the electrodes prepared from lyophilized catalysts (at 150° and P = 0.3 mbar) electrodes 1, electrodes 2, electrodes 3 and non-lyophilized catalysts electrodes 6 and electrodes 7. Electrolyte: 1M Na₂SO₃ + 18g.l⁻¹NaCl, t = 20°C.

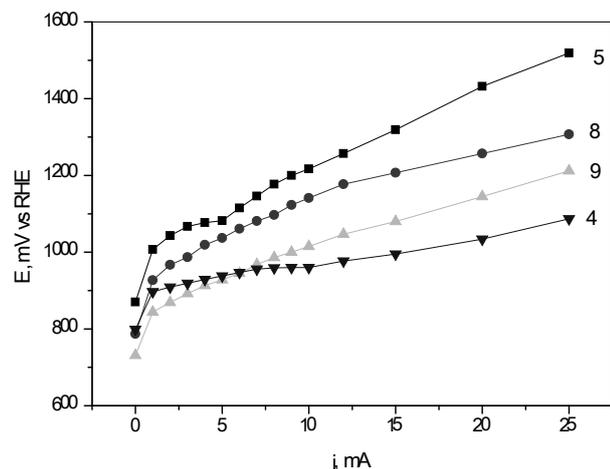


Fig. 19. Polarization curves of electrodes containing pristine DWCNTs - 4 and MWCNTs - 5, as well as electrodes incorporating thermally treated manganese acetate: 8 - [DWCNTs + manganese acetate], 9 - [MWCNTs + manganese acetate]. The electrodes were pressed at 300 kg/cm². The electrolyte was 1 M Na₂SO₃ + 18g.l⁻¹ NaCl, t = 20°C.

On the other hand the comparison between the electrodes incorporating pristine MWCNTs - 5 and DWCNTs - 4 shows that DWCNTs manifest superior catalytic characteristics. In addition we should note, that the much larger quantity of pristine DWCNTs incorporated in electrodes 4 clearly outweighs in terms of its catalytic activity the presence of manganese in electrodes 8 and 9, thus yielding lower overpotentials.

The catalysts prepared were investigated not only for the oxidation of SO₃ to SO₄, but also for the reduction of nitrates:



The qualitative analytical measurements show, that reactions (7) yield only NO₂ while N₂ has not been detected [17]. The results presented in Fig. 20 confirm that a reduction is manifest and therefore it is clearly possible to electrochemically purify nitrite polluted aquatic environments.

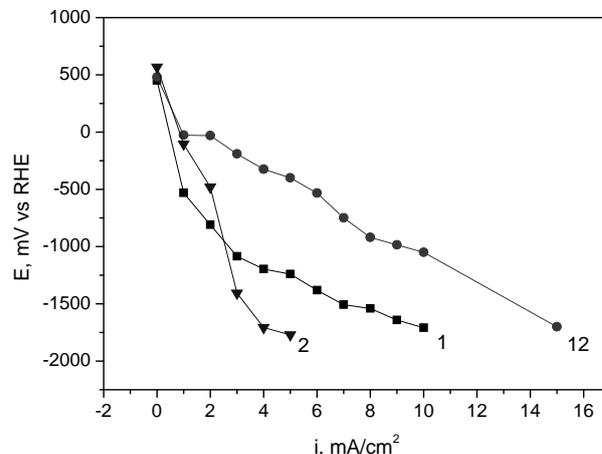


Fig. 20. Polarization curves of the electrodes comprised of lyophilized catalysts: 1, 2 and 12. The electrolyte at reduction was 0.1 M KNO₃, t = 20°C.

A comparison of the reduction and oxidation curves (Fig. 21) shows that the reduction curves are more negative, in other words at this stage it is not possible to build a fuel cell. However, in the future by utilizing microbes to increase the reaction conversion rate it should be possible to build a S/N based fuel cell.

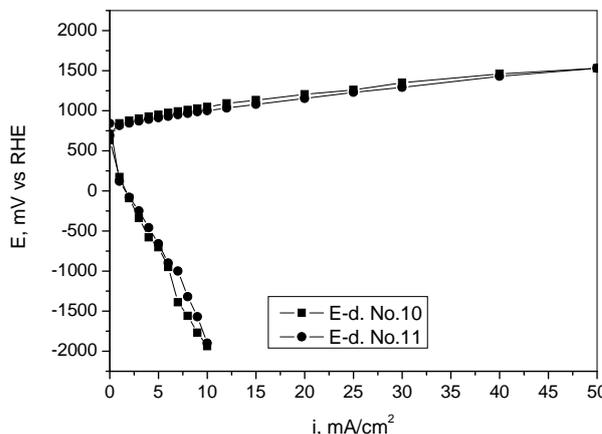


Fig. 21. Polarization curves of electrodes with catalysts prepared differently and measured at oxidation and reduction: electrodes 10 [with a pressure of 100 kg applied at room temperature], electrodes 11 [with a pressure of 300 atm. applied, while heated to 150° for 5 minutes]. The electrolyte at oxidation was 1 M Na₂SO₃ + 18g.l⁻¹ NaCl, while at reduction it was 0.1 M KNO₃, t = 20°C.

CONCLUSIONS

Higher fullerenes, DWCNTs, MWCNTs and C₆₀/C₇₀ appear to play a major role in the synthesis

of more effective catalysts. A diverse catalyst surface with well dispersed manganese particles leads to improved catalyst characteristics. The lyophilized material containing only higher fullerenes and manganese oxide was shown to have the highest activity in the oxidation of SO₃. The catalyst with a content combination of DWCNTs, higher fullerenes and manganese oxide yields the highest activity in the reduction of nitrates. The results presented confirm that it is possible to electrochemically purify nitrite polluted aquatic environments utilizing electro-catalysts incorporating fullerenes and nanotubes. At this stage, because the catalytic activity is not high enough and there are very high diffusion limitations of both reactions it is not possible to build a S/N based fuel cell. However, in the future by utilizing microbes to increase the reaction conversion rate of the catalysts studied it should be possible to successfully create a fuel cell such as the one outlined above.

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SO _x /NO _x	SO ₃ SO ₄	NO ₃ NO ₂ N ₂ ,	
	(DWCNTs)	(HFs)	/ (SEM)
	(XRD).		n/HFs
n/HFs/DWCNTs	E/V .		
		SO _x /NO _x	