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Physical and Electrochemical Characterization of Nsutite

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Abstract

Manganese oxides are of interest as, among a number of other applications, supercapacitor materials for energy storage systems. Nsutite, a naturally occurring Manganese Oxide was studied as a possible high-volume source of materials for supercapacitor applications. X-ray diffraction and thermal analysis (DSC/TGA) measurements were carried out to characterize its physical properties, and Cyclic Voltametry and galvanostatic charge-discharge measurements were carried out to obtain its electrochemical properties. The XRD and thermal results support transitions of nsutite, upon heating which were attributed to conversion to MnO_2, and to Mn_2O_3 and eventually to Mn_3O_4. The electrochemical results of the as mined material show supercapacitance behaviour, suggesting that nsutite, with some heat processing, is to be a promising high-volume source of manganese oxides for supercapacitor applications.

Keywords

Nsutite, Manganese Oxides, Supercapacitors, Cyclic Voltammetry, Specific Capacitance

1. Introduction

Nsutite is a naturally occurring Manganese Oxide of the composition $Mn^{4+}_{1-x}Mn^{2+}_{x}O_{2-2x}(OH)_{2x}$ where x = 0.06 - 0.07 [1]. In recent years, manganese oxides have been the subject of numerous studies because of their applications in energy storage systems, as catalysts for specific applications, as purification agents in drinking water, and the steel industry. In addition to battery applications, manganese oxides have been found to be promising in electrochemical supercapaci-

tors [2] [3] [4] [5]. In this paper, we performed physical, thermal, and electrochemical characterization of nsutite material for possible supercapacitor applications.

2. Experimental

We acquired samples of various grades of nsutite materials from the Ghana Manganese Company, Nsuta, Ghana. Nsutite is named after the village, Nsuta, where the material was first discovered.

Physical characterizations of the acquired nsutite material were carried out by powder X-ray diffraction (XRD) studies using a Rigaku Mini flex-II diffractometer. The thermal analysis, (Differential Scanning Calorimetry/Thermogravimetry) was carried out using a TA Instruments STA Q600.

The electrochemical properties of nsutite were studied using a Squidstat plus potentiostat (Admiral Instruments, USA). The electrochemical measurements were conducted in standard three-electrode configuration, where a platinum wire/foil and an Ag/AgCl electrode were used as a counter and a reference electrode respectively. Slurries of nsutite coated onto nickel foam were used as working electrode. All the electrochemical measurements were performed in 1 M Na_2SO_4 solution. The slurries were prepared by mixing 80 wt% of the nsutite, 10 wt% of carbon black and 10 wt% of Polytetrafluoroethylene (PTFE) binder, using ethanol as a solvent. After thoroughly mixing, the slurry was applied to a pre-cleaned nickel electrode. The mass loading of the material was obtained by measuring the mass of the nickel foam before and after electrode preparation, using an analytical balance. Electrochemical properties of the synthesized samples were investigated using cyclic voltammetry (CV) and galvanostatic charge-discharge studies.

3. Results

Figure 1 shows the XRD patterns of nsutite annealed at three temperatures, 350˚C, 500˚C and 650˚C. The results support reports in the literature of the various transitions as the material is heated [6].

From **Figure 2**, the cyclic voltammogram of nsutite materials showed capacitive behaviour at various scan rates from 20 mV/s to 200 mV/s. **Figure 2** also shows the rectangular shaped cyclic voltammogram typical of pseudocapacitive oxides [7], indicating that nsutite has pseudocapacitive properties. The specific capacitance of the samples was calculated using the following equation:

$$C_{sp} = \int I \cdot \mathrm{d}V / \Delta V \times \vartheta \times m \tag{1}$$

where, I is the current, ΔV is the potential window, ϑ represents the scan rate and m is the mass of the samples. The specific capacitance of nsutite obtained from the cyclic voltammetry studies is given in **Table 1**.

The specific capacitance of nsutite materials electrodes was calculated from the galvanostatic charge-discharge measurements, using the following equation:

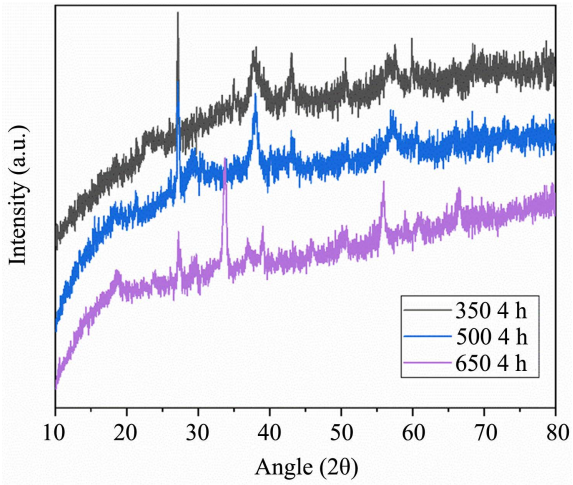

Figure 1. X-ray diffraction pattern of nsutite , annealed at various temperatures.

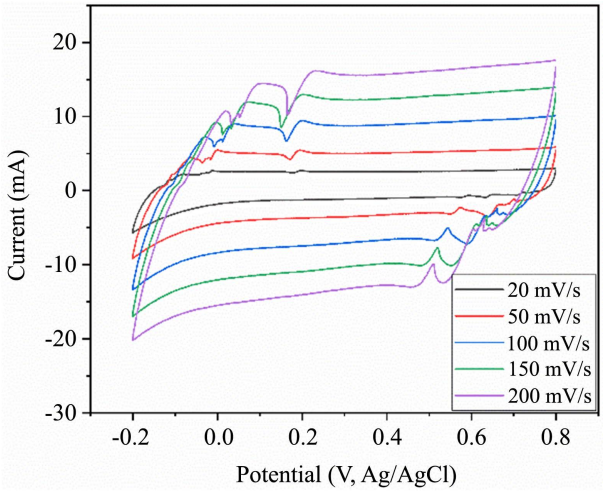

Figure 2. Cyclic voltammogram of nsutite at various scan rate.

Table 1. Specific capacitance of nsutite from cyclic voltammetry studies.

S. No.	Scan rate (mV/s)	Specific capacitance (F/g)
1	20	19.29
2	50	16.70
3	100	14.57
4	150	13.19
5	200	12.10

$$C_{sp} = I \times \Delta t / \Delta V \times m \tag{2}$$

where, I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window (V) and m is the mass (g) of the samples. Figure 3 represents the galvanostatic charge discharge of nsutite electrodes and the specific capacitance of nsutite at various current densities is given in Table 2.

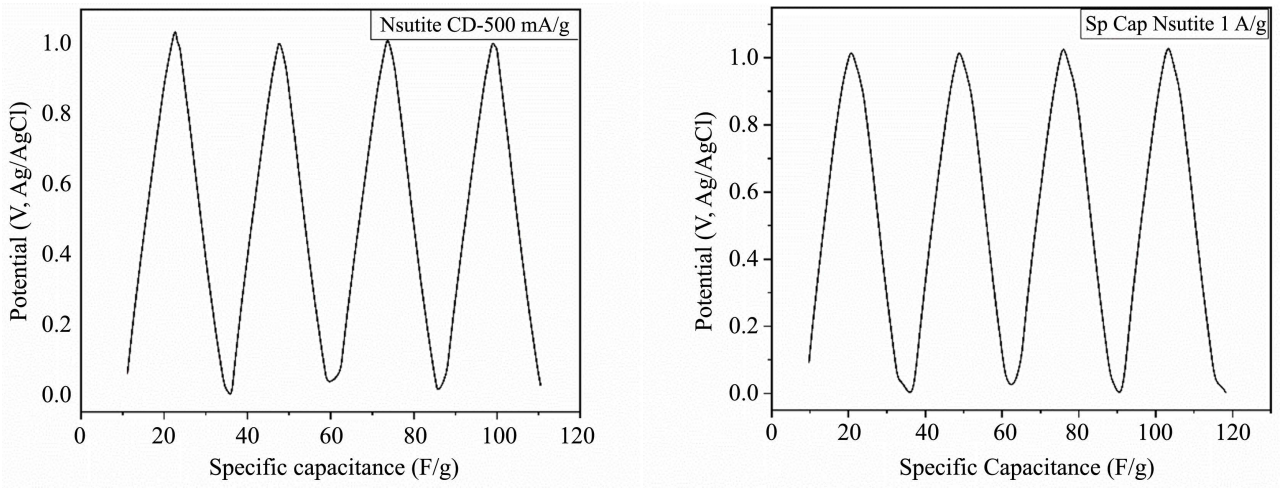

Figure 3. Galvanostatic charge discharge of nsutite.

Table 2. Specific capacitance of nsutite at various current densities.

No. of cycle	Specific capacitance (F/g) at current density 500 mA/g	Specific capacitance (F/g) at current density 1 A/g
1	13.03	15.08
2	11.5	14.16
3	14.5	14.276
4	11.5	15.107
Average Specific Capacitance	12.63	14.65

It can be seen from Table 2 that average specific capacitance of nsutite materials was found to be as 12.63 F/g and 14.65 F/g at current density of 500 mA/g and 1 A/g, respectively. It was reported earlier that the specific capacitance of pure MnO_2 was 300 F/g and 290 F/g at current density of 500 mA/g, and 1 A/g, respectively [8]. The low specific capacitance of nsutite materials compared to pure MnO_2 can be ascribed to the structural report that nsutite is not a pure MnO_2 material and may contain other manganese oxides [9] and impurities present in the nsutite materials.

Figure 4 shows the differential scanning calorimetry (DSC) and Thermogravimetric Analysis (TGA) of nsutite. The DSC and TGA results show three transitions between 200˚C and 1000˚C. The first transition at 351˚C and the corresponding mass loss can be attributed to loss of physiosorbed and chemisorbed water, and formation of MnO_2 with 4.5% mass loss. This is followed by the reduction to Mn_2O_3 [9] [10] at about 583˚C with a mass loss of about 5.9%. The thermal transformation of nsutite to Mn_2O_3 results in about 10.4% mass loss. This result is in agreement with results of about 11% obtained by Mohapatra *et al.* [9]. Finally, we observed a transformation from Mn_2O_3 to Mn_3O_4 with a mass loss of about 3.1% at about 870˚C. The observed mass loss of 3.3%, is in agreement with stoichiometric values of conversion of Mn_2O_3 to Mn_3O_4 given by

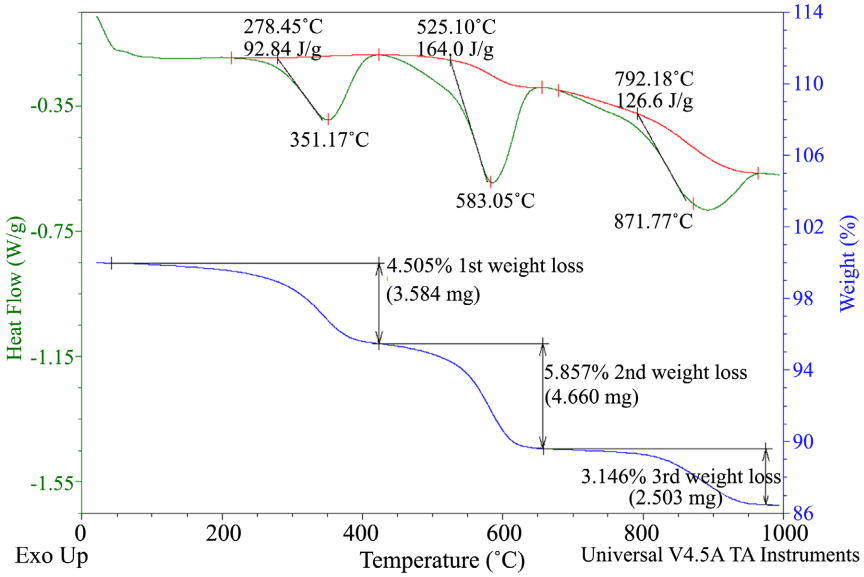

Figure 4. DSC (heat flow) and TGA (weight %) of nsutite vs. temperature.

$$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2$$

and is due to loss of oxygen. The suggestion by Bish *et al.* [10] that heating reduces Mn to lower valence states is also in line with our observed thermal transformations.

In our future work, we plan to use our thermal analysis results as a guide and will anneal the naturally acquired nsutite materials at the transition temperatures and study the physical and electrochemical behavior of the annealed samples. This work is significant because nsutite is naturally occurring and is readily available, and so its thermal modification for supercapacitor application will be highly beneficial in the search for readily available high-volume materials for such energy storage systems.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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