

## Synthesis of single-crystalline $\alpha$ -MnO<sub>2</sub> Nanotubes as electrode material for Supercapacitors

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### 1. Introduction

The research on electrochemical supercapacitors, which fall in between conventional capacitors and batteries are getting more attention owing to its high power density, moderate energy density and long cycle life. Various transition metal oxides with 'd' shell electrons and conducting polymers are suitable for the electrochemical charge storage based on Faradaic reaction or pseudocapacitance phenomena. However, for the large scale use, the factors such as environmental friendliness, low cost, higher capacitance and stability of electrolyte are very important to meet the various requirements of modern devices. Among all metal oxides supercapacitors, hydrous RuO<sub>2</sub> possesses a capacitance as high as 720 Fg<sup>-1</sup> [1]. But its, scarcity and environmental hazardous limits its use for large scale application. Henceforth, the keen on other transition metal oxides such as MnO<sub>2</sub> is getting more attention due to its low cost, environmental friendliness and primarily it's theoretically proved capacitance is 1370 Fg<sup>-1</sup> [2]. Sofar, various research groups have made attempts to get better results for the variety of morphologies of MnO<sub>2</sub> such as thin films, nanotubes, nanorods and layered nanostructures synthesized by various physical, chemical and electrochemical routes. In the present work, we have reported the growth of MnO<sub>2</sub> nanotubes with nanopore dimension by hydrothermal method and studied its supercapacitive properties by constructing a single electrode in a 6 M KOH electrolyte.

### 2. Experimental section

MnO<sub>2</sub> nanotubes were prepared by using Hydrothermal method. 2.25 mmol KMnO<sub>4</sub> was dissolved in 250 ml distilled water. The solution was kept in a sealed autoclave after adding 10 mmol concentrated HCl and then treated at 140°C in an air oven under atmospheric pressure for 12 hrs. The as-obtained powder was cleaned with distilled water and then dried at 40°C in a rotary vacuum. The obtained MnO<sub>2</sub> product was characterized by XRD, FE-SEM and FT-IR analysis.

The composite electrode with 55 wt% MnO<sub>2</sub>, 35 wt% MWCNT and 5 wt% PCVDF binder was prepared by mechanical mixing and then casted onto Ni foam current collector. The electrodes were dried over night and then kept at 40°C in a rotary vacuum to have a good adhesion of electroactive material with the current collector. The electrodes were roll pressed to further improve the contact between active material and Ni foam.

### 3. Electrochemical characterization

The electrochemical study of the electrode was tested by using a half cell arrangement in a vessel containing 6 M KOH as electrolyte at ambient temperature with Ag/AgCl reference, 2×2 cm<sup>2</sup> Pt counter and the prepared composite electrode as working electrodes. The potential was cycled between 0 to 0.4 V at various scan rates. The stability of the active materials was performed by cycle test for 10,000 numbers of cycles. Impedance spectra were obtained before and after the cycle test in the frequency range of 1 MHz to 0.01 Hz at 0 V.

#### 4. Results and discussion

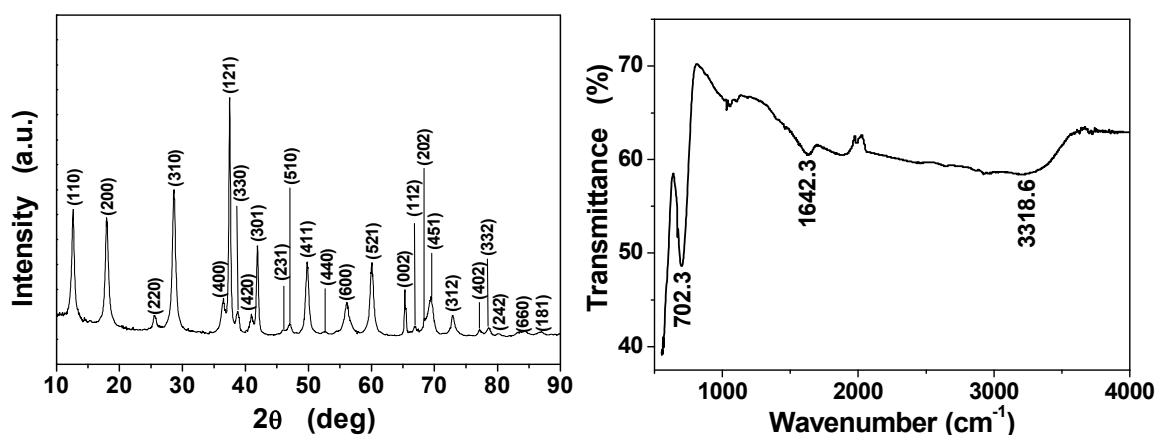


Fig.1(a,b). (a) XRD and (b) FT-IR spectra of MnO<sub>2</sub> Nanotubes.

X-ray diffraction pattern of the prepared MnO<sub>2</sub> NTs is shown in Fig 1a. The result shows sharp crystalline peaks and all the reflections can be indexed to single-crystalline body-centered tetragonal  $\alpha$ -MnO<sub>2</sub> with lattice constants  $a = 5.752$ ,  $b = 9.426\text{\AA}$ , which corresponds to the JCPDS (card no:72-1982). Similar reflections were also observed by Chen et al [3]. No detectable signal for any impurity phase was noticed.

The FT-IR spectrum in transmittance mode was recorded for the as-obtained MnO<sub>2</sub> as shown in Fig 1b. It is noticed that the obtained spectrum is relatively simple, which attributed to its highly structural symmetry. The appearance of bands at around 3318.6 and 1642.3 cm<sup>-1</sup> correspond to the O-H stretching vibration mode of traces of absorbed water. The bands located at 702.3 cm<sup>-1</sup> can be assigned to the Mn-O stretching vibrations of  $\alpha$ -MnO<sub>2</sub> nanotubes. The absence of signals corresponding to other phases such as  $\beta$  and  $\gamma$ -MnO<sub>2</sub> indicate the prepared sample contains single-crystalline  $\alpha$ -MnO<sub>2</sub> phase.

The SEM images of MnO<sub>2</sub> product clearly show well aligned nanotubes with nanoporous size and an average aspect ratio of 75 nm.

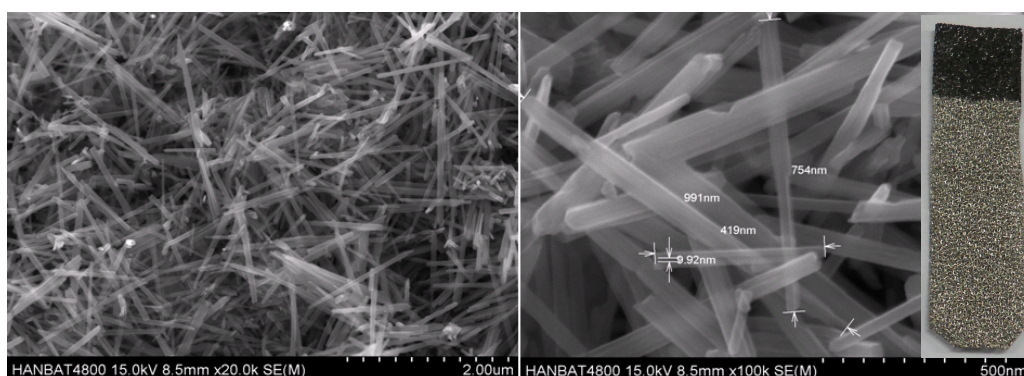


Fig.2. FE-SEM image of MnO<sub>2</sub> Nanotubes. Inset shows the photograph of the prepared single electrode.

The cyclic voltammogram (CV) were recorded at various scan rates and the obtained results are shown in Fig 3(a,b). The obtained CVs show strong oxidation-reduction peak which is a characteristic

of faradaic redox charge storage mechanism. The principle reaction involved in the charging and discharging process of  $\text{MnO}_2$  in alkaline electrolyte can be represented as follows [4]:

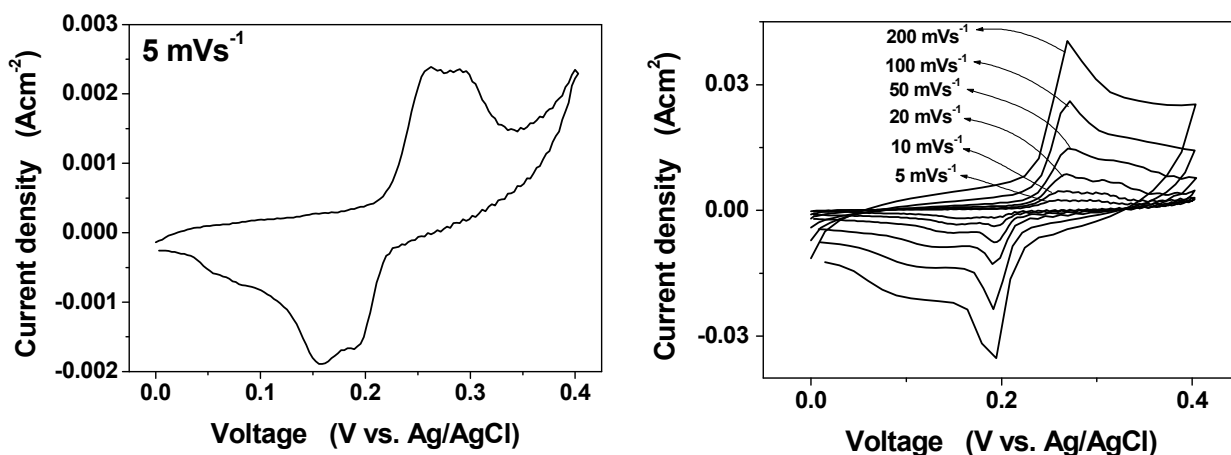


Fig.3(a,b). CVs of the electrode in 6M KOH at (a)  $5 \text{ mVs}^{-1}$  and at (b) various scan rates

The redox reaction is reversible for CVs recorded at all scan rates. But at higher scan rates, the redox peaks have become weak. Consequently, one can expect the decrease of specific capacitance. This is because; at high scan rate, the diffusion of cations into the bulk of  $\text{MnO}_2$  is lessened. But the diffusion is enhanced at the more accessible outer surface of the electrode. The values of specific capacitance ( $C_{\text{sp}}$ ) were calculated from CVs as referred in the literature [5]. The calculated  $C_{\text{sp}}$  of  $\text{MnO}_2$  single electrode at various scan rates such as 5, 10, 20, 50, 100, 200, 300, 500 and  $700 \text{ mVs}^{-1}$  are 363.1, 332.6, 239.5, 206.3, 197.9, 178.41, 169.5128.5 and  $99.1 \text{ Fg}^{-1}$ , respectively. At a higher scan rate of  $700 \text{ mVs}^{-1}$ , the  $C_{\text{sp}}$  is decreased by 72.7% from the value obtained at lower scan rate of  $5 \text{ mVs}^{-1}$ . This shows that the capacitance value has significantly decreased at higher scan rates and it indicates the electroactive material (composite of  $\text{MnO}_2$  & MWCNT) equally fail to utilize the  $\text{K}^+$  cations from KOH electrolyte used in the present investigation.

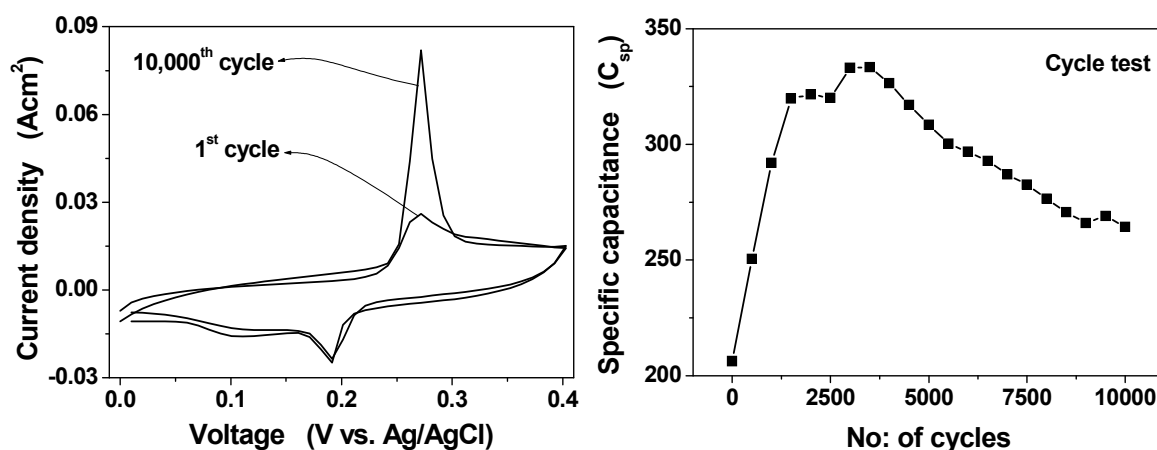


Fig.4(a,b). (a) Comparative CVs during 1<sup>st</sup> and 10,000<sup>th</sup> cycles at  $100 \text{ mVs}^{-1}$  and (b) the variation of capacitance as a function of number of cycles.

The electrode stability was analyzed by performing CVs for 10,000 cycles. As in Fig 4a, irreversibility was noticed for 10,000<sup>th</sup> cycle, which is unlike the case of 1<sup>st</sup> cycle. This may be due to the loss of active material. It results in the simultaneous decrease in intercalation and adsorption of K<sup>+</sup> cations as reflected in the area under reduction peak. The variation of capacitance as a function of cycle number as in Fig. 4b indicates 25% increment of capacitance during 10,000<sup>th</sup> cycle when compared to that of 1<sup>st</sup> cycle. This enhancement in capacitance shall be due to the improvement in the complete utilization of the active material with increase of cycle number.

The real and imaginary part of impedance was plotted at different frequency range before and after the cycling test for electrode as in Fig 5. The plots give information about the charge transfer resistance or interfacial ( $R_{ct}$ ) resistance. From this, it is very obvious that the  $R_{CT}$  before and after the cycling test is evaluated as 0.45 and 8.55  $\Omega$ , respectively. This implies that the contact resistance between active material and the Ni foam is much increased after 10,000 cycles.

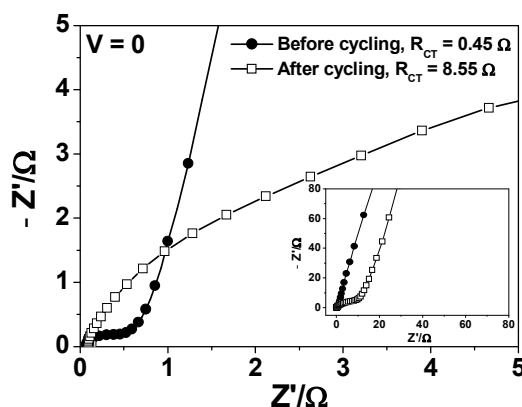


Fig 5. Nyquist plots

#### 4. Conclusion

In conclusion, MnO<sub>2</sub> Nanotubes were prepared by a Hydrothermal method and its microstructure was confirmed by FE-SEM analysis. XRD analysis showed single-crystalline body-centered tetragonal  $\alpha$ -MnO<sub>2</sub>. FT-IR spectrum showed an evidence for the Mn-O and O-H vibration bands from  $\alpha$ -MnO<sub>2</sub> and from traces of H<sub>2</sub>O, respectively. The electrochemical study revealed that the prepared composite electrode showed a highest specific capacitance of 363.1 Fg<sup>-1</sup> at 5 mVs<sup>-1</sup>. Good retention in capacitance even after 10,000 cycles indicated the stable nature of the active material. Extensive studies are underway in our laboratory to further improve the capacitance.

#### References

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