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Characterization and electrochemical performance of Manganese oxide with carbon nano tubes as negative electrode for lithium batteries

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Abstract. Different ratios of Mn₃O₄/CNT (carbon nano tubes) samples were prepared by ultrasonic and hydrothermal reactions. The added ratios of CNT: Mn wt./wt. were 0, 5, 15, 25, 35 and 50%. The phases of the samples were identified by X-ray diffraction (XRD). The particle morphology was studied with a field emission scanning electron microscope (FESEM). The lowest charge transfer resistance, Rₓ was 19.18 Ω with cell of Mn₃O₄/35% CNT. For Li/ Mn₃O₄- 35% CNT cell, the specific discharge capacity was about 688 mAhg⁻¹ after 100 cycles, which was the highest value among the other cells at discharge current density 0.02Acm⁻².

Keywords: Lithium battery anode, Mn₃O₄/CNT.

1. Introduction

Small and Portable electronic devices such as laptops, mobile telephones, camcorders, etc. use Lithium-ion Battery (LIB). They are considered the essential electric power component for these devices due to their excellent properties like long durability, high energy density, easily handling and safe for the environment. A variety of metals and metal oxides are intensively studied in order to obtain high-capacity anode materials for LIBs [1–4].

The synthesis of Mn₃O₄ with CNT was reported in some researches [5–16]. Manganese oxide with multi-wall carbon nanotubes (MWCNTs) was prepared by hydrothermal method using CH₃COONa. Mn3O4 nano-crystals were introduced inside MWCNTs [6]. The nanocomposite performed good cycling stability and rate capability. The initial reversible capacity was 1380 mAh g⁻¹ at a current density of 100 mAg⁻¹. The reversible cycle discharge capacity was 592 mAhg⁻¹ after 50 cycles. The good performance of Mn₃O₄/MWCNTs was discussed.

It was reported that Mn₃O₄nano-particles anchored on continuous super-aligned carbon nanotube (SACNT) films were obtained by decomposition of Mn(NO₃)ₓ[9]. The electrochemical performance of the Mn₃O₄/SACNT composite electrode is greatly affected by the grain size of Mn₃O₄. For smaller particle size, the electrode displayed smaller voltage hysteresis and much improved reversibility and rate capability. Mn₃O₄ with particle size of less than 10 nm inside the Mn₃O₄/SACNT electrodes showed a capacity of 342 mAh g⁻¹ at 10 C. This composite material has more advantages than the commercial graphite anode and promising in practical applications.
Mn₃O₄ / CNT was synthesized by a simple hydrothermal method [10]. MnO / CNT was obtained by heating Mn₃O₄/CNTs at 500°C for 3 h in flowing Ar/H₂. After 30 cycles, the discharge capacity of MnO electrode is only 280 mAh g⁻¹, whereas that of Mn₃O₄/CNTs electrode can still remain with 548 mAh g⁻¹ at current density 100 mAh g⁻¹. While MnO / CNT cell has 600 vs. 200 mAh g⁻¹ for Mn₃O₄ electrode.

Carbon nanofiber/Mn₃O₄ (CNF/Mn₃O₄) coaxial nano-fibers with a three-dimensional (3D) structure were prepared for lithium ion batteries by electrophoretic deposition on an electrospun CNF cathode followed by heat treatment in air [11]. The CNF/Mn₃O₄ coaxial nanocables showed a high reversible capacity of 760 mAh g⁻¹ at 100 mA g⁻¹ even after 50 charge discharge cycles without capacity fading.

A facile and green chemistry route was developed to prepare a Mn₃O₄ nanoparticles (NPs)/exfoliated graphite (EG) composite by artfully tuning the traditional fabrication process of EG [12]. During this treatment, Mn₃O₄-NPs with high crystallinity and uniform dimension of 7 nm were found to be homogeneously and firmly anchored on the surface of EG. The composite as an anode material of Li-ion batteries exhibited suitable specific discharge capacity of 655 mAhg⁻¹ extending to more than 100 cycles.

2. Experimental

2.1. Materials preparation and characterization

Different ratios of carbon nano tubes (CNT), (99%, Ad-Nano Technologies Private Limited, India) 0, 5, 15, 25, 35 and 50% were added to stoichiometric amounts of (CH₃CO₂)₂Mn·4H₂O (Aldrich, 99.5%) dissolved in distilled water to prepare the samples. The ratios of CNT were calculated as Mn: C. The suspended CNT of each mixture solution was stirred and heat-treated at 80°C for 2 hours. Furthermore, the mixture was exposed to ultrasonic vibration for one hour. After that, the mixture was transferred to an autoclave vessel (250 cm³) and heat-treated at 200°C for 24 hours.

The crystalline phases of the samples were identified by X-ray diffraction (XRD) using a step size of 0.02° and at a scanning rate of 0.16°/min on a Bruker axis D8 diffractometer with crystallographic data software Topas 2 using Cu Ka (λ = 1.54056 Å) radiation operating at accelerating voltage and applied current were 40 kV and 80 mA, respectively. The diffraction data was recorded for 2θ values between 10° and 80°. The particle morphology was studied with a field emission scanning electron microscope (FESEM QUANTAFEG 250). The magnetic properties of some of the samples powders were measured at room temperature using a vibrating sample magnetometer (VSM, 7410 Lakeshore, USA) in a maximum applied field of 20 kOe.

2.2. Electrochemical measurements

The homogeneous slurry used to form the electrodes was composed of 85 wt% active materials, 10 wt% acetylene black, and 5 wt% sodium carboxy methyl cellulose (SCMC) as binder dissolved in distilled water. It was then spread onto Cu foil substrates. The area of each coated electrode was 1 cm². The electrodes were dried in a vacuum oven at 110°C for 12 h. The electrodes were then pressed at a pressure of 2000 kg/cm². The active material loading was about 5 mg for each individual electrode. CR2032 coin cells were then assembled in an argon filled glove box (Mbraun, Unilab, Germany), using lithium metal foil as the counter electrode. The electrolyte was 1M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK). The cells were galvanostatically charged and discharged over a voltage range of 0.0~3 V using a current of 0.02 A/ cm² for both processes. Cyclic voltammetry (CV) measurements were performed using a Multi-stat CHI660 Electrochemical Workstation at a 0.1 mVs⁻¹ scanning rate, and...
the potential windows were 0 and 3 V versus Li/Li+ electrode. The Galvanostatic charge-discharge measurements were performed on a Neware Battery Tester. The frequency range of the AC impedance measurement was 1MHz – 10 mHz and 10 mV amplitude.

3. Results and Discussion

3.1 Structural Characterization

X-ray diffraction patterns of the manganese oxide and manganese oxide with CNT samples show suitable crystallinity as shown in Figure 1. Samples diffraction peaks exhibited good crystalline structures. Their structures were indexed to the tetragonal system with space group of I41/amd (JCPDS No. 24–0734). The peak at 2θ =26.4° can be achieved to (002) of the hexagonal carbon in CNT (JCPDS No. 26–1079). Mainly, there is no other phase that observed in the patterns. The main diffractions are (103), (211) and (224) for Mn3O4. The crystallite sizes of Mn3O4, Mn3O4 with 25% CNT and Mn3O4 with 35% CNT are 22.07, 13.58 and 11.03 nm, respectively at 2θ =37° according to the Debye-Scherrer equation [2,3]:

\[ L = \frac{0.94 \lambda}{w \cos \theta} \]  

where \( \theta \) and \( w \) are the Bragg angle and the full width at half maximum peak, measured in radians, of each diffraction peak, respectively. Also, \( \lambda \) is the X-ray wavelength (1.54056Å), and \( L \) is the effective particle or grain size.

Figure 1. XRD of (a) Mn3O4, (b) Mn3O4 + 25% CNT and (c) Mn3O4 + 35% CNT.

Figure 2 shows a FESEM image of the samples. The powder of Mn3O4 itself has an average particle size of ~1 μm as shown in Figure 2(a). On the other hand, the small nano particles of Mn3O4 entered inside CNT particles and formed morphology like distal colon of rabbit due to sonication and hydrothermal treatment that degraded the particles of Mn3O4. So, CNT diameter without Mn3O4 has a diameter of 41.2 nm (Figure 2b) but samples with 25 and 35% CNT have 108.4 and 88.6 nm, respectively as shown in Figure 2c,d. Thus, 35% CNT has less particle size than 25% CNT. The preparation of Mn3O4 without using CNT gives agglomeration of the grains with large particle size. However, the use of CNT enhances the formation of nano-particles of Mn3O4 under ultrasonic technique. Similar reported results were published explaining that HRTEM (high resolution transmission electron microscope) images indicated the presence of the Mn3O4 nano-particles enclosed and encapsulated within the carbon nanotubes [4].
3.2. Electrochemical Impedance Spectroscopy and magnetic properties measurements

Electrochemical impedance spectroscopy (EIS) may be considered as one of the most sensitive tools for the study of differences in electrode behavior due to surface modification. The electrochemical impedance spectra of the cells, as presented in Figure 3, show an intercept at high frequency on the real axis $Z'$ for the resistance of the electrolyte, $R_e$, followed by a semicircle in the high-middle frequency region, and a straight line in the low frequency region. The numerical value of the diameter of the semicircle on the $Z_{real}$ axis is approximately equal to the charge transfer resistance, $R_{ct}$, and therefore, it can be seen that there is a marked decrease in $R_{ct}$ with the addition of CNT until 35% ($R_{ct} = 127 \Omega$), but 50% CNT increases $R_{ct}$, 928 $\Omega$. So, the increase of CNT percentage decreases the $R_{ct}$ until 35% CNT and after that the charge resistance increases again with the increase of CNT. i.e. 35% CNT is the optimum condition of these experiments.

**Figure 2.** SEM of (a) Mn$_3$O$_4$, (b) CNT, (c) Mn$_3$O$_4$ + 25% CNT & (d) Mn$_3$O$_4$ + 35% CNT.
Figure 3. EIS of cells prepared from: (a) Mn$_3$O$_4$, (b) Mn$_3$O$_4$ + 5% CNT, (c) Mn$_3$O$_4$ + 15% CNT, (d) Mn$_3$O$_4$ + 25% CNT, (e) Mn$_3$O$_4$ + 35% CNT and (f) Mn$_3$O$_4$ + 50% CNT. Full Scale: A Scale Part B up to $Z' = 2000 \, \Omega$ and Scale Part C for Mn$_3$O$_4$ + 35% CNT only.

The straight line in the low frequency region is attributed to the diffusion of the lithium ions into the bulk of the electrode material, or the so-called Warburg diffusion. The plot of the real part of the impedance, $Z_{\text{re}}$, versus the reciprocal root square of the lower angular frequencies is displayed in Figure 4.
Figure 4. Relationship between real impedance with the low angular frequencies for Li/ Mn$_3$O$_4$-CNT cells.

Figure 5. The relation between the magnetization and the magnetic field of the samples.

Table 1. Electrochemical Impedance parameters of of lithium cells using anodes prepared from Mn$_3$O$_4$ with and without different percentage of CNT.

<table>
<thead>
<tr>
<th>Cell sample</th>
<th>$R_e$ [Ω]</th>
<th>$\sigma_w$ [Ω.s$^{0.5}$]</th>
<th>D [cm$^2$s$^{-1}$]</th>
<th>$i^o$ [A]</th>
<th>$C_{dl}$ [F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_3$O$_4$</td>
<td>6095.71</td>
<td>8182.5</td>
<td>5.29E-14</td>
<td>4.22E-06</td>
<td>1.64E-07</td>
</tr>
<tr>
<td>5% CNT</td>
<td>1872.9</td>
<td>1984.51</td>
<td>8.99E-13</td>
<td>1.37E-05</td>
<td>4.26E-10</td>
</tr>
<tr>
<td>15% CNT</td>
<td>1545.17</td>
<td>1841.95</td>
<td>1.04E-12</td>
<td>1.66E-05</td>
<td>8.18E-10</td>
</tr>
<tr>
<td>25% CNT</td>
<td>164.51</td>
<td>451.496</td>
<td>1.74E-11</td>
<td>1.56E-04</td>
<td>4.85E-07</td>
</tr>
<tr>
<td>35% CNT</td>
<td>127.0218</td>
<td>3.39E+02</td>
<td>3.09E-11</td>
<td>2.02E-04</td>
<td>6.28E-07</td>
</tr>
<tr>
<td>50% CNT</td>
<td>928</td>
<td>3.44E+02</td>
<td>2.99E-11</td>
<td>2.77E-05</td>
<td>1.36E-09</td>
</tr>
</tbody>
</table>

The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode material, or the so-called Warburg diffusion. This relation is governed by equation 2. It is observed that the Warburg impedance coefficient, $\sigma_w$ is 339 $\Omega$.s$^{0.5}$ for cell composed from Mn$_3$O$_3$ with 35% CNT cell, and it is the lowest value among the other cells. The parameters of the electrochemical impedance spectroscopy are presented in Table 1. Also, the diffusion coefficient values of the lithium ions for diffusion into the bulk electrode materials have been calculated using Equation (3) and are recorded in Table 1.

$$Z_{re} = R_e + R_{ct} + \sigma_w \cdot \omega^{-0.5}$$ \hspace{1cm} (2)

$$D = 0.5\left(\frac{RT}{A F \sigma_w C}\right)^2$$ \hspace{1cm} (3)

where: $R_e$: charge transfer resistance, $R_e$: electrolyte resistance, $\omega$: angular frequency in low frequency region, D: diffusion coefficient, R: the gas constant, T: the absolute temperature, F: Faraday’s constant, A: the area of electrode surface, and C: molar concentration of Li$^+$ ions [2,15]. The obtained diffusion coefficient, 3.09x10$^{-13}$ cm$^2$s$^{-1}$ for Mn$_3$O$_4$ with 35% CNT cell explains the higher mobility for Li$^+$ ion diffusion than in the other cell. Furthermore, the exchange current density is given by the following formula:$i^o = \frac{RT}{nF R_{ct}}$, where n is the number of electron involved in the electrochemical reaction. It is observed that $C_{dl}$ for cell "Mn$_3$O$_4$ with 35% CNT " has the highest value: 1.66 x 10$^{-8}$ F.
The magnetic properties of Mn$_3$O$_4$ and Mn$_3$O$_4$ with 35% CNT samples are shown in Figure 5. It is observed that the magnetization of Mn3O4 with 35% CNT sample is higher than Mn$_3$O$_4$ one. The magnetic coercivities (Hc) are 322.98 and 365.39 G for samples without CNT and with 35% CNT, respectively as shown in Figure 5. This means that the presence of 35% C increases the Hc, i.e. Mn$_3$O$_4$ with 35% CNT is more ferromagnetic than Mn$_3$O$_4$ itself.

Figure 6. Cyclic voltammograms of Li/ Mn$_3$O$_4$-CNT cells.

3.3 Potentiodynamic and galvanostatic measurements

Cyclic voltammetric (CV) measurements were carried out between 0 and 3 V as shown in Figure 6. The cyclic voltammogram of the investigated Mn$_3$O$_4$ sample shows two cathodic reduction peaks at 0.9 (broad) and 0.3 V vs. Li+. The first peak for formation of a solid electrolyte interphase (SEI) film owing to the decomposition of electrolyte on the Mn$_3$O$_4$ particle surface and reduction of Mn$^{3+}$ to Mn$^{2+}$ [8], while the second one (0.3V) for Mn$^{2+}$ to Mn(0) and the formation of amorphous Li$_2$O based on the electrochemical conversion reaction as follows:

On the other hand, the anodic oxidation peaks take place at 1.3 and 2.6V vs. Li+. These peaks are attributed to the oxidation of Mn$^0$ to Mn$^{2+}$ and the other is assigned to the re-oxidization of Mn$^{2+}$ to higher oxidation state manganese [13]. It is observed that the addition of the CNT with 25 or 35% increases the current intensities of the peaks.

The first discharge/charge capacity plateaus versus the working voltage between 3 and 0.01V vs. Li$^+$ are shown in Figure 7. The first discharge capacities of the cells are nearly about 1050 mAhg$^{-1}$. The profiles for the first discharge curves look fairly similar for the investigated cells. There is a small transient and slope plateau between 1.5 and 0.25V vs. Li$^+$ for the formation of solid electrolyte interface (SEI) film and the reduction of Mn$_3$O$_4$ to Mn$^{2+}$, respectively. A plateau at 0.25 V is observed that corresponded to further reduction of Mn$^{2+}$ to Mn(0) [7–9,16].

Figure 8 shows the curves of the specific discharge capacity vs. the cycle number of the different cells samples in the discharge voltage range of 3 and 0.01 V. For Li/ Mn$_3$O$_4$- 35% CNT cell, the capacity can be retained to about 90% of the discharge capacity after 100 cycles with respect to 2$^{nd}$ cycle and the specific discharge capacity is about 688 mAhg$^{-1}$, which is the highest value among the other cells. The initial capacity loss is attributed to the surface film formation, which is known as solid electrolyte interface (SEI) film. This is due the formation of irreversible reaction as: 8Li$^+$ + 8e$^- + Mn$_3$O$_4$ → 4Li$_2$O
+ 3Mn [17,18]. It is observed from CV measurements (Figure 6) that the 2nd and the followed cycles of Mn₃O₄ have no cathodic reduction peaks at 1V but Mn₃O₄ with 25 and 35% CNT have this type peak. This means that quasi-reversible of Mn₃O₄/CNT composite is formed as reported with similar Mn₃O₄/Graphite composite [17]. It can be explained that the reaction is an intercalation reaction when the discharge voltage was limited at 1.5V, the frame structure of material almost was not destroyed, and however, the reaction was a probable redox reaction when the discharge voltage went to lower potential (i.e. 1.5–0.01 V), then the structure of the materials is entirely destroyed at very low potential and cannot be recovered. It can be expected that the charge/discharge voltage is the key factor to affect the cyclic performance.

![Figure 7. Capacity- voltage profile of Li/ Mn₃O₄-CNT cells.](image1)

![Figure 8. Cycle life performance of Li/ Mn₃O₄-CNT cells.](image2)

4. Conclusion

Different ratios of Mn₃O₄/CNT (carbon nano tubes) samples were prepared by hydrothermal reaction. Their crystal structures of the samples aretetragonal system. The cell of Mn₃O₄/35% CNT has lowest charge transfer resistance, Rₚ, 19.18 Ω. The magnetic coercivities (Hₑ) are 322.98 and 365.39 G for samples without CNT and with 35% CNT, respectively. For Li/ Mn₃O₄- 35% CNT cell, the capacity can be retained to about 90% of the discharge capacity after 100 cycles and the specific discharge capacity is about 688 mAh g⁻¹, which is the highest among the other cells at discharge current density 0.02Acm⁻².

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