Trimanganese Tetraoxide as a Negative Electrode Material for Li-ion Battery

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Abstract
A novel crystalline nanostructured Mn\(_3\)O\(_4\) was successfully synthesized by a basic molten salt technique at 300 °C using a commercial MnCl\(_2\)·2H\(_2\)O as a structuring agent. The formation, structure and morphology of Mn\(_3\)O\(_4\) nanopowder were confirmed by thermo-gravimetric analysis (TGA), X-ray Diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). TGA result revealed that the composite is formed at a low temperature of 300 °C. The as-synthesized composite structure is a mixed of tetragonal (Mn\(_3\)O\(_4\)) and orthorhombic (MnO\(_2\)) phases. SEM-EDX observations demonstrated that the morphology of compound is consisting of manganese oxide substance with very fine particles exist in form of clusters, and the average size of particle is less than 50 nm. The electrochemical performance of as-prepared powder was studied. The discharge capacity at 93 mA g\(^{-1}\) for the first 10 cycles was in the range of 1645 and 667 mAh g\(^{-1}\). The excellent cyclebility and high capacity storage of as-prepared powder make it a promising candidate as an anode material for the application in rechargeable lithium ion batteries.

Keywords: Trimanganese Tetraoxide; Molten salt method; Low temperature synthesis; Lithium-ion battery
1. Introduction
Manganese oxides compounds have been largely studied in many applications attributable to their low cost, environmental merit and ease of preparation (Haegyeom, Sung-Wook, Jihyun, Young-Uk, & Kisuk, 2011). Among manganese oxides, trimanganese tetraoxide Mn$_3$O$_4$ is known to be an active catalyst in many redox reactions and frequently used as a catalyst in the oxidation of ethane (Metev & Veiko, 1998) and carbon monoxide (Breckling, 1989), the decomposition nitrogen oxides(Yamashita & Vannice, 1996), the selective reduction of nitrobenzene (Zhang, Zhu, Sin, & Mok, Nov. 1999), and the catalytic combustion of organic compounds (Baldi, Finocchio, Milella, & Busca, 1998). In battery research the Mn$_3$O$_4$ has been considered as a potential candidate for anode materials in lithium-ion batteries (LIBs) due to their high theoretical specific capacity of 937 mAh g$^{-1}$, non-toxicity and low production cost (Fang et al., 2010; Pasero, Reeves, & West, 2005; Wang et al., 2010). Its conversion reaction with lithium to form lithium oxide and metal nanoparticles is similar to other transition metal oxides (FeO, NiO, CoO, Co$_3$O$_4$, and Fe$_3$O$_4$): $\text{MO} + 2\text{Li}^+ + 2e^- = \text{Li}_2\text{O} + \text{M}$. (Armand & Tarascon, 2008; Bruce, Scrosati, & Tarascon, 2008; Poizot, Laruelle, Grugeon, Dupont, & Tarascon, 2000). Throughout this reaction, the metal oxides can react with more than one Li ion and exhibits high capacity, while the development of metallic lithium can be reduced when more positive reaction potentials for metal oxides (vs Li$^+/Li$) occurred during insertion/de-insertion process.

On the contrary, the disadvantage of trimanganese tetraoxide is low electronic conductivity which limiting it to be a potential anode material in Li rechargeable battery electrode (Pasero et al., 2005; Thackeray, David, Bruce, & Goodenough, 1983; Wang et al., 2010). Recently, producing trimanganese tetraoxide in nanosized structure and/or incorporated it with conductive materials have gained prominence. Potentially, reducing the particle size could shorten the traverse time of ionic species, resulting large surface area for electrochemical reaction. On the other hand, doping with conductive elements such as amorphous carbon, carbon nanotube and conducting polymer also could enhance the electronic conductivity of the composite materials (Jie, Michael, & Hector, 2011; Strobel et al., 2006). Various approaches have been applied to synthesis Mn$_3$O$_4$ in nano-sized: one approach involves the fabrication of nanostructured Mn$_3$O$_4$ through a hydrothermal route, and another involves a simple precipitation method. Li and co-workers successfully synthesized tetragonal Mn$_3$O$_4$ nanoparticles with dimension of $\sim 20$ nm in diameter and $\sim 80$ nm in length, via the hydrothermal technique. They have experimentally shown that their nano-sized material led to the excellent electrochemical results in terms of the discharge capacity and cycle stability (Li et al., 2010). In the precipitation technique, Gao et al have effectively synthesis Mn$_3$O$_4$ with an average domain size of 30 nm (Jie et al., 2011). As a result, the discharge capacities of 1327 and 869 mAh g$^{-1}$ at the 1st and 2nd cycle were recorded which is closer to the theoretical capacity of Mn$_3$O$_4$. The study also demonstrated that the nanosized material could overcome the hysteresis problem, provide excellent capacity retention, improve the Coulombic efficiency, even the results much better than other conversion systems like Co$_3$O$_4$ or Fe$_3$O$_4$, and much higher compared to previous reports on Mn$_3$O$_4$ and as good as carbon-coated MnO nanoparticles (Ban et al., 2010; Fan & Whittingham, 2007; Lou, Deng, Lee, Feng, & Archer, 2008; Pasero et al., 2005; Zhong et al., 2010). Obviously, the outstanding electrochemical performance of the nanostructured Mn$_3$O$_4$ could be mainly attributed to its nanosize structure. The nanoscale structure provides large surface area, which improves the utilization of active material, and the loose porous structure allows lithium ions insertion / de-insertion, this piloted to the good electrochemical performance.

In this work, nanosized Mn$_3$O$_4$ with crystalline nature was prepared by a basic molten salt method at a low temperature of 300°C. The electrochemical performance of the Mn$_3$O$_4$ as an anode in Li-ion battery was evaluated. The structure and morphology of Mn$_3$O$_4$ were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results indicate that Mn$_3$O$_4$ exhibits a high initial reversible capacity ($\sim 1200$ mAh g$^{-1}$) at $\sim 93$ mA g$^{-1}$ and its
capacity kept maintain about 27% of the initial reversible capacity after forced with a current density of 747 mA g⁻¹.

2. Experimental
2.1. Raw Materials. Lithium nitrate (LiNO₃, 99%), lithium hydroxide (LiOH·H₂O, 98%), hydrogen peroxide (H₂O₂, 30%) and manganese chloride hydroxide (MnCl₂·2H₂O, 99%) were purchased from Sigma Aldrich Chemical Reagent Company and used as received.

2.2. Synthesis of Mn₃O₄ nanopowder. The Mn₃O₄ material was synthesized by a molten salts technique. Specifically, 0.862 g (100 mmol) of LiNO₃, 0.106 g (20 mmol) of LiOH·H₂O and 0.364 g (10 mmol) of MnCl₂·2H₂O were hand grinded in an agate mortar for a few minutes. Then 0.607 g (50 mmol) of H₂O₂ was added gradually where the mixture turned into dark brown color, and further grinded until the mixture become homogenous. The mixture was then heated at 100 °C for 24 h in a vacuum oven, and further heated at 300 °C for 3 h in a muffle furnace in air. The muffle furnace was cooled down naturally at the end of this period. The dark brown product was collected and washed with distilled water and alcohol to ensure total removal of the inorganic ions. The wet product was dried at 100 °C for 12 h under a vacuum pressure. The overall schematic model of the preparation procedure is described in Figure 1.

2.3. Material Characterization. Thermogravimetric analysis (TGA) was carried out with Mettler TGA/sDTA 851e equipment at a heating rate of 10°C min⁻¹ in air. X-ray diffraction (XRD) measurement was recorded using a MiniFlex II diffractometer equipped with an X’celerator using CuKα radiation (λ= 0.1542 nm), operated at 40 kV and 40 mA in the 2θ range between 10° and 80°. Scanning electron microscope (SEM) observations and energy dispersive X-ray spectroscopy (EDS) measurement was carried out on a Hitachi S–4300 SEM. For the morphology observations, the product was pasted on studs and gold coated and then observed through a JEOL JEM–200CX scanning electron microscope at an acceleration voltage of 20 kV.

2.4. Electrode Preparation and Electrochemical Characterization. The active anode powder were mixed with activated carbon (AC) and polyvinylidene fluoride (PVDF) binder in two different weight ratios (see Table 1) in N-methyl pyrrolidone (NMP) to form a viscous slurry. The slurry was uniformly coated on a 1 cm² Cu foil. The electrode sheets were dried at 100°C for 12 hrs under vacuum. Coin cells (CR 2032) were assembled in a glove box which controlled the moisture and oxygen levels less than 0.1 ppm. The electrolyte was 1M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) at 1 : 1 volumetric ratio. Li metal foil was used as a counter electrode. The cells were galvanostatically discharged and charged at multiple current densities of 93-747 mA g⁻¹ within the cutoff voltage window of 0.01–3.0V using Neware battery tester.

3. Results and Discussion
Thermo gravimetric analysis (TGA) was carried out to ensure that the obtained product of the molten salts method is Mn₃O₄ compound without any calcination (Figure 2). The sample was heated from 100 to 305°C at a rate of 5°C min⁻¹. As can be seen in Figure 2, the precursor starts to lose weight in air as temperature increase, and maximum weight loss is found to take place around 100 to 305°C. The formation of manganese oxides compound is expected occur at temperature in range of 280 and 305°C. Specifically, the weight loss of sample starts at 100°C (point A), which could be attributed to the loss of physically absorbed water. At the point B (150–240°C), weight loss is occurred which could be ascribed to the ionic species in precursor start to react and transform into Mn₃O₄ compound. At the point C (250–305°C), all the ionic species are in the equilibrium phases to form the compound of Mn₃O₄ (Ching, Hughes, Gray, & Welch, 2004).
Figure 3 shows the X-ray diffraction pattern of the nano-crystalline Mn$_3$O$_4$ powder synthesized under molten salts conditions. The pattern is indicating that it be likely to have poor crystalline phase. The as prepared powder was identified as a co-existence of Mn$_3$O$_4$ and MnO$_2$ phases, where Mn$_3$O$_4$ compound was the majority element founded in the powder. Significant XRD peaks recorded at 2θ = 29.33, 31.25, 32.62, 36.60, 37.97, 44.84, 51.01, 54.30, 56.50, 58.83, 60.20, 64.87, 74.48, and 77.91° could be well assigned to the (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224), (314), (413), and (404) planes of Mn$_3$O$_4$. It is corresponding to the hausmannite structure (space group I41/amd) with lattice constant a=5.75 Å and c = 9.42 Å (JCPDS 02-1062). The peaks located at 2θ = 18.90, 21.23, 48.40, and 68.03° could be assigned to the (200), (101), (302), and (610), and might be correlated to MnO$_2$ ramsdellite nanostructure (JCPDS 42-1316) with space group of Pbnm lattice constant, a = 9.531 Å, b = 2.864 Å, and c = 4.70 Å. The crystallite size was calculated according to Scherrer equation (Niasari, Davar, & Mazaheri, 2008).

$$L = \frac{k}{D_0} \cos \theta_b$$  \hspace{1cm} (1)

$L$ is the crystallite size, $k$ is a constant (0.9 assuming that the particles are spherical), $l$ is the wavelength of the X-ray radiation, $D_0$ is the full width at half maximum and $\theta_b$ is the angle of diffraction. From the diffraction peaks at (211) Mn$_3$O$_4$ and (200) MnO$_2$ reflections, crystallite sizes of the as-synthesized hausmannite and ramsdellite structure were calculated to be ca. 13.57 and 28.67 nm respectively. Undoubtedly, a less crystallized structure was formed at low temperatures (300°C) and these results agree well with those studies on Mn$_3$O$_4$ and MnO$_2$ at low temperature in previous reports (Covaliu et al., 2010; Gillot, G, & Laarj, 2001; Yuan, Zhang, Du, Ren, & Su, 2003).

Scanning electron microscopy images are shown in Figure 4, which presents Mn$_3$O$_4$ nanostructure at different location. The morphology of the sample at low magnification (Figure 4a) is composed of the large agglomerated clusters with the size is between 5 and 20 µm. At higher magnification, the morphology of Mn$_3$O$_4$ (Figure 4b) consists of small groups nanosized clusters (200-400 nm) and it is also can be observed that, in each nanoclusters there is a combination of very small particles with roughly standardized in size, estimated less than 100 nm (Figure 4c). The particle morphology experimental is either spherical or cubic like with irregular shapes. Moreover, the results also indicate that the as-prepared sample has very fine structure with porous architecture among the nanoparticles as shown in the Figure 4c and 4d, respectively. Undoubtedly, these results demonstrated success in synthesizing Mn$_3$O$_4$ nanostructure through a simple and low-temperature synthesis route (Li et al., 2011).

Figure 5 illustrates the EDS mapping images of as-prepared nanopowder. The black spot in the figure is referring to the carbon tape used to adhesive the tested powder. In Figure 5c, the element of oxygen is associated to white, green and red spots that mass spreading surface of the observed image and there is only small area which covered by the black spot of carbon tape. All the existence elements are represented by the EDS graph as shown in Figure 5d. The peaks of manganese are observed located at 0.6, 5.8 and 6.4 keV, while for oxygen is at 0.5 keV. There is a peak at 0.4 keV, which is related to the peak of carbon tape. The other peaks located at 1.9, 2.1 and 9.8 keV are corresponding to the gold element, where it is used in coating process of sample. From the results, it can be clarified that the presence of Mn and O elements in the powder is in good agreement to the XRD in this study.

The electrochemical performance of nanosized Mn$_3$O$_4$ at a multiple current densities from 93.4 to 747.2 mA g$^{-1}$ is presented in Figure 6. Figure 6a demonstrates the charge and discharge curve of Mn$_3$O$_4$ anode for the first cycle at a current density of 93 mA g$^{-1}$ and cycled between 3.0 – 0.01V vs Li$^+$/Li. As can be seen in the figure, the discharge plateaus in the galvanostatic curve can be attributed to the electrochemical behavior of the as-prepared electrode. The discharge and charge curves are also similar to those previously reported (Gao, Lowe, & Abruna, 2011), which confirms that these are Mn$_3$O$_4$ curves. The capacity of the 1st discharge is found to be around 1645 mAh g$^{-1}$, which is 76% higher than the theoretical capacity of Mn$_3$O$_4$. The discharge plateau at 3.0 V is assigned to MnO$_2$ ramsdellite nanostructure and the one at 2.7 V is related to hausmannite MnO$_3$. The discharge plateau at 2.4 V is corresponding to MnO phase, while the one at 2.0 V is connected to MnO$_2$ ramsdellite nanostructure.
(Gao et al., 2011). Figure 6b shows representative discharge and charge voltage profiles of the Mn$_3$O$_4$ anode at various current densities. The cell was first cycled at a low current density of 93 mA g$^{-1}$ for 12 cycles, where the specific capacity of cycle 12th is 667 mA g$^{-1}$. The capacity is as high as 543 mAh g$^{-1}$ after the current density increased to 186 mA g$^{-1}$. The capacities are gradually decreased to 452 and 356 mAh g$^{-1}$ at the current densities of 373 and 560 mA g$^{-1}$, respectively. The capacity reached to the lowest value of 331 mAh g$^{-1}$ at the current density of 747 mA g$^{-1}$. As comparison, the cycling performance of Mn$_3$O$_4$ with lower content of activated carbon (10wt.% AC – sample A) (Figure 6d) is worsen compared to sample B (15wt.% AC) where the 1st reversible capacity is 250 mAh g$^{-1}$ and remain constant below 200 mAh g$^{-1}$ at 10th cycle. These results revealed that the electrochemical performance of Mn$_3$O$_4$ nanopowder can be improved by assisted at least 15 wt.% of activated carbon where it is experimentally believed that the existing of AC can provide the excellent interconnection between Mn$_3$O$_4$ particles and improve the electronic conductivity.(Fransson, Eriksson, Edström, Gustafsson, & Thomas, 2001)
The high capacity and rate capability, good cycling stability of our material were attributed to nanosized Mn$_3$O$_4$ and the accessible an appropriate amount of AC which known can provide the shortest traverse time of ionic species, offer more space for electrochemical reaction, deliver the continuous electrical paths and ensuring the fast electronic conduction. Further, AC’ mechanical flexibility and the nanosized of Mn$_3$O$_4$ are another important factors which contributes of capability of material to mitigate the large volume change caused by the manganese oxide displacement reaction.

4. Conclusions
In this paper, Mn$_3$O$_4$ nanopowder has been synthesized successfully by a molten salts technique. The structure, morphology, and lithium storage performances in terms of high capacity, cycling stability, and rate capability are characterized in Mn$_3$O$_4$ with different activated carbon contents. It is experimentally verified that Mn$_3$O$_4$ with the high content of AC delivered the better performance. The Mn$_3$O$_4$-acivated carbon could be further explored by different techniques for high-capacity, low-cost and non-toxic anode material for battery applications. Our molten salt approach should offer an effective and convenient method to prepare the nanosized powder to improve the specific capacities, cycling stability and rate capabilities of anode materials in the battery area.

Acknowledgment
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References


**Figures and Table**

**Fig. 1.** Schematic illustration of nanostructured Mn3O4 preparation.

**Fig. 2.** TGA curve of sample prepared by a molten salt method at 300 °C for 3 h.
Figure 3

![XRD pattern of prepared sample.](image)

Fig. 3. XRD pattern of prepared sample.

Figure 4

![SEM images of nanostructured Mn$_3$O$_4$.](image)

Fig. 4. SEM images of nanostructured Mn$_3$O$_4$. 
Fig. 5. EDS images of Mn$_3$O$_4$ nanopowder: (a) Selected area image, (b) Mn, (c) O and (d) EDS graph.
Fig. 6. (a) The first charge-discharge profiles of Mn$_3$O$_4$ nanopowder anode with 75% content of active material. (b) Representative charge and discharge curves of Mn$_3$O$_4$ at various current densities. (c) Capacity retention of Mn$_3$O$_4$ at various current densities. (d) Capacity retention of Mn$_3$O$_4$ with a low content of activated carbon (sample A) at a current density of 93 mA g$^{-1}$.

Table 1: The active anode electrodes with different weight ratios of compounds.

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<thead>
<tr>
<th>Sample/Material</th>
<th>A Weight (wt%)</th>
<th>B Percentage</th>
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<tbody>
<tr>
<td>Active material</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PVdF)</td>
<td>10</td>
<td>10</td>
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