

SYNTHESIS AND CHARACTERIZATION OF $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ AS A CATHODE MATERIAL BY A HMTA-NITRATE COMBUSTION METHOD

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ABSTRACT

$\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ has attracted a great deal of interest in the investigation of cathode material for lithium ion batteries to replace the presently popular LiCoO_2 because the combination of Ni, Co, Mn can provide advantages such as stable cycling performance, good thermal stability and excellent rate capability [1-5]. The $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode materials were synthesized by a self-sustaining HMTA-nitrate combustion method using starting materials of LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NH_4OH , $\text{C}_6\text{H}_{12}\text{N}_4$ and deionized water. The mixture of starting materials was quickly introduced in a muffle furnace, which was pre-heated to 500°C . The mixture was kept in the furnace at the set temperature for 15 min, during which time it decomposed in a smoldering (flameless) combustion process to yield a black, voluminous product of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. The product was allowed to cool, and subsequently subjected to calcinations at different temperatures for 12 hours. The morphology, structural and electrochemical behavior were characterized by means of SEM, X-ray diffraction analysis and electrochemical charge-discharge test. The cathode material synthesized by using this method showed reversible capacity of 184 mAhg^{-1} in the voltage range of 3.0-4.9 V versus Li.

INTRODUCTION

$\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ is believed to be one of the most interesting intercalation materials because this material possesses acceptable capacity and stable structure [1-3]. It has a typical hexagonal $\alpha\text{-NaFeO}_2$ structure with a space group of $R\bar{3}m$, the valence of Ni, Co and Mn in the compound are $2+$, $3+$ and $4+$, respectively [6], only divalent Ni and trivalent Co are involved in the electrochemical processes through $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$ redox couple [7,8]. Tetravalent Mn, on the other hand, has a configuration of empty $3d_{eg}$ orbital in octahedral coordination so that it is electrochemically inactive. However, Mn plays an essential role in supporting the host structure during Li^+ de-/intercalation. It was reported that the rechargeable capacity of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ was 160 mAh/g when the cell operated at 2.5-4.4 V and more than 200 mAh/g in the voltage range of 2.8-4.6 V [3, 9] and it is considered to be one of the best candidates for a positive electrode material for hybrid electric vehicle (HEV) power source system by Amine et al. [10].

In this report, Combustion HMTA-Nitrate method, which is a self sustaining

combustion process using metal nitrates as the oxidizer and HMTA as the fuel has been used to obtain an ultra-fine powder of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. By using this method, all constituents of the precursors can be homogeneously distributed at the molecular level in a solution, therefore lead to the production of homogenous, ultra-fine powders with desired composition. The synthesis method and material properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ synthesized using HMTA-nitrate combustion method will be discussed. The structure and electrochemical properties of the powders were investigated using scanning electron microscope (SEM), X-ray diffraction spectroscopy (XRD) and charge-discharge method.

METHODOLOGY

Stoichiometric mixtures of LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in a minimum amount of water. The fuel, HMTA, was added to this solution, such that the equivalent ratio, ϕ_e , defined as the ratio of total oxidizing power of the oxidizer, $[\text{O}]$, to the total reducing power of the fuel, $[\text{F}]$, was 1, so that the energy released in the combustion process was at a maximum [11]. It may be recalled that according to the concepts of propellant chemistry [11], the elements C, H, Li, Co, Ni and Mn are considered reducing elements with valencies of +4, +1, +1, +2, +2 and +2, respectively. Oxygen is considered the oxidizing element with a valency of -2. In propellant chemistry, the valency of nitrogen is considered to be 0. Accordingly, LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ will have an oxidizing power of -5, -10, -10, -10 and -10, respectively. HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$, is a highly reducing fuel with a reducing power of +36, which means that the amount of fuel required will be very small for an $[\text{O}]/[\text{F}]$ ratio of 1.

LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and HMTA ($\text{C}_6\text{H}_{12}\text{N}_4$) will be mix together for 1 hr. The mixture taken in Pyrex glass beaker was quickly introduced in a muffle furnace, which was pre-heated to 500°C . The mixture was kept in the furnace at the set temperature for 15 min, during which time it decomposed in a smoldering (flameless) combustion process to yield a black, voluminous product of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. The product was allowed to cool, and subsequently subjected to calcination at different temperatures for 12 hours. Structural properties were studied by the X-ray diffraction method (Bruker). The morphology and size of the particles were examined by field-emission scanning electron microscopy (Leo 1525).

A two-electrode electrochemical cell composed of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ as the working electrode and a lithium metal anode as the counter and reference electrode. The cathodes consist of 20 mg of accurately weighed active material and sufficient amount of conductive binder. It was pressed on a 100-mm^2 stainless steel mesh current collector. The electrode were pressed at 40 Mpa, and dried at 100°C for an overnight in an oven. The electrolyte was 1M LiPF_6 in an ethylene carbonate/dimethyl carbonate (1:2) solution. All procedures were carried out in a dry box containing an argon atmosphere. Next, the specific capacities of the material were examined using Solartron 1470.

RESULTS AND DISCUSSION

The solution combustion method offers a convenient and fast synthetic strategy for the production of metal oxides [18, 19]. The method involves the ignition of a mixture of metal nitrates with a fuel at a particular temperature. Because of the presence of the oxidant and the reductant, the mixture smolders in a self-propagating decomposition reaction, yielding the metal oxide. Once ignited, the reaction propagates through the reaction mixture at velocities from a few mm/s to tens of cm/s, and temperatures in excess of 1000°C are reached [17]. Because the mixture was heated in a furnace, the reaction was initiated in a number of spots by a process referred to as ‘thermal flash’ [17]. The decomposition process was accompanied by a copious evolution of gases such as CO₂, NO, NO₂ and H₂O, which ensured that the products had low particle sizes and large surfaces areas.

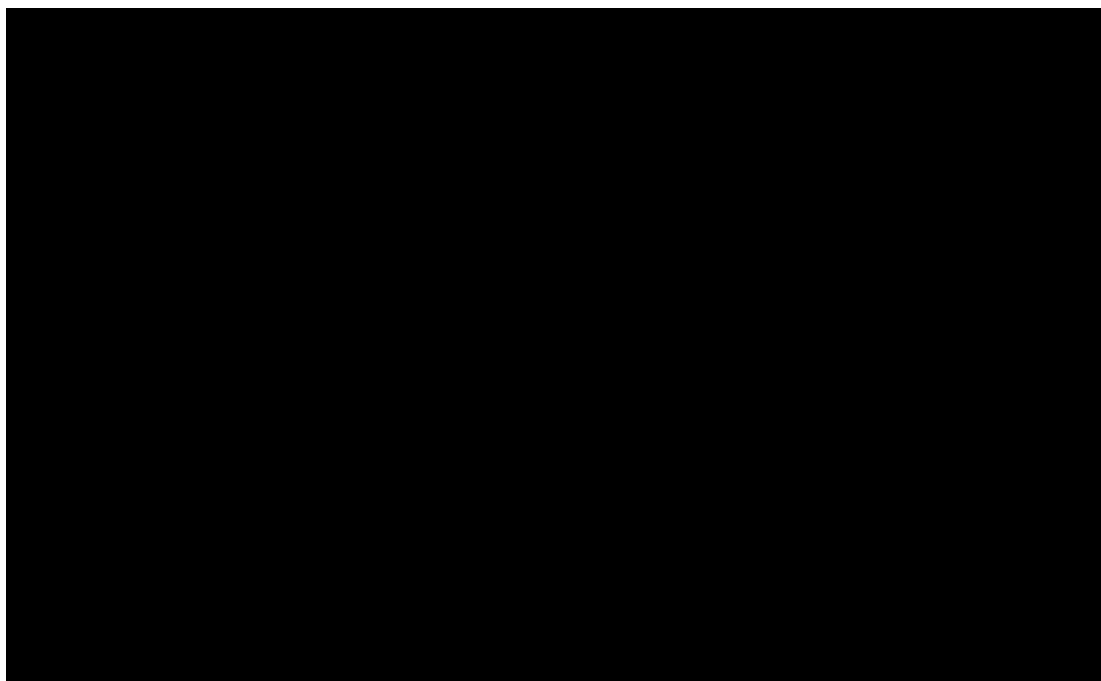


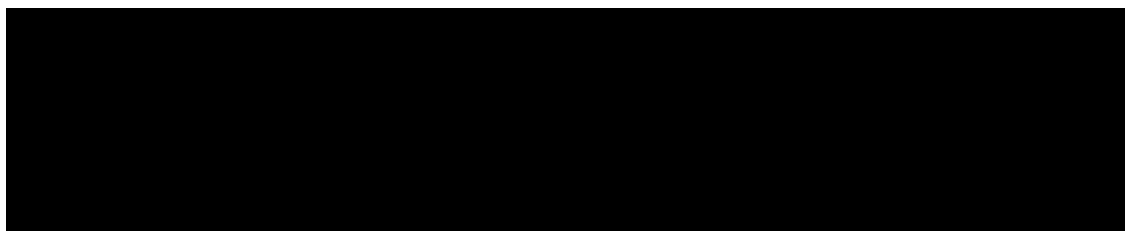
Figure 1: X-ray diffraction pattern of the Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powder synthesized at various temperatures for 12 h. (a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C; (e) 900°C; (f) 1000°C.

Figure 1 shows the XRD pattern of the Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cathode calcined at various temperatures. This sample can be indexed to the hexagonal α -NaFeO₂ structure (space group $R\bar{3}m$) without any impurities peaks. The XRD spectra recorded for the mixture heated at 500°C revealed the formation of the crystallized compound during the heating process. In order to improve the crystallinity of the powders, heat treatment of the sample was carried out at 600, 700, 800, 900 and 1000°C. With increasing the

calcinations temperature, the peak splitting (006)/(102) and (108)/(110) become clear. The splits in the (006)/(102) and (108)/(110) doublets observed in the XRD pattern, indicating that the layered $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode material has been successfully synthesized at 700°C and above. Furthermore, from Table 2, the full width at the half-maximum became narrow, which indicates the improvement on the crystallinity by the heat treatment.

The lattice parameter and other structural parameters calculated based on XRD results for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ are summarized in Table 2. Lattice parameters were calculated by a least square method from the XRD pattern of Figure 1. With increasing heat-treatment temperature, the *a*-axes and *c*-axes increased monotonously to 700°C. By the calcinations at 800°C for 12 h, the *a*- and *c*-axes parameter decreased. The opposite trends were observed for powders calcined at 900 and 1000°C. The *a*-axes parameters showed a little lower than reported values [20]. The *a*-axes value is critically related to the atomic distance between transition metal and oxygen. It is speculated that the lower value of lattice parameter is due to improvement of crystallinity of host structure by heating at higher temperature, which is clearly seen from the peak splitting of (006)/(102) and (108)/(110) peaks in the XRD pattern of Figure 1. Therefore, it is likely that the lower values would come from the higher crystallinity of the final products, because the material was fired for much longer time compared to other researcher [20].

Table 2: Calculated structure parameter for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ synthesized at various temperature



Some researchers [12, 13] used the high integrated intensity ratio of the I_{003}/I_{104} to indicate the cation mixing of the layered structure. Generally, when $I_{003}/I_{104} > 1.2$, the cation mixing is small with good layered structure. The I_{003}/I_{104} value of the sample calcined at 700 and 900°C in this work is larger than 1.2 indicating no undesirable cation mixing takes place. The powder calcined at 800°C shows acceptable value of small cation mixing. The opposite trend was observed for powder calcined at 1000°C due to decomposition of the structure (Figure 2f). Dahn et al. [14, 15] believed that the *R*-factor ($R = (I_{102} + I_{006})/I_{101}$) was an indicator of hexagonal ordering, the lower the *R*-value, the better the hexagonal ordering. The powder calcined at 700, 800 and 900°C shows good hexagonal ordering with the values is from 0.6 up to 0.9.

Figure 2 show the SEM micrograph of the powders calcined at 500, 600, 700, 800, 900 and 1000°C for 12 hours.

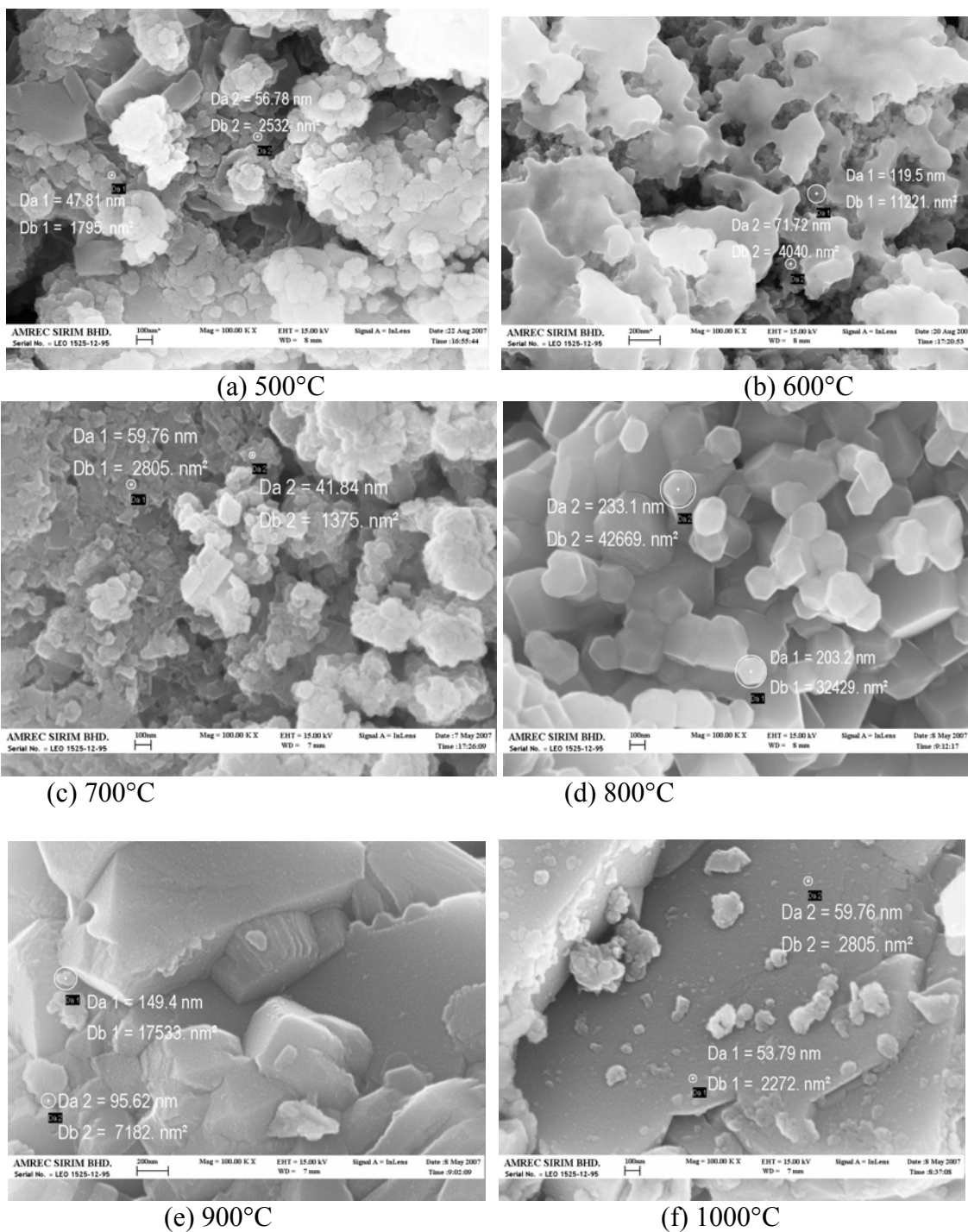


Figure 2: SEM micrograph for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ powder calcined at 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C for 12 h.

Changes of the particle shapes by the calcinations are also quite interesting in Figure 2. The loosely agglomerated primary structure changed to densely agglomerated secondary particle in Figure 2a and 2b, and calcinations at 800°C led to polyhedral shape primary structure. It is clearly shows that upon increasing the temperature, the size of the material also increasing drastically. At 700°C, the size of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ was around 60 nm. At 800°C, the size was increasing to 200 nm and above 900°C; the size of this material is in micron magnitude. Materials at 700°C and below shows different profile i.e. the material is agglomerate together while at 800° and above the material start to crystallite and show polyhedral shape. At 1000°C, the material starts to decompose.

Table 3: Capacity data for $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ powder calcined at different temperature.

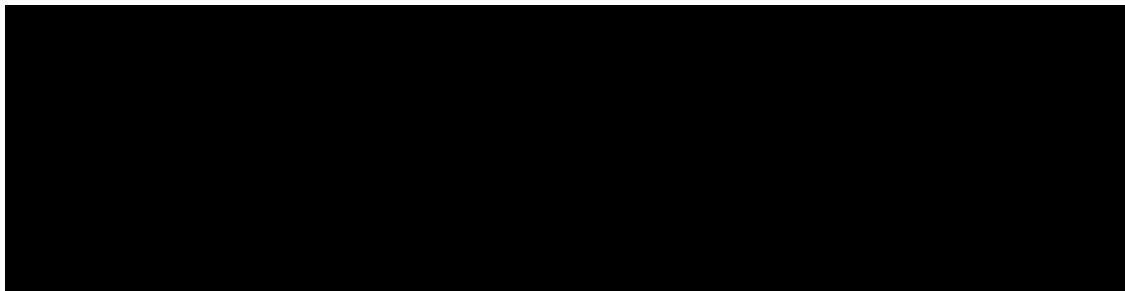


Table 3 shows charge discharge capacity data for three cycles of the prepared $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ calcined at different temperature. The $\text{Li} / \text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cell was first galvanostatically charged and subsequently discharged with a current density of 20 mA g^{-1} at 25°C. The highest coulombic efficiency at initial charge and discharge cycle was 81% delivered by the material calcined at 700°C. This material also shows the highest discharge capacity of 184 mAh g^{-1} after three cycles. Upon increasing the temperature, the capacities start to decrease. Both powder calcined at 800°C and 900°C delivers the specific capacities of 129 mAh g^{-1} . At 1000°C, the capacity is only 7 mAh g^{-1} . This result supported by SEM image (Figure 2f) show that material degraded at 1000°C.

CONCLUSION

$\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ was prepared by a HMTA-nitrate combustion method. As calcinations temperature increases, the peak splitting (006)/(102) and (108)/(110) become clear, which is the characteristic of the layered $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. The splits in the (006)/(102) and (108)/(110) doublets observed in the XRD pattern, indicating that the layered cathode material has been successfully synthesized at 700°C and above. We consider that 700°C is the proper calcinations temperature to obtain good layered and high specific capacity of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. The $\text{Li} / \text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ calcined at 700°C for 12 h delivered the discharge capacity of 184 mAh g^{-1} .

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