

Synthesis of layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode via CTAB assisted ball milling route

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Abstract: Layered cathode material lithium nickel cobalt manganese oxide, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM) was successfully prepared by ball milling assisted sol-gel route with CTAB (cetyltrimethyl ammonium bromide) as the surfactant. The influence of ball milling the precursor before calcination was studied by comparison made with the structural, morphology and cell performance of the sample made by calcination with no milling step. While ball milled sample showed phase pure structure, nickel oxide impurities were observed for the sample prepared without milling step. The half cell made using the phase pure cathode material resulted in an initial discharge capacity value of 84 mAh/g with a good capacity retention of 88% at the end of 50th cycle, in the voltage range of 2.5 to 4.4 V at 0.2 C (30 mA/g). Whereas, the half cell made with sample prepared without milling resulted in an initial discharge capacity value of only 73 mAh/g, but with better capacity retention of 97% at the end of 50th cycle. The difference in preferential growth of particles along (003) direction as observed in diffraction pattern was found to be the key factor in determining lithium ion intercalation/deintercalation mechanism.

Keywords: cathode, ball milling, lithium battery, electrochemical performance, discharge capacity

1. INTRODUCTION

Layered LiCoO_2 has been broadly used in lithium secondary cells as cathode materials for nearly two decades due to its easy preparation and stable electrochemical performance. However, issues like toxicity, and safety problems have led to considerable effort to search alternative suitable cathodes for advanced lithium ion batteries [1, 2]. Recently, the mixed transition metal oxide, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ have drawn great attention for its high capacity, low toxicity, high thermal stability and long cycle life [3]. One of the major shortcomings of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is the cation mixing and presence of Li_2MnO_3 superlattices in the structure. So far, various preparation methods have been adopted for the preparation of NCM compound like, sol-gel method, hydrothermal, co-precipitation, ion exchange, combustion method and molten salt method etc., [1, 3 & 4]. Knowing appropriate preparation conditions to achieve final product with high purity is a tedious work. In the present work, in order to know the impact of ball milling the precursor on the structural, morphological and electrochemical performance of the NCM compound, the precursor was made by CTAB assisted sol-gel route. It is well known that, surfactant can effectively reduce the surface tension and surface Gibbs free energy and result in better product [5]. So, with the aim of achieving uniform particle and high performance NCM cathode, cationic surfactant CTAB was used during the preparation process.

2. EXPERIMENTAL PART

$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ was prepared by sol-gel route with CTAB as the surfactant. All chemicals used were received from Sigma-Aldrich with 99.9% purity. Required amount of CTAB (0.105 M) was added to 100 mL of distilled water and stirred well to get viscous solution. Acetates of lithium, nickel, cobalt and manganese were mixed with the above

viscous solution at proper stoichiometric level (0.1: 0.033: 0.033: 0.033 M) and stirred well. The resultant solution was dried on a hot plate until to get powder precursors. The obtained black colour powder was ball milled with stainless steel balls for 12 h. Further, the powders were calcined at 950 °C for 10 h in the air atmosphere, at a heating rate of 3 °C/min. The sample code was given as **BM-333**. Another set of sample was prepared in the similar process as discussed above, except for ball milling the precursors. The sample code was fixed as **SG-333**.

X-ray diffraction patterns (XRD) of the samples were obtained using SHIMADZU-XRD-6000 diffractometer with $\text{Cu-K}\alpha$ radiation. Morphology analysis was made using Field Emission Scanning Electron Microscope (JEOL-JSM 6700F). The 2016 size coin cells were assembled in an Ar-filled glove-box at O_2 and H_2O level of less than 1 ppm. The cyclic voltogram (CV) was made in the voltage range 3.0-4.5 V using Macpile II (Biologic, France) system. Galvanostatic cycling was carried out at room temperature (25 °C) by using a Bitrode multiple battery testers (Model SCN, Bitrode, USA).

3. RESULT & DISCUSSION

3.1 XRD analysis

Powder XRD pattern of the as prepared $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ compound is shown in Fig. 1. Both the diffraction patterns were indexed on the basis of $\alpha - \text{NaFeO}_2$ hexagonal layer structure with space group $R-3m$. The XRD pattern of BM-333 was relatively quiet narrow, indicating high crystalline nature of the samples, and shows no impurities. Whereas, SG-333 shows extra broad peaks which is attributed to NiO impurities (indicated by * symbol).

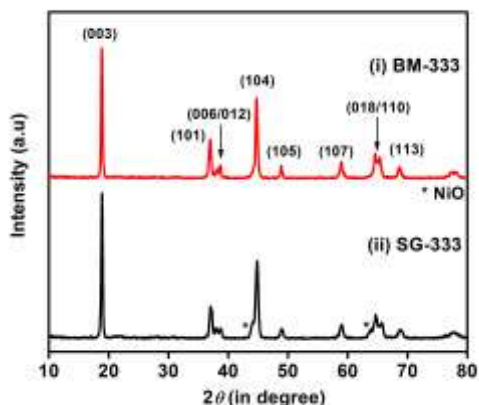


FIGURE 1. Powder XRD patterns of NCM compounds prepared by sol-gel method, (i) ball milling the precursor (ii) with no ball milling

The degree of cation mixing (interchange between $\text{Li}^+/\text{Ni}^{2+}$) in the sample can be calculated from the integrated intensity ratio of (003) and (104) planes. In general, the intensity ratio I_{003}/I_{104} is greater than 1.2 indicate less amount of cation mixing in the sample [3, 5]. Both BM-333 and SG-333 samples shows the integrated intensity ratio is greater than 1.2 indicating low cation mixing, but the integrated intensity of SG-333 was found to be 1.9, which is slightly higher than BM-333 (1.7) suggesting that very lower cation mixing was obtained.

3.2 FESEM analysis

In order to evaluate the effect of ball milling on morphology of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ compound FE-SEM were taken and images are shown in Fig.2 a, b. As can be seen in these figures, the particle size of the BM-333 was relatively smaller than that of SG-333 with less agglomeration, but in both cases the primary particles are much finer.

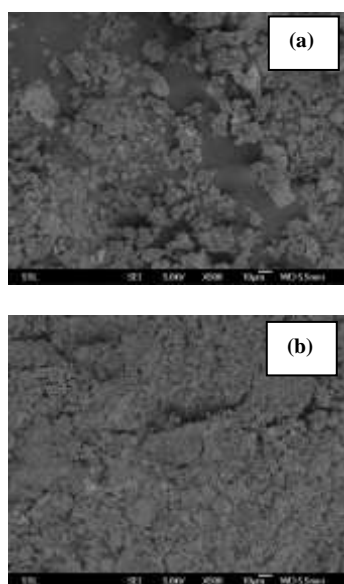


FIGURE 2. SEM images of a) BM-333 and b) SG-333

3.3 Electrochemical analysis

Fabricated CR2016 coin cells with as prepared $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode were charged and discharged at a current density of 30 mA/g in the voltage range, 2.5-4.4 V vs. Li at room temperature, and the first and 50th charge discharge profiles are shown in Fig. 3 a, b. The single plateau region during charge and discharge process was observed at 3.9 V and 3.8 V vs. Li, respectively and was matched with the results from CV (inset of Fig.4). The half cell made with sample BM-333 delivers an initial discharge capacity of 84 mAh/g, whereas SG-333 delivers only 73 mAh/g. A discharge capacity of 71 mAh/g was observed in the 50th cycle indicating 12% of capacity fading for cell made with BM-333. But in the case of cell made with SG-333, the capacity fading was only 3%. In both cases the discharge capacity at 50th cycle shows similar values. The capacity vs. cycle number graph for BM-333 and SG-333 are shown in Fig. 4. We can observe from the graph that the reversible discharge capacity for cell made with SG-333 remains stable from cycle 1 to the end of 50 cycles. It indicates the better electrochemical stability of the cell made with SG-333 sample, owing to its lower cation disorder.

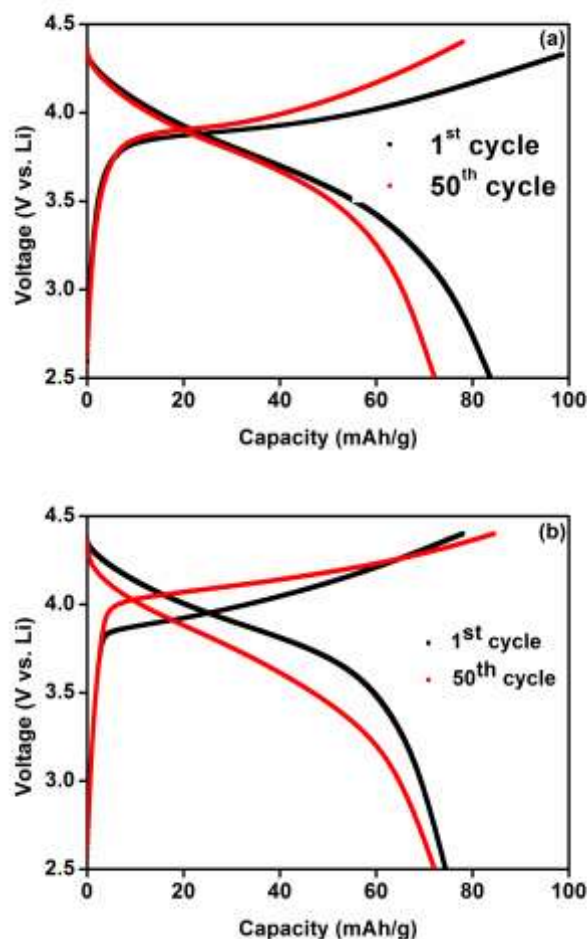


FIGURE 3. Galvanostatic charge discharge curve of half cells made using a) BM-333 and b) SG-333

Cyclic Voltammograms (CV) were measured in the voltage range of 3.0 to 4.5 V at a scan rate of 0.058 mV/s and shown in Fig. 4(inset). The CV plot shows broad anodic peak (oxidization, deintercalation of lithium) at ~ 4.2 V vs. Li and

corresponding cathodic peak (reduction, intercalation of lithium) of ~ 3.8 V vs. Li in the first cycle for both the cells. The redox peak was due to the presence of electrochemical active nickel ($\text{Ni}^{2+}/\text{Ni}^{4+}$).

4. CONCLUSION

The influence of ball milling the precursor before calcination, for the compound $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared by CTAB assisted sol-gel method was investigated; Ball milling the precursor was found to control the formation of impurity phases, but resulted in slight increase in cation disorder. The SEM analysis of the prepared materials showed much finer primary particles with less agglomeration for sample made by ball milling the precursor. It was found that even though SG-333 shows NiO impurity phase and agglomerated particles, it delivers better electrochemical stability than ball milled one due to the very low cation disorder than BM-333, but still the capacity need to be improved. Overall, the present works reveals the effect of ball milling with respect to phase purity and cation disorder. Further work is required to optimize the parameters like total metal ion: CTAB ratio and ball milling duration to achieve the best electrochemical performance.

6. REFERENCES

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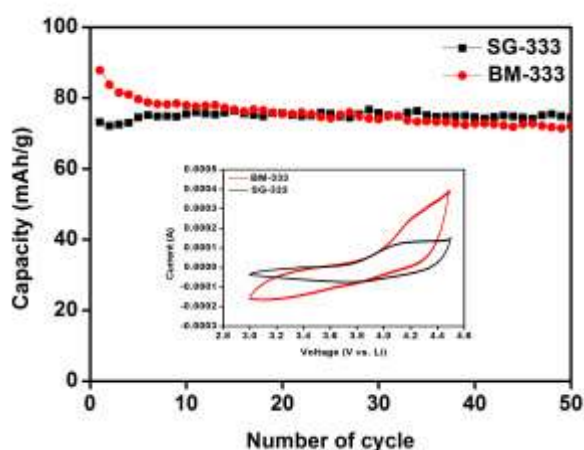


FIGURE 4. Capacity vs. cycle number graph (inset: CV curve) for half cells made using BM-333 and SG-333

5. ACKNOWLEDGEMENT

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