COMPARATIVE STRUCTURAL STUDIES OF LIN_{0.8}CO_{0.1}MNO_{0.1}O_{2} CATHODE MATERIALS PREPARED BY SOL-GEL VERSUS SOLID-STATE-REACTION METHOD.

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Abstract

In the present work, the layered structure oxide LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} (NCM 811) is synthesized by sol-gel auto combustion and solid state reaction methods. Microstructural and optical properties are investigated by XRD, FE-SEM with EDS, FT-IR and bonding nature studies. Characterization of the crystalline powders, phase identification, particle size examination, and morphological studies are done using XRD and FE-SEM. From FT-IR and UV-NIR studies, vibrational bands are identified in the range of 400-2000 cm\(^{-1}\) representing the MO\(_2\) (M = Ni, Co & Mn) layers.

Introduction:

Lithium-ion batteries (LIBs) have been predominately applied in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high energy density, long cycle life, and energy safety and good rate capability [1-5]. Some researchers have been found Ni-rich cathode materials are the power of Lithium-ion batteries superior energy density due to its high capacity and low cost [6-8]. But, these materials are so many problems are there, such as poor cycling, commercially poor thermal stability, cation mixing [9-10]. Such as these problems are rectify in cations (substitute Ni ions by Ti, Cr, Na, Zr, Mg and non-metallic ion, like F) [11-13] bulk doping (obviously increase the lithium layer spacing, resulting in rapid lithium-ion diffusion into the electrode) [14-15] and surface coating (achieve superior performances due to less unwanted surface functional groups, hydrogen fluoride (HF) scavenger and physical obstacle and conducting media for lithium-ion and electron) [16-18] have been solved these issues. Therefore, great efforts have been reported that it can cause long cycle life owing to enhanced thermal and structural stability and reduced transition metal dissolution [19-20].

Finally, in this paper, we prepared LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} (NCM-811) cathode materials prepared by two different methods such as sol-gel auto-combustion and solid-state reaction methods. Therefore, we believe that the NCM-811 cathode material is a beneficial approach for high performance and reliability of lithium-ion batteries.

Preparation and Characterizations

Sol-gel auto-combustion method: We synthesized LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} cathode materials by using the sol-gel method. A stoichiometric amount of LiNO\(_3\) (AR) and Ni(NO\(_3\))\(_2\).6H\(_2\)O (AR), Co(NO\(_3\))\(_2\).6H\(_2\)O (AR) and MnC\(_2\)H\(_4\).4H\(_2\)O (AR) are dissolved in distilled water. The aqueous solution of citric acid which is acting as chelating agent is added to the mixer of the metal ion solution according to their molar ratio of 1:1. At the same time, an Ammonia solution as a precipitation agent is separately added. The reaction temperature is kept at 80\(^\circ\)C and pH is
controlled by ammonia solution to $8 \sim 9$. The solutions are added together under stirring at $130{^\circ}C$ for 10 hours, forming a sol solution. The sol solution is vaporized at $130{^\circ}C$ till the dry gel is formed, followed by the heat treatment at $500{^\circ}C$ for 6h in the air with a $5{^\circ}C$/min heating rate to eliminate the organic residues. The powders are thoroughly ground and then sintered at $850{^\circ}C$ for 20 hours in the air to obtain the required compounds.

**Solid-state reaction method:** The cathode compositions are synthesized by a solid-state reaction method from stoichiometric amounts of Li$_2$CO$_3$ (Merck 99.9%) and NiO (Merck 99.9%), CoO (Merck 99.9%) and MnO (Merck 99.9%). A slight excess amount of lithium (5%) was used to compensate for any loss of the metal which might have occurred during the calcination at high temperatures. The mixture of the starting materials is sufficiently mixed and after grinding the powder it is then heat-treated in the air at $500{^\circ}C$ for 5 h and it is again ground and mixed, and calcined again at $750{^\circ}C$ for 20 h. Then, this powder was cooled at a rate of $5{^\circ}C$/min. Finally, the powder was ground and mixed, and calcined again at $850{^\circ}C$ for 20 h in the air using a muffle box furnace.

The powder X-ray diffraction (XRD) data of the samples are collected on a Rigaku Cu-Kα diffractometer with diffraction angles of $20^\circ$ and $80^\circ$ in increments of 0.02°. The unit cell lattice parameter is obtained by the least square fitting method from the d-spacing and (hkl) values. Further, the crystal size of the sample is obtained using the Scherrer's equation from the XRD pattern. The particle morphology of the powders is observed applying the field effect scanning electron microscopy images taken from CarlZeiss, EVOMA 15, Oxford Instruments, Inca Penta FETx3.JPG. Fourier transform infrared (FT-IR) spectra are obtained on a Shimadzu FT-IR-8900 spectrometer using KBr pellet technique in the wavenumber range between 350 and 800 cm$^{-1}$.

**Results and Discussions:**

**TG studies**

Figure 1 represents the TG curves of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ gel precursors synthesized by sol-gel auto combustion method using citric acid as a chelating agent. The formation of synthesized material takes place around $500{^\circ}C$, which is observed from the TG curve. The major weight loss (around 50%) occurs from $290 \sim 485{^\circ}C$, which leads to the decomposition of acetates corresponding exothermic peak appears around $485{^\circ}C$. After $485{^\circ}C$ TG curves become flat which indicates that no weight loss occurs in this region; further heating only assists the crystallization event of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ material. Similarly, solid state reaction method the first weight loss region from 0 to $100{^\circ}C$ corresponds to the loss of absorbed water molecules. The next weight loss region ($100 \sim 290{^\circ}C$) indicates that the decomposition of the chelating agent. From figure 2 shown from the curves, there is an initial weight loss in the temperature range from room temperature to $310{^\circ}C$. This corresponds to the evaporation of methanol used during grinding to homogenize the mixture and the moisture absorbed during storage [21]. TG curve of the synthesized materials are shows significant weight loss (17.8%) between the temperatures $310{^\circ}C$ and $570{^\circ}C$. This loss may be due to the decomposition of the precursors Li$_2$CO$_3$, NiO$_2$, Co$_3$O$_4$, and MnO$_2$, and the reaction between the decomposed materials thereby to produce crystalline materials. Though, Li$_2$CO$_3$ is stable in air up to $750{^\circ}C$ and the melting point is $723{^\circ}C$, some studies have point out that Li$_2$CO$_3$ already reacts below $300{^\circ}C$ [22]. At the proposed temperature, the TG curve becomes more flattened, indicating stable phase is formed.

![Figure 1: TG/DTG curve for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ material is prepared by sol-gel auto-combustion method](image-url)
XRD studies

X-ray diffraction patterns for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_{2}$ sample prepared by sol-gel and solid-state reaction methods are shown in Figure 3. Both XRD patterns of the powders prepared by sol-gel auto-combustion and solid-state method show X-ray peaks corresponding to LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_{2}$ can be indexed to a phase-pure hexagonal structure with the space group of R3m and match well with diffraction file (JCPDS) 74-0919 [23]. The synthesized material is with no evidence of any impurities, indicating that the uniform solid solution has been formed in the compounds [24]. The crystal lattice parameters of the compounds are calculated by using the unit cell program and presented in Table 1. Li$_{0.6}$, MO$_{0.4}$ where M=Ni, Co and Mn occupy 3b, 3a positions and O is in the 6c position in Fig. 1. Which should be related to the larger radii of Li$^+$ (0.72Å) is thus their cell volume should be expanded according to Vegard's law. We believe that this would be attributed to the decrease in the Ni$^{2+}$ (0.69Å), Co and Mn (ionic radii) content caused by the charge compensation for the compound in both methods to remain in electrically neutral. The overall high-intensity ratio of the (0 0 3) and (1 0 4) peaks and the clear splitting of the (0 1 8) and (1 1 0) peaks indicate that the compounds have a good structure [25].

The a-axis increases linearly from 2.893 to 2.896 Å and the c-axis decreases from 14.238 to 14.23 Å. The ratio of c/a decreases from 4.922 to 4.915Å due to the substitution of Ni ions by Co and Mn ions probably result from the severe cation mixing because it has the lowest intensity ratio of (0 0 3) to (1 0 4) peaks as given in Table 1. The unit-cell volume also increases from 103.205 to 103.371 Å$^3$. The crystallite sizes of the cathode powders are prepared from the sol-gel auto-combustion and solid-state reaction methods are shown in 9.8 nm and 12.67 nm. The Bragg intensity ratio of I(0 03)/I(1 04), which is a signature of the cation-mixing and Its values are 1.1602 and 1.1361. It has been reported that if this value is < 1.2 for the undesirable cation mixing would occur in the lattice. The crystallite size can be estimated using Scherrer’s formula given in eq. (1).

$$D = \frac{0.9}{\beta \cos \theta} \quad (1)$$

where, $\lambda$ is the wavelength of X-ray used, which is CuK$\alpha$ radiation ($\lambda$= 1.5406 Å), and $\beta$ is the full width at half-maximum of the diffraction peak corresponding to 20. Using the above equation the sizes of the crystallites are found to be in the range of nanometer [26]. The crystallite size is measured by taking the average of three mainline widths, which are obtained from the XRD patterns. The crystallite size calculated using the Debye Scherrer’s formula is listed in the table. 1.

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**Figure 2**: TG/DTG curve for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_{2}$ material is prepared by solid state reaction method

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**Table 1**: The sol-gel and solid state reaction methods

| Samples     | a(Å)  | c(Å)  | c/a   | Cell volume (Å$^3$) | $I_{003}$/I$_{104}$ | R-factor ((I$_{006}$+I$_{102}$)/I$_{110}$) | Crystallite size (nm) |
|-------------|-------|-------|-------|---------------------|---------------------|------------------------------------------|---------------------|
| NCM811 (SG) | 2.875 | 14.336| 4.921 | 103.31              | 1.67                | 20.6                                     | 7.43                |
| NCM811 (SSR)| 2.893 | 14.243| 4.923 | 103.26              | 0.99                | 20.8                                     | 10.77               |
Figure 3: X-ray diffraction patterns for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ material is prepared by sol-gel auto-combustion and solid state reaction methods.

**FE-SEM with EDS studies**

Figure 4 and 5 shows the FE-SEM images of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ compound in sol-gel auto-combustion and solid-state reaction method. Both compounds have a smooth, well-shaped and particle-agglomerated morphology [27]. The average size of the primary particle is about 500 nm and 2 µm. These samples have the accumulation morphology, but the primary particles become well-shaped and their size increases. In this results suggest that foreign metal ion doping could improve the crystallinity of the synthesized samples. The precursor powders with spherical shape and dense morphologies were necessary to prepare the cathode powders with spherical shape and dense structure by both methods with a lithium component. Figure 3 and 4 shows the EDS spectra, qualitative results and elemental analysis that confirms the presence of Ni, Co, Mn and O in LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathode material. It is clearly observed that the spectra show the appropriate ratios of the elements. Lithium is not observed in the EDS spectrum because it has too low of an atomic number to be detected with EDS.
Figure 5: FE-SEM with image for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ material is prepared by solid state reaction method.

Figure 6: FT-IR spectra LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ material is prepared by sol-gel auto-combustion and solid state reaction methods.

FT-IR studies
From the figure 6 represents the mode of vibrations for transition metals LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ in the 400–1000 cm$^{-1}$ region which is largely associated with the vibrations of MO$_6$ where M= Ni, Co and Mn and LiO$_6$ octahedral units. The peaks at 613 cm$^{-1}$ and 614 cm$^{-1}$ are listed in the table. 2 the vibration bending modes of MO$_6$ i.e. $\nu$ [(M–O–Li)], the weak band around 430 cm$^{-1}$ is assigned for the asymmetric stretching of Li–O in LiO$_6$ environments. The structure of the synthesized sample by the ion-exchange reaction was further characterized by FT-IR. Figure 4(b) shows the IR spectra of the synthesized sample prepared by solid state reaction method at air atmosphere. It can be seen that strong absorption peaks are observed in the region 400-1000 cm$^{-1}$. The typical absorption peaks at 515.2 cm$^{-1}$ and 859.4 cm$^{-1}$ which are in agreement with those for LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ prepared by solid-state reaction at high temperature, are observed. The LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ crystal can be considered to be composite metallic oxidant in which Li-ion layer is sandwiched between Ni, Co and Mn and O layers.

Optical properties
It was carried out by measuring the diffuse reflectance spectroscopy in UV-Vis range. The spectrum was taken in the range of 200-700 nm. Fig.1 shows the prepared LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 nano-powders synthesized by sol-gel auto-combustion method of the diffused reflectance spectra (absorbance as a function of wavelength). The absorption edges are homogeneous with no other band observed, which confirm that the prepared samples (both methods) are LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 layered structure. Those absorption band at around 364.5 nm to 385.5 nm may be due to the MO (M=Ni, Co and Mn) nanoparticles. The absorption edge of the bulk spinel cathode material is around 320 nm and 472 nm [31-32]. The band gap energy was calculated from the diffuse-reflectance spectra by plotting the square of the Kubelka-Munk function given as [33],

\[ K = \frac{(1 - R)^2}{2R} \]

where \( K \) is reflectance transformed according to Kubelka Munk, \( R \) is reflectancy (%), \( h\nu \) is the photon energy. The \( E_g \) were measured with the help of reflectance spectra plotting graphs of \((K^2\nu)^2\) versus \((\nu)\).

**Figure 1:** UV-visible spectra of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 material is prepared by sol-gel auto-combustion

**Conclusions:**
The layered structure material LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 is synthesized by sol-gel auto-combustion and solid-state reaction method. The cathode material resembled the hexagonal \( \alpha \)-NaFeO_2 structure which was confirmed from the XRD pattern. This result strongly supports the results obtained for the preparation method is sol-gel.

**References:**
1. J. Eom, M. G. Kim, J. ChoStorage characteristics of LiNi_{0.8}Co_{0.1+x}Mn_{0.1-x}O_2 (x=0, 0.03, and 0.06) cathode materials for Lithium batteries, J. Electrochem. Soc., 155 (2008), p. A239
2. J.-Y. Liao, A. ManthiramSurface-modified concentration-gradient Ni-rich layered oxide cathodes for high-energy lithium-ion batteries, J. Power Sources, 282 (2015), pp. 429-436
3. Y. Su, Y. Yang, L. Chen, Y. Lu, L. Bao, G. Chen, Z. Yang, Q. Zhang, J. Wang, R. Chen, S. Chen, F. WuImproving the cycling stability of Ni-rich cathode materials by fabricating surface rock salt phase, Electrochim. Acta, 292 (2018), pp. 217-226
4. J. Fu, D. Mu, B. Wu, J. Bi, H. Cui, H. Yang, H. Wu, F. WuElectrochemical properties of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode material modified by Lithium tungstate under high voltage, ACS Appl. Mater. Interfaces, 10 (2018), pp. 19704-19711
5. L. Zhang, H. Wang, L. Wang, Y. CaoHigh electrochemical performance of hollow corn-like LiNi_{0.8}Co_{0.1}M_0.1O_2 cathode material for lithium-ion batteries, Appl. Surf. Sci., 450 (2018), pp. 461-467
6. S. Chen, T. He, Y. Su, Y. Lu, L. Bao, L. Chen, Q. Zhang, J. Wang, R. Chen, F. Wu
   Ni-rich LiNi0.8Co1.2Mn0.2O2 oxide coated by dual-conductive layers as high performance cathode material for Lithium-ion batteries, ACS Appl. Interfaces, 9 (2017), pp. 29732-29743.

7. X. Xiong, Z. Wang, P. Yue, H. Guo, F. Wu, J. Wang, X. Li
   Washing effects on electrochemical performance and storage characteristics of LiNi0.8Co1.2Mn0.2O3 as cathode material for lithium-ion batteries, J. Power Sources, 222 (2013), pp. 318-325.

8. T. Li, X. Li, Z. Wang, H. Guo
   A short process for the efficient utilization of transition-metal chlorides in lithium-ion batteries: a case of Ni0.8Co0.2Mn0.1O2 and LiNi0.8Co0.2Mn0.2O2, J. Power Sources, 342 (2017), pp. 495-503.

9. Y. Su, G. Chen, L. Chen, W. Li, Q. Zhang, Z. Yang, Y. Lu, L. Bao, J. Tan, R. Chen
   Exposing the {010} planes by oriented self-assembly with nanosheets to improve the electrochemical performances of Ni-Rich Li[Ni0.8Co0.1Mn0.1]O2 microspheres, ACS Appl. Interfaces, 10 (2018), pp. 6307-6414.

10. Du R., Bi Y., Yang W., Peng Z., Liu M., Liu Y., Wu B., Yang B., Ding F., Wang D.
    Improved cyclic stability of LiNi0.8Co1.2Mn0.2O2 via Ti substitution with a cut-off potential of 4.5V, Ceram Int, 41 (2015), pp. 7133-7139.

11. J. Cho, T.-J. Kim, J. Kim, M. Noh, B. Park
    Synthesis, thermal, and electrochemical properties of ALPO4-coated LiNi0.8Co0.1Mn0.1O2 cathode materials for a Li-Ion Cell, J. Electrochem. Soc., 151 (2004) A1899-A1904.

12. D. Phan, V. Tran, N. Tran, T. Pham, N. Tran, T. Do
    Enhanced electrochemical properties of lithium-reactive V2O5 coated on the LiNi0.8Co0.2Mn0.2O2 cathode material for lithium-ion batteries at 60 °C, J. Power Sources, 292 (2015), pp. 1284-1288.

13. J. Cho, H. Kim, B. Park
    Comparison of overcharge behavior of ALPO4-coated LiCoO2 and LiNi0.8Co0.2Mn0.2O2 cathode Materials in Li-Ion Cells, J. Electrochem. Soc., 151 (2004).

14. S.W. Lee, M.S. Kim, J.H. Jeong, D.H. Kim, K.Y. Chung, K.C. Roh, K.B. Kim
    LiNi0.8Co0.2Mn0.2O2 surface coating on Ni-rich LiNi0.6Co0.1Mn0.3O2 by a citric acid assisted sol-gel method: improved thermal stability and high-voltage performance, J. Power Sources, 360 (2017), pp. 206-214.

15. J.D. Steiner, L. Mu, J. Walsh, M.M. Rahman, B. Zydelwski, F.M. Michel, H.L. Xin, D. Nordlund, F. Lin
    Accelerated evolution of surface chemistry determined by temperature and cycling history in nickel-rich layered cathode materials, ACS Appl. Mater. Interfaces, 10 (2018), pp. 23842-23850.

16. P. Yan, J. Zheng, J. Liu, B. Wang, X. Cheng, Y. Zhang, X. Sun, C. Wang, J.-G. Zhang
    Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries, Nature Energy, 3 (2018), pp. 600-605.

17. L.S. Zhang, K. Jin, L.Z. Wang, Y. Zhang, X.F. Li, Y.H. Song
    High capacity Li1/2Mn0.5Ni0.5O2 cathode materials synthesized using mesocystal precursors for lithium-ion batteries, J. Alloys Compd., 638 (2015), pp. 298-304.

18. L. Zhang, H. Wang, L. Wang, Y. Cao
    High electrochemical performance of hollow corn-like LiNi0.8Co0.2Mn0.2O2 cathode material for lithium-ion batteries, Appl. Surf. Sci., 450 (2018), pp. 461-467.

19. Min Nie, Yunfei Xia, Zhenbo Wang, Fuda Yu, Yin Zhang, Jin Wu, Bing Wu
    Effects of precursor particle size on the performance of LiNi0.5Co0.5Mn0.5O2 cathode material, Ceram. Int., 41 (2015), pp. 15185-15192.

20. Ilkyu Hwang, Chul Wee Lee, Jae Chang Kim, Songhun Yoon
    Particle size effect of Ni-rich cathode materials on lithium-ion battery performance Mater. Res. Bull., 47 (2012), pp. 73-78.

21. Minmin Chen, Enyue Zhao, Dongfeng Chen, Meimei Wu, Songbai Han, Qingzhen Huang, Limei Yang, Xiaolin g Xiao, Zhongbo Hu
    Decreasing Li/Ni disorder and improving the electrochemical performances of Ni-rich LiNi0.8Co0.2Mn0.2O2 by Ca doping, Inorg. Chem., 56 (2017), pp. 8355-8362.

22. Duc-luong Vu, Jae-won Lee
    NaN-doped layered LiNi0.8Co0.1Mn0.1O2 with improved rate capability and cycling stability, J. Solid State Electrochem., 22 (2018), pp. 1165-1173.
27. Kang Wu, Guofeng Jia, Xuehui Shangguan, Guowei Yang, Zenghu Zhu, Zhengjun Peng, Qin Zhuge, Faqiang Li, Xiaoling Cui: Improved high rate performance and cycle stability for LiNi_{0.8}Co_{0.2}O_{2} by doping of the high valence state ion Nb^{5+} into Li^+ sites, J. Alloy. Comp., 765 (2018), pp. 700-709

28. H.Q. Pham, G. Kim, H.M. Jung, S.-W. Song, Adv. Funct. Mater., 28 (2018), p. 1704690

29. G. Socrates, Infrared Characteristic Group Frequencies, Table and Charts, (second ed.), John Wiley & Sons, New York (1994)

30. A. Vijayamari, K. Sadayandi, Suresh Sagadevan, Preeti Singh, J. Mater. Sci.: Mater. Electron., 28 (2017), pp. 2739-2746.

31. Lehlohonolo F. Koao, Setumo V. Motloung, Tshwafo E. Motaung, Mesfin A. Kebede, Physica B: Condensed Matter, 535 (2018) 323-329.

32. H. Bai, Z. Liu, D.D. Sun, Int. J. Hydrog. Energy, 37 (2012), pp. 13998-14008.