SYNTHESIS AND CHARACTERIZATION OF NOVEL P-2 TYPE LAYERED OXIDES FOR ELECTRODES

Soumava Palit

TIFR Centre for Interdisciplinary Studies, Hyderabad, (India)

ABSTRACT

This paper is about the synthesis and characterization of the P-2 type layered oxides that hold a lot of promise in the making of electrodes for sodium ion rechargeable batteries,a possible successor of the lithium ion battery.However, the selection of materials for electrodes has been a challenge.Herein, a novel, Na+ion intercalation material, NFMO issynthesized by a high temperature solid state reaction. Characterization studies using XRD,SEM,EDAX, was undertaken to confirm the structure that accommodates sodium insertion.Two more variants of the layered oxides,nfco and nmco werealso taken up to see the similarities in structure with nfmo likewise, for possible battery applications.

Keywords: Characterization, Layered Oxide, NFMO, NFCO, NMCO, Solid State Reaction.

I. INTRODUCTION

Secondary or rechargeable batteries can be recharged instead of disposing by reversing their electro chemical reaction. The rapid growths of the worldwide demand of lithium for batteries (LIBs) canpossibly lead to a shortage of its reserves. Sodium batteries represent a promising alternative because they enable much higher energy densities than other battery systems, with the exception of LIBs, and are not limited by sodium availability. NIB can be applied for large scale storage of energy. In this study, we synthesize and characterize a promising layered material for cathode$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$.NFMO by a high temperature solid state reaction.

II. CHALLENGES

The large cation radius of Na (1.02 Å) versus Li (0.76 Å) and its general preference for octahedral or prismatic coordination limits the structural variability and choice of Na insertion materials in crystalline materials. However, since sodium is so abundant (4th most abundant element in the Earth crust) sodium-based batteries operating at ambient temperature could provide a low-cost energy storage option. Thus a search for new intercalation host materials to help enable high-performance batteries is essential to push forward the implementation of new Na-ion battery technologies.

2.1 Methodology

NIB is still an experimental field and it is going to be a while before it is commercialized. The literature reveals a hierarchy of materials for cathodes. A promising material reported in the journal Nature, $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ is chosen for this study. Komaba and colleagues investigated the sodium intercalation process in P2−$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$. These results will contribute to development of rechargeable batteries from the earth-abundant elements operable at room temperature. Novel materials are synthesized taking cue from the latest literature by solid state reaction. Also simultaneously $Na_{2/3}Fe_{1/2}Co_{1/2}O_2$ and $Na_{2/3}Mn_{1/2}$ $Co_{1/2}O_2$ are made as additional cathodes to compare the characterization and performance. Detailed characterization was embarked upon for these electrode materials namely using XRD, SEM, TEM.

2.1.1 Classification of Electrodes

Fig 1 shows the different reaction mechanism of electrode materials.

Intercalation electrodes: This is most common. Electrode is essentially a host structure that can contain Li. Example:$LiCoO_2$, $LiFePO_4$, and Graphite.

Conversion electrodes: This is less common. Electrodes undergo a chemical reaction where its structure is created and destroyed during operation. Example: FeF_3, Li_2O_2.

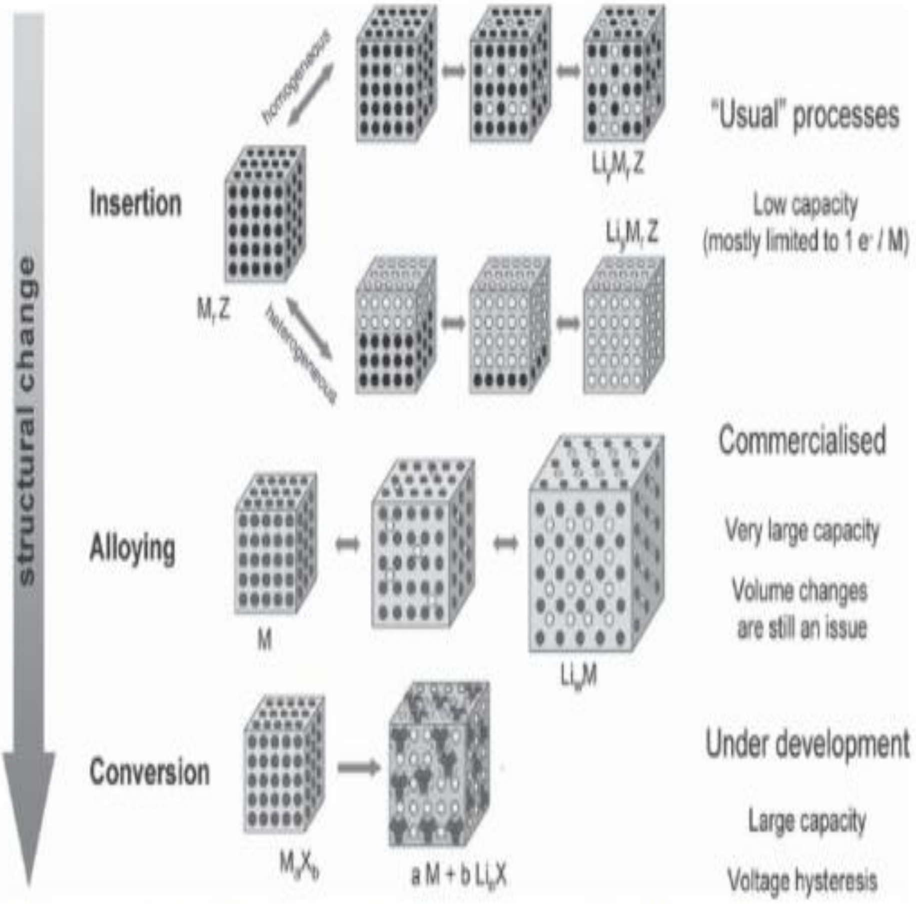


Figure 5. Schematic illustration of the reaction mechanisms of electrode materials with Li ions in LIB. Reproduced with permission.[7] Copyright 2009, Royal Society of Chemistry.

Fig 1 Different Reaction Mechanism of Electrode Materials

[Ref. Adv.Energy Mat.2012.2, 710-721]

Various categories of compounds used as electrodes in NIB are shown below in **Table 1**.

Table 1 Various Categories Of Compounds Used As Electrodes In NIB.

Different aspects of Na Ion chemistries			
ANODES		**ELECTROLYTES**	**CATHODES**
Metallic Sodium		Liquid Electrolyte	Oxides : Na0.44MnO2 tunnel structure oxides. Layered Na0.7MnO2 Vanadium Oxides- Eg: Layered V2O5 or tunnelled NaxV2O5 and Iron Oxides – Fe3O4 inverse spannel Layered sodium transition metal oxides. Type AMO2 (A=Li, Na. M=CoMnNi, Cro).
Sodium Alloys	Na^nM form of alloys. Eg: M=Pb		
Carbon Based Materials (non graphitic)	Hard Carbons from Various sources		
	Glassy Carbons and other amorphous Carbons like carbon black	Sold Electrolyte	Polyanion NASICON type compounds NaTi2(PO4)3, Na2FePO4F
Metal oxide materials	Ti based intercalation compounds. eg: $Na_2Ti_3O_7$		Sulphides & Sulphates TiS2(Intercalation)
	Conversion compounds of cobolt. eg: $NiCO_2O_4$		Florides & Phosphates NaFeF3 (Perovskite)
Intermetallic Anodes	Multi component Na alloying reactions with metals. Eg: SnSb/C nanocomposites		

2.1.2 Introduction to Layered Materials as Cathode

Layered oxides are the subject of intense studies either for their properties as electrode materials for high-energy batteries or for their original physical properties due to the strong electronic correlations resulting from their unique structure. Here we would synthesize and use $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ and characterize it.

The layered Na_xMO_2 materials can be categorized into two major groups which are P2 and O3 type. The first letter P or O refers to the nature of the site occupied by alkali ion (prismatic or octahedral), and 2 or 3 refers to the number of transition metal layers in the repeat unit perpendicular to the layering.

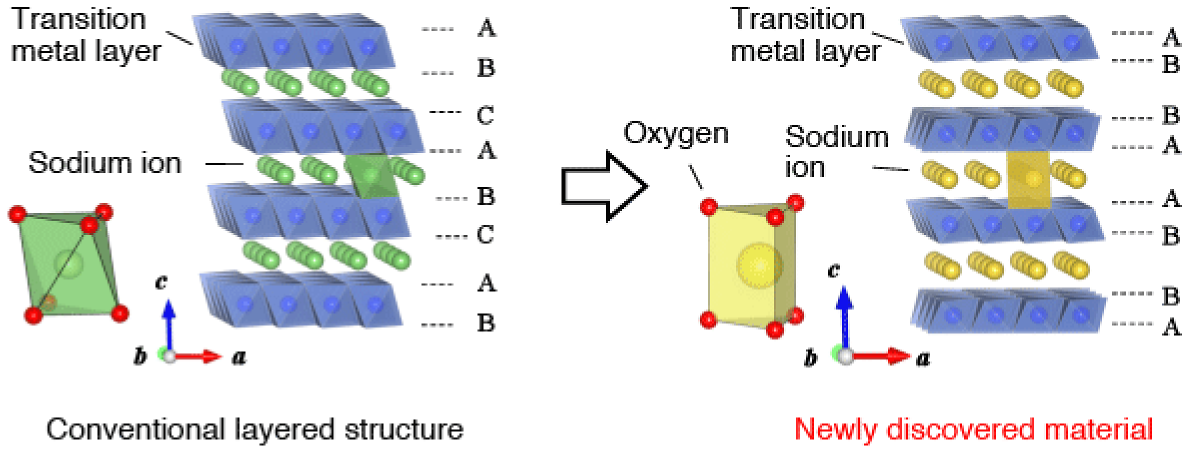


Fig1.1Comparison of conventional layered oxide (left) and the newly discovered Fe-based layered material (NFMO). [Ref: Spring.8 Press Release 30 Apr 2012]

2.1.3 Classification of P2 Type for NIB

Recent investigations have shown that especially 2D-layered transition metal oxides are promising candidates as cathodes materials in sodium-ion batteries. For the development and design of layered cathode materials three major trends are visible here:

1. Replacing toxic and expensive transition metals like in $NaCrO_2$ by environmentally friendly and cheaper Mn-based materials, such as P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ or $Na[Ni_{0.33}Fe_{0.33}Mn_{0.33}]O_2$. A Comparison of conventional layered oxide and the newly discovered Fe-based layered material (NFMO) is shown in **Fig1.3**. One of the key differences lies in the oxygen coordination environment in relation to sodium ions.

2. Taking advantage of transition metal intermixing, like in $NaNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, in order to combine the several advantages of the different metals while erasing the drawbacks and challenges related to the pure oxides and

3. Stabilizing the sodium layered oxides by implementing smaller cations inside, such as $Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_2$.

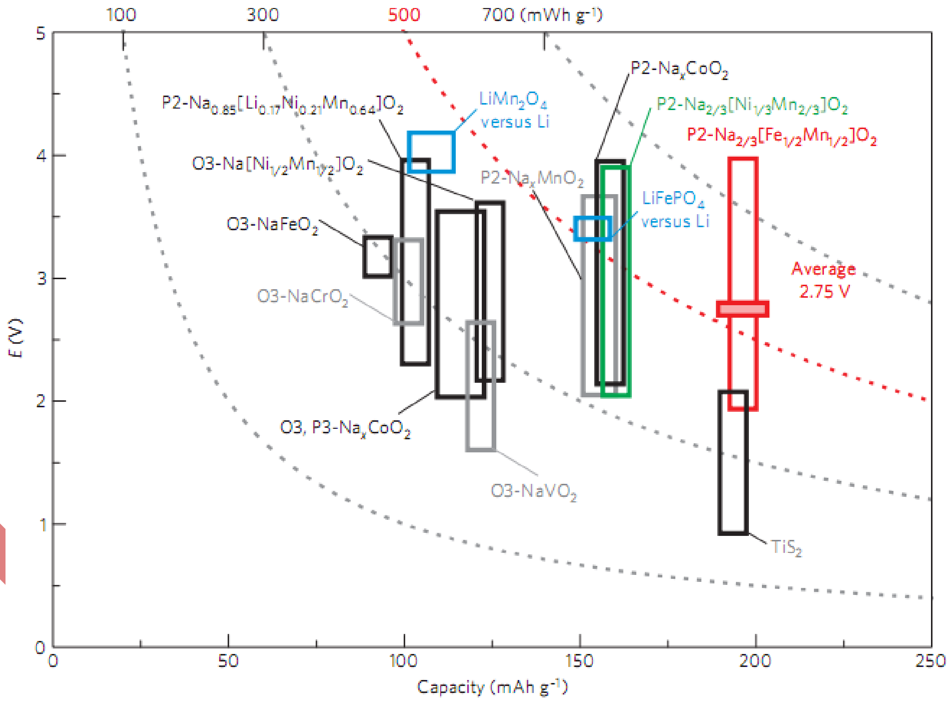


Fig 1.2 A Comparison Of Reversible Capacity And Operating Voltage Ranges Of The Layered Sodium Insertion Materials [8]

2.2 Experimental

In our choice of cathode toxic and expensive transition metals are replaced by environmentally friendly, earth abundant and cheaper Mn-based materials. The cathode is chosen for this work. This is prepared by a high temperature solid state reaction.

2.2.1 Synthesisofcathode

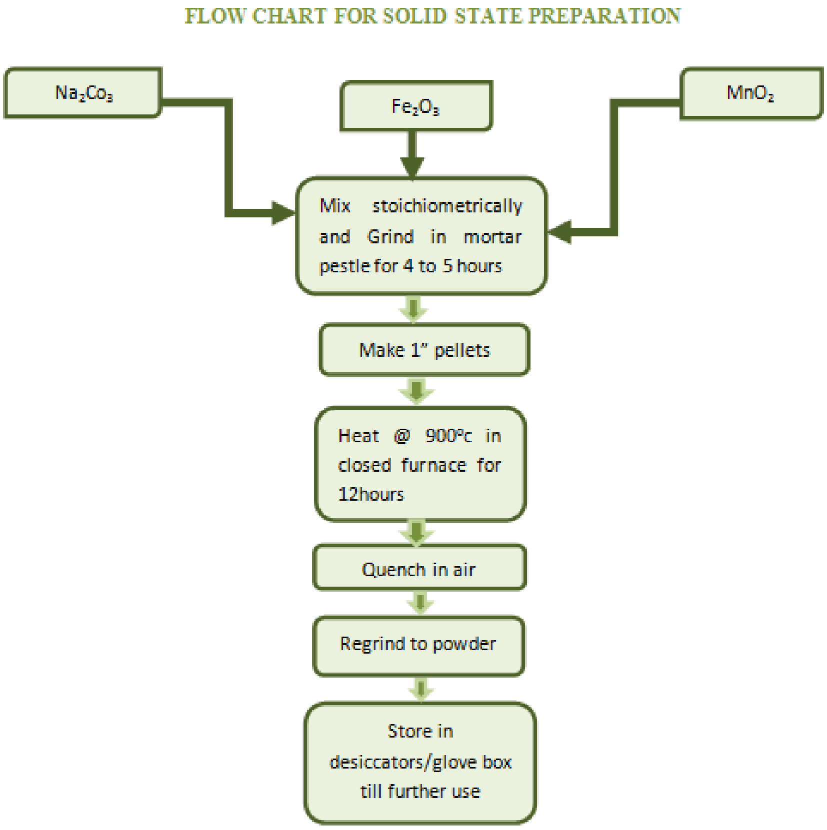


Fig 1.3 Flow Chart for Solid State Preparation

2.2.2 Solid State Reaction

The mostly widely used method for the preparation of polycrystalline solids (i.e. powders) is the direct reaction, in the solid state, of a mixture of solid starting materials. Herein we use the same method at high temperatures. Solids do not usually react together at room temperature over normal timescale and it is necessary to heat them to much higher temperature often 1000 to 1500^{o}C, in order for reaction to occur at an appreciable rate. This shows both the thermodynamics and kinetic factors are important in solid state reaction; thermodynamics consideration show whether or not a particular can occur and kinetic factors determine the rate at which the reaction occurs. The following two points are noteworthy.

a. There is a considerable differences in structure between reactants and products and
b. That there is a large amount of structural reorganization that is involved in forming the product: bonds must be broken and reformed and atoms must migrate, perhaps over considerable distances (on an atomic scale). Only at very high temperature do such ions have sufficient thermal energy to enable them occasionally to jump out of their normal lattice sites and diffuse through the crystal.

Fine grained materials should be used to maximize surface areas and hence reaction rates. Hence the grinding of the powder is very important. Mixtures should be heated first at a temperature for a few hours so that decomposition occurs in a controlled manner. This is because during heating, sintering and grain growth of both reactant and product phases usually occur in addition to the main reaction, causing a reduction in the surface area of the mixture. The reaction rate may also be speeded up by pelletizing the samples prior to heating, thereby increasing the areas of contact between the grains. The products of solid state reactions are usually in the form of a powder or a sintered, polycrystalline piece. The flow chart depicts the vital steps in the synthesis.

The XRD serves to indicate whether the reaction is complete, therefore, by showing that the original reactants have disappeared and by showing that unwanted side-products or intermediates have not formed.

2.2.3 Types of Layered Compounds

The layered Na_xMO_2 materials can be categorized into two major groups which are P2 and O3 type. The first letter "P" or "O" refers to the nature of the site occupied by alkali ion (prismatic or octahedral), and "2" or "3" refers to the number of transition metal layers in the repeat unit perpendicular to the layering. The larger Na-ion is stable in the more spacious prismatic site. The material chosen as cathode in this work is $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ which was reported in the journal NATURE and shows a better electrode performance. The reversible capacity reaches 190mAhg^{-1}, which corresponds to approximately 72% of the theoretical capacity. It was also revealed that the diffusivity of Na-ions in P2 structure is higher than that in the corresponding O3 structured compounds.

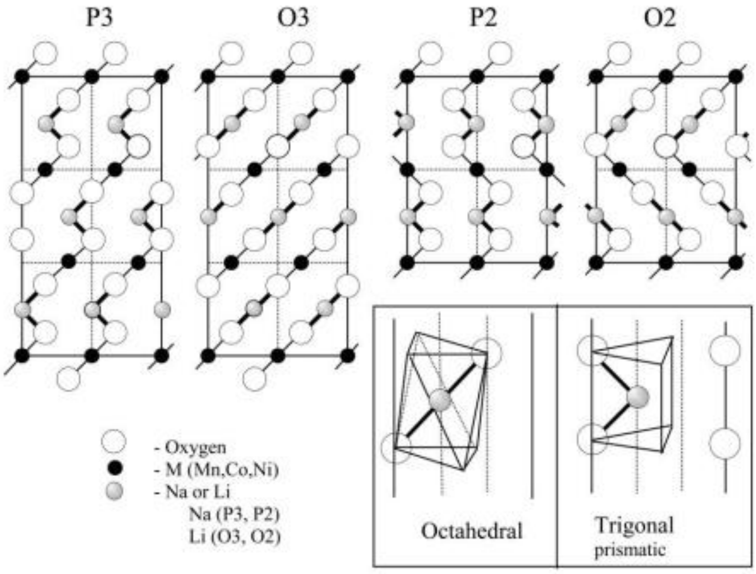


Fig 1.4 Different Types of Layered Structures: P3, O3, P2, O2 & Octrahedral & Prizmatic sites are shown

2.2.4 XRD

The XRD of NFMO obtained is in good agreement with the reported literature. In comparison NFCO shows multiphases due to the temperature being 900°C for the solid state reaction. NFMO has a stacking fault and hence is a defect structure and thus cannot be fit by available functions (like pseudo VOIGT).

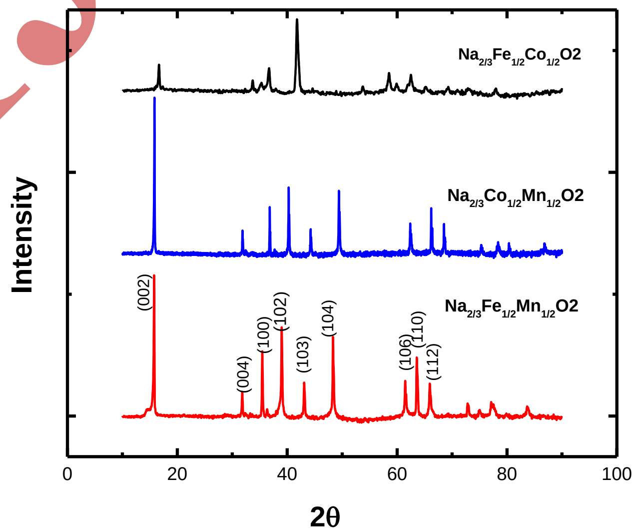


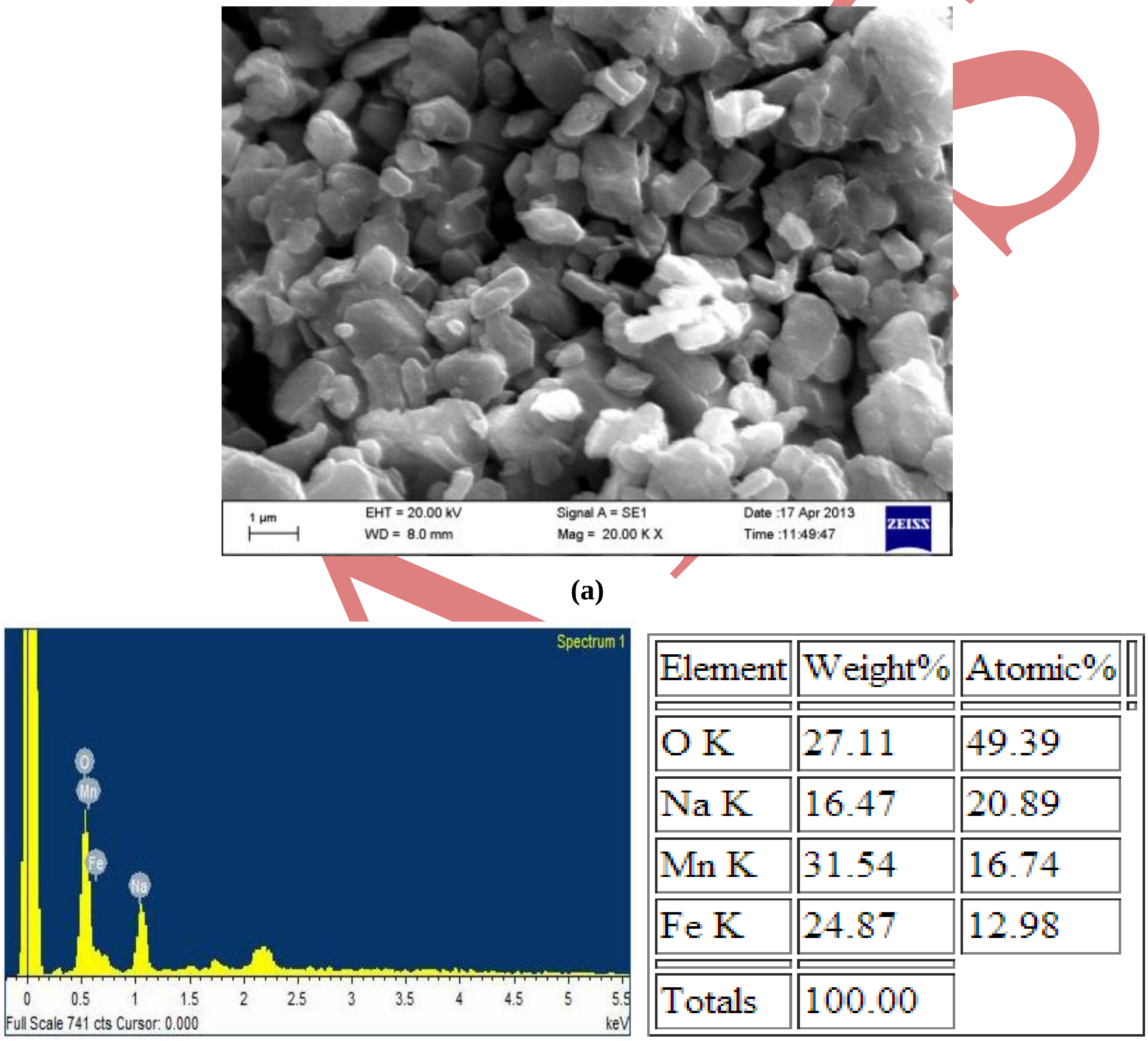
Fig 1.5 XRD Of The Cathode Materials

2.2.5 EDAX

For compositional analysis, we have carried out energy dispersive X-ray analysis (EDX) for all the samples. Scans were performed in both point and area scan modes. The EDX spectra resulted identical composition within the experimental limit for measurements at various locations, thus conforming the chemical homogeneity of the samples. Although, the sodium loss that occurs during the heat treatment of the samples is unavoidable, a significant improvement in the sodium content can be realized by adopting different preparative techniques.

2.2.6 SEM

2.2.6.1 SEM of NFMO



(a)

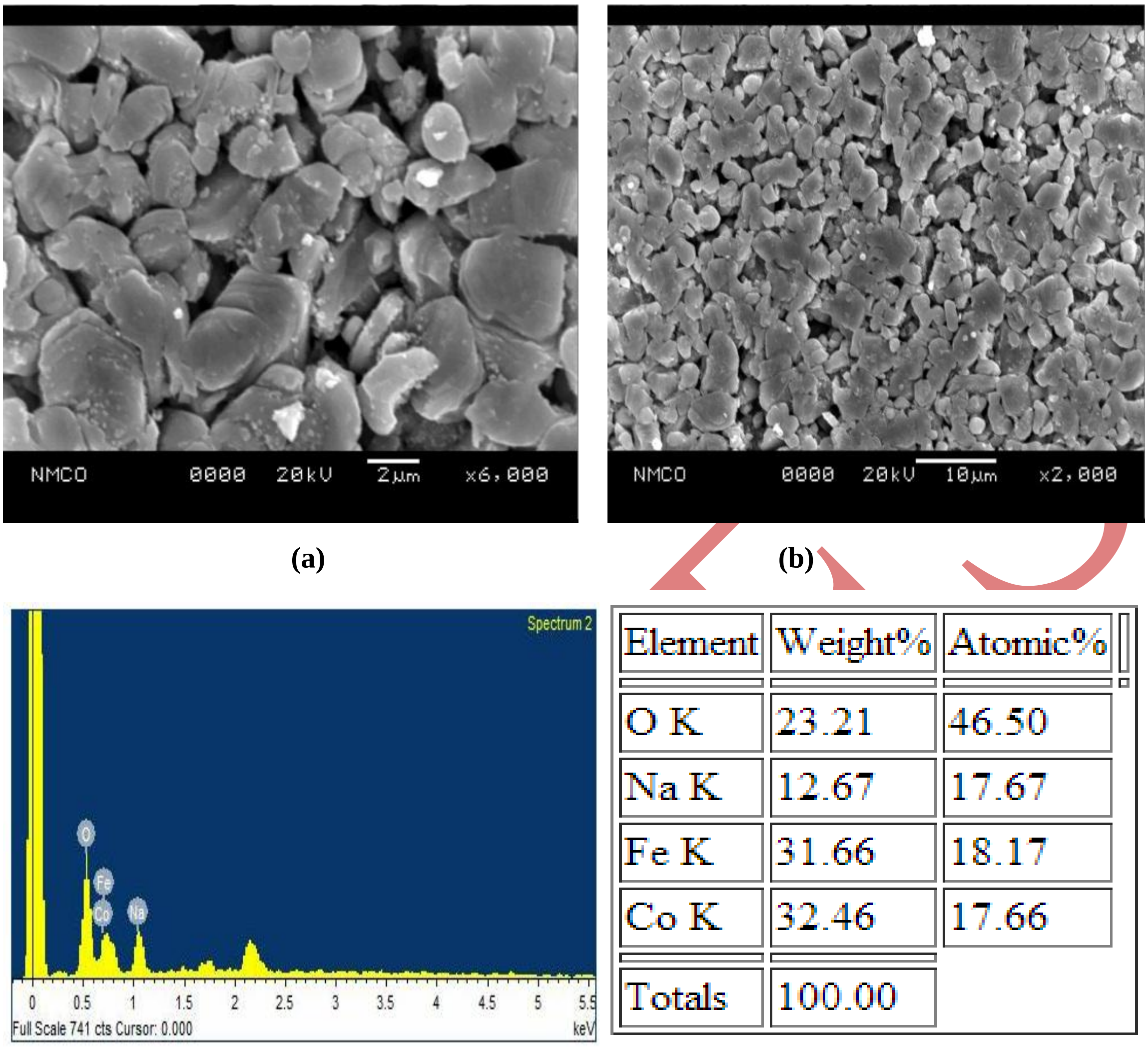
Element	Weight%	Atomic%
O K	27.11	49.39
Na K	16.47	20.89
Mn K	31.54	16.74
Fe K	24.87	12.98
Totals	100.00	

(b) (c)

Fig 1.6 A-SEM, B-EDAX, C-Percentage Composition of NFMO

The SEM images show the surface morphology of sample $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ prepared by the solid state synthesis. A dispersion of irregular shaped, agglomerated particles is seen. The average particle size is 0.5 to 1 µm. As the particles are agglomerated to each other, they form several µm-sized secondary particles. Hence the actual particle size is of the order of 500nm. Different sizes and shapes can be obtained by other synthesis methods and post treatments like ball milling and firing.

2.2.6.2 SEM of NMCO



Element	Weight%	Atomic%
O K	23.21	46.50
Na K	12.67	17.67
Fe K	31.66	18.17
Co K	32.46	17.66
Totals	100.00	

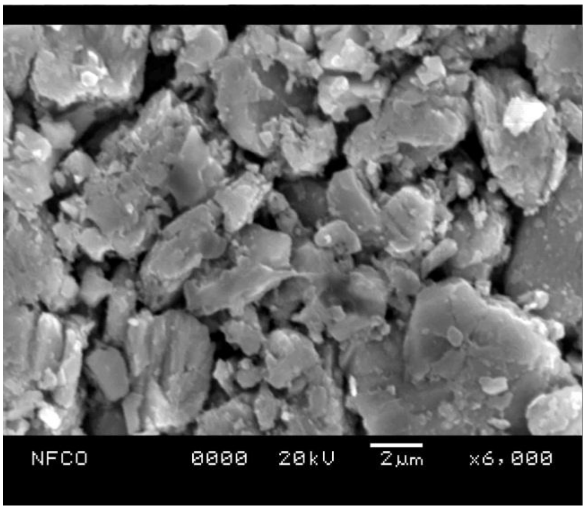
(a) (b)

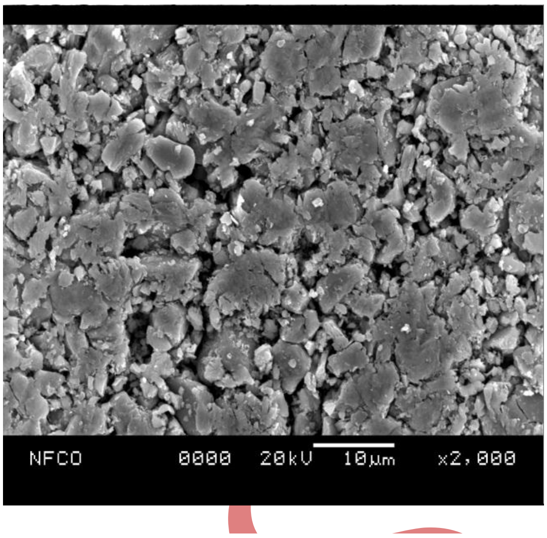
(c) (d)

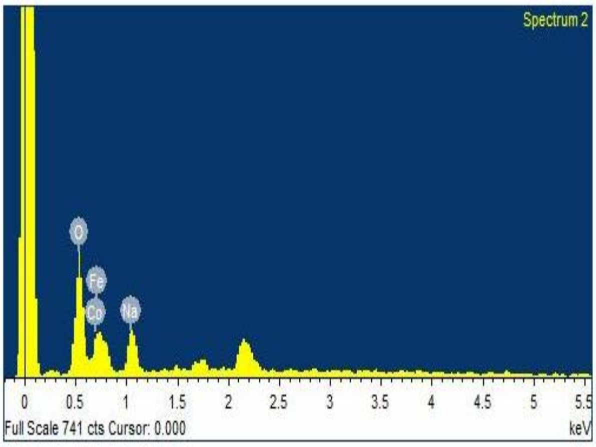
Fig 1.7 a,b-SEM, c-EDAX, d-Percentage Composition of NMCO

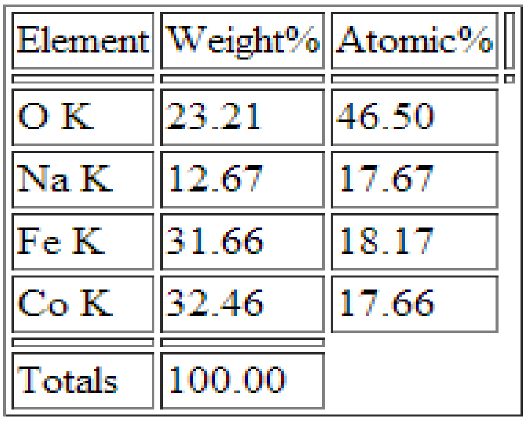
The relative particle size is larger than NFMO. It is of the order of 2-10 µm. The particles are more rounded in shape and distributed randomly. The smaller particles are more irregular in appearance.

2.2.6.3 SEM of NFCO





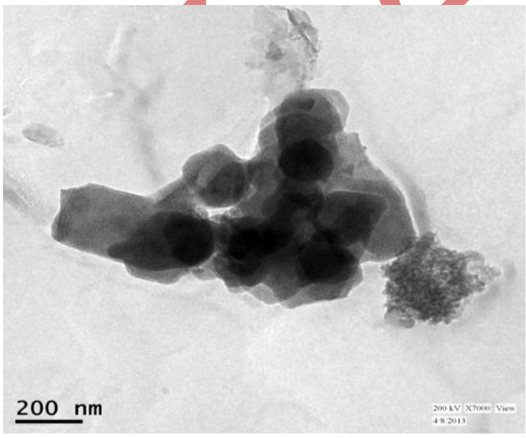


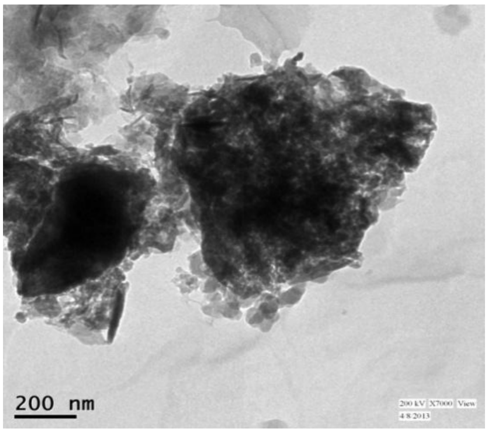


Element	Weight%	Atomic%
O K	23.21	46.50
Na K	12.67	17.67
Fe K	31.66	18.17
Co K	32.46	17.66
Totals	100.00	

The SEM of NFCO shows elongated as well as irregular particles dispersed. The average particle size is 10 - 15µ.

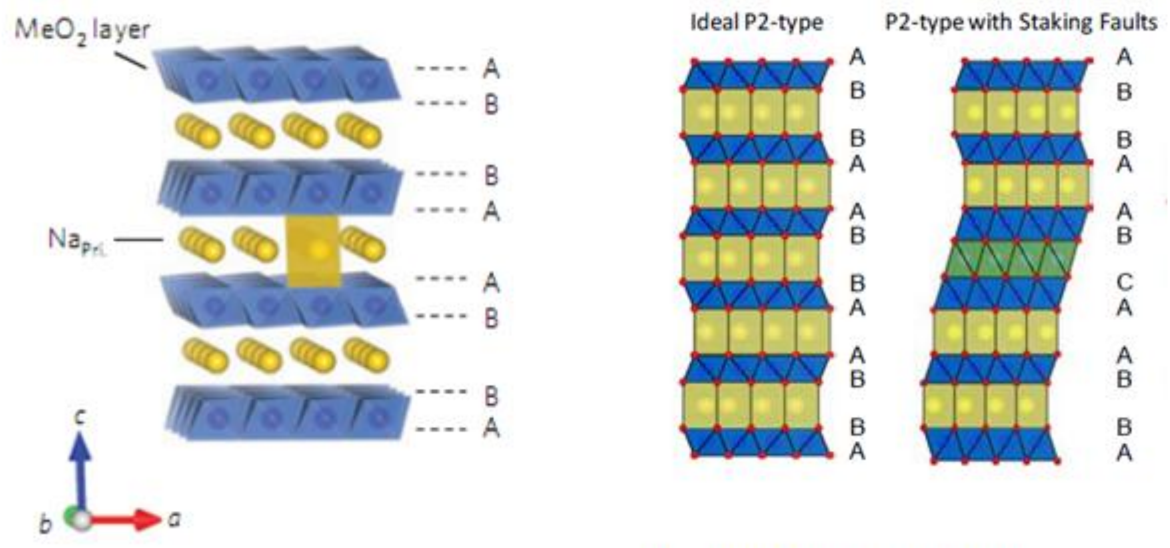
2.2.7 TEM





The TEM images of NFMO show the nanometer sized individual particles as well as the agglomerated bigger sized particles. These are unevenly distributed and are not of regular shapes due to the high temperature sold state reaction.

III. STRUCTURE

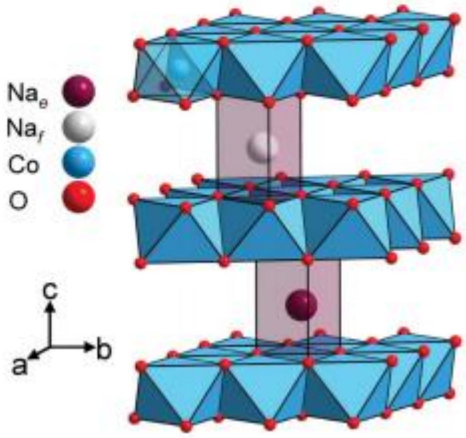


$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ structure

The $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ structure consists of a hexagonal lattice with space group P63/mmc, which is structural with P2-type Na_xCoO_2. The a, b, c parameters a=2.9335(3) and c=11.224(1)Å) can be given, . Sodium ions are accommodated in prismatic sites. Symbols A and B in the schematic diagram depicts the two different oxygen layers described by the AB notation. A longer interlayer distance is observed for the P2 phase because of the repulsive electrostatic interaction of the AA-type oxygen stacking to form prismatic sites. If one had tried to increase the Fe percentage instead of Mn then, Fe4+ cannot be stabilized in the oxide-ion frame under ambient conditions. Hence the compound is regarded as a manganese (substituted) version of $NaFeO_2$.

3.1 Existence of a Stacking Fault

It is interesting to note that the peak profile of $Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$ cannot be fitted by a conventional profile function, such as a pseudo-Voigt function. From the XRD it is observed that the peak profile of (10l) lines is distinctly broad, especially at the bottom of each peak, whereas a typical peak profile is observed for (hk0) and (00l) lines, which are normal and parallel to the metal planes, respectively. Therefore a through plane stacking fault is observed in this p-2 type layered compound. The model for the stacking fault is shown in the figure.



Structure of NMCO

3.2 Structure of NMCO

The structure of Na_xCoO_2 type materials consists of CoO_2-slabs made of edge-sharing CoO_6-octahedra.This structure is followed by NMCO. The sodium ions are sandwiched between these CoO_2-slabs so as to occupy trigonal prismatic sites (denoted by P). Based on the number of theCoO_2-layers in the unit cell and the Na^+ ions' site symmetry, the structure of NaxCoO2 phases can be either P2, P3, P¢3, orO3 structural types (P2 stacking is shown in Fig.).In P2-Na_xCoO_2, the sodium ions occupy two distinct prismatic sites: the Na (1) position shares faces with the CoO_6 octahedral in the layers above and below, while the Na(2) position shares edges only. (These two positions will be further noted as Naf (for face sharing) and Nae (for edge sharing).) The distribution of the sodium ions over the two positions depends strongly onthe sodium content and can be described as resulting from the competition between the Na^+ –$Co3^+/4^+$ electrostatic repulsions and the in-plane Na^+ –Na^+ electrostatic repulsions. Several groups reported various Na^+/vacancy ordered structures in the P2-Na_xCoO_2 systems. Dolle et al. prepared Mn rich $Na_{0.7}$CoyMn1-yO2+z phases (up to y = 0.2) and observed P2 and P3 stacking inter growths. The sodium ions occupy both Naf and Nae sites with a preferential occupancy of the Nae site. From the electrostatic point of view, the Nae site is energetically more favorable in comparison with the Naf site. The simultaneous occupancy of both sites allows the in-plane Na^+ -Na^+ electrostatic repulsion to be minimized leading globally to stable configurations [30].

3.3 NFCO

P2 and 03 phases seem to be present together. Pure phase p2 would depend on the experimental sintering temperature. Here 900 degree c has been used of the high temperature solid state reaction for all the samples to compare the various properties like dielectric and magnetic behaviors. Controlling the amount of substituted cobalt is another way to get only p2- layered structure.

CONCLUSION

a) After a detailed survey of the literature the cathode was decided. $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ was selected as cathode. After preparation characterization were undertaken using XRD, SEM, TEM, RAMAN, and resistivity, magnetic and dielectric studies. Similar investigation extended to related compounds $Na_{2/3}Mn_{1/2}Co_{1/2}O_2$ and $Na_{2/3}Fe_{1/2}Co_{1/2}O_2$ that hold good potential in sodium ion battery.

b) The XRD results are obtained in good agreement with the reported literature but if the same temperature of heating is used for all the samples, certain samples may be more phases. This can be prevented by using a different temperature of synthesis or varying the proportion of the constituent elements.

c) The SEM images provide a good indication to the average sizes and shapes of the cathode powders which agrees with the XRD.

d) The solid state reaction allows for easier synthesis of the samples.

e) Coin cells or beaker cells may be designed with appropriate anodes like hard carbon to test NIB battery operation and compare with LIB.

REFERENCES

[1] S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries, Advance Energy Materials 2 (2012) 710.

[2] V. Palomares, P. Serras, I. Villaluenga, K.B. Hueso, J. Carretero-González, T.Rojo, Na-ion batteries, recent advances and present challenges to become low cost energy storage systems, Energy & Environmental Science 5 (2012)5884.

[3] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices, Science 334 (2011) 928.

[4] S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, Electrochemical intercalation activity of layered $NaCrO_2$ vs. $LiCrO_2$, Electrochemistry Communications 12 (2010) 355.

[5] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, P2-type $Na_x.[Fe_{1/2}Mn_{1/2}]O_2$ made from earth-abundant elements for rechargeable Na batteries, Nature Materials 11 (2012) 512.

[6] D. Kim, E. Lee, M. Slater, W. Lu, S. Rood, C.S. Johnson, Layered $Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2$ cathodes for Na-ion battery application, electrochemistry Communications 18 (2012) 66.

[7] M. Sathiya, K. Hemalatha, K. Ramesha, J.M. Tarascon, A.S. Prakash, Synthesis, structure, and electrochemical properties of the layered sodium insertion cathode Material: $NaNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, Chemistry of Materials 24 (2012) 1846.

[8] D. Kim, S.-H. Kang, M. Slater, S. Rood, J.T. Vaughey, N. Karan, M. Balasubramanian, C.S. Johnson, Enabling sodium batteries using lithium-substituted sodium layered transition metal oxide cathodes, Advanced Energy Materials 1 (2011) 333.

[9] D. Buchholz, A. Moretti, R. Kloepsch, S. Nowak, V. Siozios, M. Winter, S. Passerini, Towards Na-ion batteries – synthesis and characterization of a novel high capacity Na-ion intercalation material, Chemistry of Materials 25 (2013) 142.

[10] M.S. Whittingham, Lithium batteries and cathode materials, Chemical Reviews 104 (2004) 4271.

[11] P.G. Bruce, J. Nowinski, Sodium Intercalation into WO2Cl2, Journal of Solid State Chemistry 89 (1990) 202.

[12] P.G. Bruce, F. Krok, P. Lightfoot, J.L. Nowinski, Multivalent cation intercalation, Solid State Ionics 53–56 (1992) 351.

[13] P.G. Bruce, F. Krok, J. Nowinski, V.C. Gibson, K. Tavakkoli, Chemical intercalation of magnesium into solid hosts, Journal of Materials Chemistry 1 (1991)705.

[14] Ma X, Chen H, Ceder G. Electrochemical properties of monoclinic NaMnO2. JElectrochemSoc 2011;158:A1307.

[15] Bhide A, Hariharan K. Physicochemical properties of NaxCoO2 as a cathode for solid state sodium battery. Solid State Ionics 2010;192:360.