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Electrochemical Performance of Li(NMC)O2 Cathode Materials for Li-ion Batteries

by

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Abbreviation and Terminology

1 C rate	The current density needed to charge up the battery in one hour
CV	Cyclic Voltammetry
GITT	Galvanostatic Intermittent Titration Technique
PITT	Potentiostatic Intermittent Titration Technique

Abstract

Li-ion batteries are widely used in portable electronic industry, and have been considered for large scale applications in electric or hybrid electric vehicles. The rapid development in electronics industry calls for better batteries of higher energy storage, lower capacity decay, and lighter weight. A better understanding on materials' electrochemistry would help us optimize the battery's performance. This project is therefore focused on the electrochemical performance of a LiNi_yMn_zCo_{1-y-z}O₂ type cathode material.

LiNi_vMn_zCo_{1-v-z}O₂ powder was successfully synthesized through co-precipitated hydroxide route, with a resultant composition of LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ determined from EDX. The particle morphology was examined by SEM. It was found that the particles possessed a polyhedral geometry with an average size of 1 µm. XRD analysis on lattice parameters, I₀₀₃/I₁₀₄ parameter and R-factor showed a well layered structure in this material with little cation mixing between Li⁺ and Ni²⁺. Both particle morphology and well indexed diffraction pattern pointed to the formation of highly crystallized and pure compound. This material's electrochemical properties were characterized with various electrochemical measurements. Cyclic voltammetry was performed at different scan rates. The oxidation and reduction peaks were found to be at ~3.8 V and ~3.7 V, respectively, which corresponds to the redox reaction of Ni^{2+}/Ni^{4+} . No Mn^{3+} was found in this compound due to a lack of redox peak at 3.0 V; and this confirms that the major oxidation state of Mn ion is 4+. Cycling charge-discharge performance was carried at two rates: 0.5 C (80 mA/g) and 2 C (320 mA/g). The corresponding discharge capacity was 154 mAh/g and 143 mAh/g at 0.5 C and 2 C rate, respectively. By the end of the 30th cycle, the discharge capacity decays to 137 mAh/g and 122 mAh/g, respectively. The Coulombic efficiency after the first cycle was over 100%. A linear capacity fading model was adopted for this material, and the capacity decay rate was 0.52 % per cycle. Li-ion chemical diffusion coefficient was determined as a function of cell voltage using both GITT and PITT techniques, yielding D_{Li} of ~10⁻¹⁰ cm²/s from GITT and ~10⁻¹¹ cm²/s from PITT. This range is consistent with the D_{Li} obtained using CV curves at different scan rates, which yielded a value of 2.4×10^{-11} cm²/s. The equilibrium voltage vs. amount of lithium extraction showed a change of slope at 30% lithium de-intercalation. Finally, a brief investigation on crystal structural change after 30 cycles at 0.5 C and 2 C rates was carried out using XRD, which revealed severe cation mixing and low hexagonal ordering upon cycling by analyzing the I₀₀₃/I₁₀₄ parameter, R-factor and the *c/a* ratio. The increase of (110) over (108) peaks intensity might infer an irreversible Li loss which accounts for the deterioration of the layered structure.

1. Introduction

The objective of this project it to synthesize Li(Ni_yMn_zCo_{1-y-z})O₂ type cathode through hydroxide co-precipitation route, and to study its crystal structural and electrochemical performances, including capacity and reversibility at different charge-discharge rates. Li-ion kinetics during charging is another area of principal investigation in this project. The cathode crystal structural change due to charge-discharge cycling has also been studied.

High energy density and design flexibility have rendered lithium ion batteries (LIB) a wide variety of applications in portable electronic devices. The need for turning to clean energy has also made LIB a promising candidate in powering future electric vehicle (EV) and hybrid electric vehicle (HEV). LiCoO₂, which has a α-NaFeO₂ structure, was first introduced by SONY in 1990s, and continues to have a strong presence in today's LIB market. Nevertheless, the thermal instability, poor rate performance, and the toxicity and high cost of cobalt associated with LiCoO₂ prohibit its use in large-scale applications. In view of this, various alternative LIB cathode materials have been developed. Among them Li(Ni_yMn_zCo_{1-y-z})O₂ system has attracted much attention due to its high rate performance and improved safety. Ohzuku and Makimura introduced the first of its kind with a stoichiometry of equal amounts of Ni, Mn, Co, which demonstrates a stable capacity of 150 mAh/g cycled between 3.5 and 4.2 V and a capacity over 200 mAh/g upon charging to 5.0 V[2]. A comprehensive study of Li-ion kinetics on this composition has been done using GITT and

EIS measurements by Shaju et al.[1]. However, there is no clear reason why 1:1:1 amount of transition metals has to be adopted for this system beside symmetry in composition. Therefore, it is worthwhile to explore other compositional possibilities within this system, from which a general guide may be established on the possible comparable choices, if not better, of transition metal composition for different application requirements.

In this project, a LiNi_yMn_zCo_{1-y-z}O₂ type compound was synthesized through a co-precipitation hydroxide route. The morphology was examined by SEM, composition by EDX, and crystal structure by XRD. Cyclic voltammetry was employed to study the redox couple as well as the Li-ion diffusion coefficient. Cyclic charge-discharge tests were carried out to test this cathode material's cycling performance. GITT and PITT methods were employed to investigate Li-ion kinetics during charging. This compound's structural change after cycling was studied using XRD.

2. Literature Review

2.1 Development of lithium batteries

A battery is a power source that converts chemical energy into electrical energy, and the reversible reaction carry out in rechargeable batteries. It consists of an anode, a cathode and an electrolyte. In the case of lithium batteries, the anode is the source of lithium ions whereas the cathode is the sink, the two electrodes are separated by an electrolyte that has high conductivity for ion but low for electron. Li⁺ is released from the anode and transported to the cathode during discharging, and the process is reversed during charging.

The energy storage capacity of batteries is usually expressed as specific energy (Wh/kg) and energy density (W/L); and the rate capability uses terms of specific power (W/kg) and power density (W/L). There are usually two requirements for electrode materials in terms of high energy density and high specific energy: the first one is that the electrodes should have a high specific charge (in Ah/kg) and charge density (in Ah/L); and the other requires the cathode and the anode to form a high potential redox couple.

The development of a battery technology based on Li metal as anode was initially motivated by the fact that Li is the most electropositive (-3.04 V versus standard hydrogen electrode) and the lightest (equivalent weight M=6.94 g mol⁻¹, and specific gravity ρ =0.53 g cm⁻³) metal. In the 1970s, the use of Li metal was first demonstrated to be of advantage in the assembly of primary (non-rechargeable) Li cells whose high capacity and variable discharge

rate were well received in a variety of applications[3]. A comparison of different battery technologies in terms of energy density is shown in Fig. 1. During the same era, numerous inorganic compounds, later on identified as intercalation compounds, were demonstrated to react with alkali metals reversibly, which opened the door for developing high-energy rechargeable Li systems. The problem with the use of the Li-metal/liquid electrolyte was soon exposed - dendritic Li growth as the metal was replated during each subsequent discharge-recharge cycle, which led to explosion hazards. To overcome the safety issues, several approaches were attempted. The first approach[4] was to replace the metallic Li with a second insertion material, which gave birth to the so-called Li-ion or rocking-chair technology at the end of the 1980s and early 1990s. The dendrite problem was solved because Li is in its ionic rather than metallic state. The second approach [5] modified the electrolyte by substituting it by a dry polymer electrolyte, which led to the so-called Li solid polymer electrolyte (LI-SPE) batteries. However, this technology was only limited to large systems. Several groups later on attempted to avoid this drawback by developing Li hybrid polymer electrolyte (Li-HPE) battery which ended up with the same Li-metal dendritic growth problem. The first reliable and practical rechargeable Li-ion HPE battery was developed by Bellcore researchers who introduced polymeric electrolytes in a liquid Li-ion system[6].



Figure 1. A comparison of different battery technologies in terms of volumetric and gravimetric energy density. (Picture adopted from [7])

Presented with a historic development of lithium batteries, the following sessions will be devoted to materials employed in anodes, cathodes, and electrolytes.

2.2 Anode

Carbons are commonly used as the anode for commercial rechargeable lithium batteries. It has demonstrated a capacity of 450 mA h g^{-1} and very good cycling performance. The carbon host is able to form a lithium/carbon intercalation compound Li_xC_n when lithium ions transport through the electrolyte, which is a reversible reaction and accounts for the better cycling performance. Graphite are layer-structured carbons which has a lower capacity of 350 mA h g^{-1} [7].

Concurrent with the development of carbon anodes, lithium alloys have attracted much $$\mathsf{Page}\,\mathsf{5}$$

effort in research. Table 1 presents a comparison of a few lithium alloys and the carbon compound anodes. The lithium alloys are more attractive in specific charge and charge density relative to carbon compounds. However, excessive lithium[8] is needed for metallic lithium to compensate for the low cycling efficiency (less than 99%) in order to achieve decent cycle life, which makes its practical capacity comparable with that of the carbon compounds. Besides, the great volume change during each charge/discharge cycle rendered metallic lithium unviable for rechargeable batteries because the mechanical stress induced by the volume variation will eventually lead to anode disintegration.

	Specific charge	Charge density	Volume
Alloy	(Ah/g)	(Ah/cm ³)	variation(%)
Li	3.861	2.06	_
Li_2Sn_5	0.79	2.023	259
Li_2Si_5	2.012	2.374	312
Li ₃ Sb	0.564	1.788	147
Li ₃ As	0.84	2.041	201
LiAl	0.79	1.383	94
LiC ₆	0.339	0.76	10

Table 1. Characteristics of a few anode materials for lithium batteries[9]

Attempts to employ nanotechnology in anodes have shown encouraging results. The Si-C nanocomposites have shown attractive characteristics of 1000mA h g⁻¹ capacity for more than 100 cycles[10]. Thin amorphous silicon films deposited on a specially roughened copper foil surface by a sputtering process demonstrated[3] an almost 100% reversibility at capacities

larger than 3000 mA h g^{-1} . Nevertheless, the use of primary nanoparticles comes with side-reactions with the electrolyte, resulting in safety issues and short calendar life.

2.3 Cathode

A lot of effort has been devoted to cathode materials in search for a system with high output voltage, light weight, high energy density, excellent cycle life, low self-discharge and absence of environmentally hazardous elements. The following passages will give a comprehensive review on different kinds of cathode materials.

2.3.1 Transition-metal dioxides

The general formula for this kind of material is $LiMO_2$ with M being V, Cr, Fe, Co or Ni, and it adopts the α -NaFeO₂-type structure (Fig. 2). In cubic close-packed oxygen array the lithium and transition-metal atoms are distributed in the octahedral interstitial sites in such a way that MO₂ layers are formed consisting of edge-sharing [MO₆] octahedral. The lithium resides in octahedral [LiO₆] coordination, forming a layer between adjacent MO₆[9].



Figure 2. Layered oxides structure of $LiCoO_2$ and $LiNiO_2$. Spheres represent the lithium ions, and the polyhedra represent MO_6 . (Adopted from [11])

2.3.1.1 LiCoO₂

Lithium cobaltite is most widely used for commercial battery cathodes. It has a layered structure (Fig. 2) and produces high potential. Since only half lithium can be liberated for each Co and cycled reversibly without causing structural changes, it has a relatively low capacity of 130 mA/g [11]. A very good cycling behavior has been obtained, which shows 80-90% capacity retention after being cycled for more than 500 times[9]. One disadvantage of this cathode is the high cost of cobalt which is more expensive than nickel and manganese. Doping with other elements has been performed in order to lower the cost and improve the reversibility at the same time.

2.3.1.2 LiNiO₂

Isostructural with LiCoO₂, LiNiO₂ has lower cost and higher specific capacity of 200 $${\rm Page \ 8}$$

mAh/g during the first charge[9]. However, high exothermic reactions occur when the cathode is overcharged (Li_xNiO_2 , x<0.25)[12], which imposes potential hazards to safety. Doping has also been used to overcome these disadvantages.

2.3.1.3 LiMnO₂

The structure of lithium manganese dioxide is only similar to that of $LiCoO_2$. It also has a layered structure but the configuration of $[LiO_6]$ and $[MnO_6]$ octahedral is in a zigzag manner, as shown in Fig. 3. An overall capacity of 210 mAh/g has been reported [13] on the initial charge between 3.4 and 4.5 V. The orthorhombic-LiMnO₂ shows very good reversibility. However, this structure converts to spinel structure when charged over a certain potential[14], which accounts for the poor recycling capability.



Figure 3. The structure of orthorhombic-LiMnO₂ (Adopted from [15]).

2.3.2 $LiFePO_4$

 $LiFePO_4$ is one of most appealing cathode materials with low cost and environmental friendliness. It has an olivine phase structure, shown in Fig. 4. The discharge potential is

around 3.4 V relative to lithium metal, which is relatively high. LiFePO₄ has a high theoretical capacity of 170 mAh/g[11] but could hardly be achieved unless at very low current[16] density or elevated temperature charging[17]. No obvious capacity fading was observed after several hundred cycles. One drawback of this material is its low electronic conductivity (10⁻⁹ S/cm)[18]. Doping has shown significant increase in conductivity, and this material is a promising candidate for lithium batteries.



Figure 4. The crystal structure of olivine LiFePO₄ (Adopted from[7]).

2.3.3 LiMn₂O₄

A spinel structure is adopted by $LiMn_2O_4$, shown in Fig. 5, which has the same cubic closed-packed oxygen ions with the α -NaFeO₂ structures but differs in the distribution of the cations among the available octahedral and tetrahedral sites. The discharge process exhibits two plateaus, one around 4 V, which is commonly used, and the other around 3 V. When cycled in the 4 V plateau, its reversible capacity is only 120 mAh/g. More than one thousand

charge/discharge cycles have been reported [19] with decent capacity fading rate at low specific capacity. The low capacity of $LiMn_2O_4$ has deterred its entrance to the market.



Figure 5. Spinel structure of LiMn₂O₄ (Adopted from [9]).

2.3.4 $Li(Ni_{1-y-z}Mn_yCo_z)O_2$

The first synthesis of this mixed Ni-Mn-Co dioxide was reported in 1999 by Liu et al[20]. A typical composition of this type of cathode is the symmetric amount of transition metals, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, which was first introduced by Ohzuku and Makimura in 2001[2] and displayed very good performances. It delivers a capacity of 200 mAh/g in the voltage window 2.5-4.6 V with improved safety, and a low capacity fading is maintained even with high power rate. This upper potential limit is not attained by other transition metal oxides such as $LiNiO_2[21]$ and $LiCoO_2[22]$ due to various reasons. A comparison between $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and other transition metal oxides is shown in Table 2.

Cathode	Specific capacity (mAh/g)	Potential (V)
LiCoO ₂	140	3.0-4.2
LiMnO ₂	190	2.0-4.25
LiNiO ₂	200	2.5-4.2
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	200	2.5-4.6

Table 2. Characteristic comparison between $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and some traditional transition metal oxides.

Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ cathode, like other LiMO₂ layered materials, has the α -NaFeO₂-type structure as shown in Fig. 2. The oxygen atoms stack in ABCABC sequence. One of the models proposed by Koyama et al.[23] suggests regularly alternating slabs of CoO₂, NiO₂ and MnO₂ as illustrated in Fig. 6. The same author concluded, based on his calculation [24], a higher potential than LiNiO₂, long cycle life and better reversibility than LiNiO₂ and LiCoO₂ for this structure.



Figure 6. An extremely regular structure of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ having alternating slabs of CoO₂, NiO₂ and MnO₂. Oxygen layers are stacked in ABC sequence.

Due to its various possible combinations of the transition metals, $Li(Ni_{1-y-z}Mn_yCo_z)O_2$ has offered a great chance to building better batteries by optimizing its composition.

2.4 Electrolyte

In an all-solid-state construction, polymers have been developed as the material for solid electrolyte. An ideal electrolyte should have a high ionic conductivity, a negligible electronic conductivity and stability in contact with the electrodes. Unfortunately, solid polymer electrolytes have suffered from a poor ionic conductivity at ambient temperature. Despite this drawback, solid polymer electrolyte has offered several advantages[25]: (1) excellent processability and flexibility that enables the fabrication of thin film electrolyte; (2) higher safety relative to organic solvent electrolyte; (3) possible prevention of dendritic growth upon lithium replating; and (4) a high dimensional stability. At present, an amorphous lithium phosphorous oxynitride, also known as Lipon, has been widely used as thin film electrolyte in thin film batteries. It has a lithium ionic conductivity of 2×10^{-6} S/cm, and withstands both metallic lithium and the transition metal electrodes at potentials up to 5.5 V[9]. Besides, a high electric resistivity minimizes the short circuit self-discharge of the battery.

3. Experimental procedures

3.1 Synthesis of Li(Ni_yMn_zCo_{1-y-z})O₂ through co-precipitation

The $(Ni_vMn_zCo_{1-x-v})(OH)_2$ precursor was prepared using $Ni(NO_3)_2 \cdot 6H_2O_1$ $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and NaOH as starting materials. Ni(NO₃)₂ · 6H₂O, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ were mixed with a molar ratio of 1:1:1, and this mixture was dissolved in distilled water to obtain a 2 mol/L solution. The molarity of NaOH needed was twice as much as the molarity of the three metal salts combined and was also made into a 2 mol/L solution. NaOH solution and the desired amount of NH₃ • H₂O was added separately in a drop-wise manner into the metal salts solution under an Ar atmosphere along with constant stirring. The solution was stirred for 10 hours at 50 $^{\circ}$ C, and the pH was controlled at around 11. The precipitated solution was then washed and filtered, followed by an overnight drying at 50 $^{\circ}$ C in a drying furnace. The dried precursor was thoroughly mixed with 10% excess LiOH which was used to compensate for possible loss of Li during calcination. The mixed powder was ground in a mortar by hand, and the powder was pressed into pellet. The pellet was initially heated at 500°C for 6 hours and subsequently calcined at 950°C for 15 hours. Powders were obtained by breaking down and regrinding the pellet.

3.2 Preparation of the cathode

Polyvinylidene fluoride (PVdF) dissolved in 1-methyl-2-pyrrolidone (NMP) solution was

used as a binder. The slurry consisting of uniformly mixed 80 wt.% $Li(Ni_yMn_zCo_{1-y-z})O_2$, 10 wt.% acetylene black, and 10 wt.% PVdF was casted on a piece of pressed Al foil used as current collector. The cathode was dried in vacuum for 2 hours at 80 °C before it was pressed at 14.7 MPa (150kg/cm²). The pressed cathode was then heated to 120°C for 12 hours in vacuum. The completely dried cathode material was then cut into round foils with a diameter of 9/16 inch (1.43 cm).

3.3 Physical characterization

The as-prepared powders were examined using a scanning electron microscope (SEM) equipped with energy dispersive spectrometry. The X-ray diffraction patterns of the powder as well as the cycled samples were obtained from a Cu K α radiation (Siemens D500) at 2θ rate of 0.01 °per second ranging from 10 ° to 90 °. For the examination of cycled cathode, cells were dismantled and washed with diethyl carbonate (DEC) two times to ensure the removal of absorbed Li salt and dried at 50 °C.

3.4 Electrochemical measurements

Electrochemical measurements were carried out on Li / $Li(Ni_yMn_zCo_{1-y-z})O_2$ cells with a lithium metal foil as anode. The electrolyte consisted of 1M LiPF₆ dissolved in ethylene carbonate-diethyl carbonate (1:1 in weight). Cells were assembled into CR2025 coin cells

with a glass fiber separator in Ar-filled glove box where the concentrations of oxygen and water were kept at 0.1 ppm and 0.5 ppm, respectively.

The charge-discharge tests were carried out between 2.5V and 4.3V at current densities of 0.5 C and 2 C (1C is defined as 160 mA/g) for 30 cycles with an Arbin 2000 testing system. The galvanostatic intermittent titration technique (GITT) measurement was carried out at room temperature. The cell was charged at a constant current flux of C/25 for an interval of 1 hour followed by an open circuit stand for 5 hours to allow the cell voltage to relax to its steady-state value. This procedure was repeated for the voltage window of 2.5 - 4.5V. Potentiostatic intermittent titration technique (PITT) measurement was performed from 3.72 to 4.10 V. 10 mV height steps were applied in the 3.8 - 3.9 V range, 20 mV height in the range of 3.72 - 3.8 V and 3.9 - 4.0 V, 50 mV height in the 4.0 - 4.1 V range.

4. Results and Discussion

4.1 Morphology and Structure

The SEM images of the synthesized Li(Ni_yMn_zCo_{1-y-z})O₂ particle are shown in Fig. 7. The particle size distribution was not uniform and covered a broad range of dimensions. The appearance of many small particles might be resulted from the grinding process which mechanically broke particles apart. The average particle size is around 1 μm if smaller broken pieces were omitted. The particle displays a polyhedral morphology as revealed in Fig. 7(b). The composition is determined by energy dispersive x-ray spectroscopy, revealing the atomic ratio of Ni:Mn:Co to be 36: 29: 35 although an equal distribution is expected. It is noted, however, that the relative accuracy of EDX will be as bad as 50% for samples of small particles[26]. Therefore, more advanced techniques have to be employed to give more accurate measurement. And this material is hereafter denoted as LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂.



Figure 7 (a) and (b). Scanning electron micrographs of the as-prepared $\text{Li}(\text{Ni}_{y}\text{Mn}_{z}\text{Co}_{1-y-z})\text{O}_{2}$ powders synthesized through co-precipitation method at different magnifications.

Fig. 8 shows the XRD pattern of $LiNi_{0.36}Mn_{0.29}Co_{0.35}O_2$ powders synthesized through Page 17

co-precipitation hydroxide route. All peaks are indexed in a hexagonal α-NaFeO₂-type structure, indicating high purity of the as-synthesized powder. Table 3 lists calculated lattice parameters (Jade 5 software) and a comparison to that of a LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ material. Smaller a and c are found in this compound. Since none of the transition metal's atomic compositions is held constant to 1/3, it is difficult to conclude how each transition metal affects the lattice parameters, merely from a comparison with LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂. However, it should be noted that by holding either Mn or Ni constant, a and c decrease with an increasing amount of Co[27]. In an α-NaFeO₂-type structure, the oxygen sub lattice is regarded as distorted from cubic symmetry in the hexagonal *c*-axis[28]. This distortion is accountable for the split of (006)/(102) and (108)/(110) doublets in the XRD pattern which are distinctive of the layered structure [29]. It is well known that c/a is $2\sqrt{6}$ (4.899) in an ideal c.c.p. lattice. A distortion in c would yield deviation from this value. Therefore, the closer the value is to 4.899, the larger amount of transition metals is present in the lithium layer. A comparison of c/a values in Table 3 suggests the less layeredness of LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂. Nevertheless, c/a in this compound is well above 4.93, the threshold value for a clear separation of the doublets[28], which suggests formation of the layered structure. The peak intensity ratio of $I_{(003)}/I_{(104)}$ is used to measure the degree of cation mixing between Li⁺ and Ni²⁺. A ratio $I_{(003)}/I_{(104)} < 1.2$ means undesirable cation mixing[30]. The ratio $I_{(003)}/I_{(104)} = 1.68$ obtained from this compound is an indicator of very little cation mixing. The R factor, which is defined as $(I_{(006)}+I_{(012)})/I_{(101)}$, reflects the hexagonal ordering. The smaller the R, the better the hexagonal ordering and thus less deviation from hexagonal to cubic structure [31,32]. Since this material has a larger R value, it is believed that the hexagonal ordering of its lattice is not as good as LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂. And this finding is consistent with what has been concluded previously from the *c/a* ratio analysis.



Figure 8. X-ray diffraction pattern of $LiNi_{0.36}Mn_{0.29}Co_{0.35}O_2$ synthesized through co-precipitation method.

Table 3. Calculated parameters of LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ and comparison with LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

Material	$LiNi_{0.36}Mn_{0.29}Co_{0.35}O_{2}$	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2}[33]$
<i>a</i> (Å)	2.851	2.8602
<i>c</i> (Å)	14.173	14.2260
<i>c/a</i> (Å)	4.971	4.9738
$I_{(003)}/I_{(104)}$	1.68	1.5624
R	0.69	0.4073

4.2 Electrochemical properties

The cyclic voltammetries (CV) of LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ cathode material for the first 4 cycles are shown in Fig. 9. The CV shows only one couple of redox peaks between 3 and 4.3V, which corresponds to oxidation and reduction of Ni²⁺ /Ni⁴⁺[34]. The oxidation peak of the first CV curve occurs at a higher potential of 3.852 V with a higher current. The potential polarization of the second cycle between the anodic and the cathodic peaks is less than that of the first cycle. There is no distinctive difference among oxidation peaks and reduction peaks of subsequent CV cycles, suggesting a good electrochemical reversibility. Table 4 lists potentials of each redox peaks as well as related polarization. The decreasing polarization with increasing cycle number also indicates good reversibility. No peak is found around 3 V which corresponds to Mn^{3+}/Mn^{4+} redox reaction[35,36], as shown in Fig. 10. This phenomenon indicates no or very little presence of Mn³⁺ in this material. Since fully oxidized Mn ions (Mn⁴⁺) do not participate in the electrochemical reaction, they are inactive and thus stabilize the structure. Different CV scan rates were also performed in the potential window 2.5-4.6V, as shown in Fig. 10. As expected, both polarization and redox peak values increase with increasing scan rate.



Figure 9. Cyclic voltammetry of the first 4 cycles at a scan rate of 0.1mV/s from 3 to 4.3 V.

Table 4. Redox pe	eak potentials and	polarizations for the	e first 4 cycles obtained	from CV.
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Cycle number	1	2	3	4
Oxidation (V)	3.852	3.828	3.821	3.816
Reduction (V)	3.689	3.685	3.687	3.684
Polarization (V)	0.163	0.143	0.134	0.132



Figure 10. CV of $LiNi_{0.36}Mn_{0.29}Co_{0.35}O_2$ at scan rates of 0.1mV/s, 0.5mV/s, 1mV/s, and 5 mV/s between 2.5 and 4.6V (vs. Li).

CV can also be employed to determine chemical diffusion coefficient of Li-ion using the classical Randles-Sevchik equation which is given in the following form[37],

$$I_p = 0.4463n^{3/2} F^{3/2} C_{Li} A R^{-1/2} T^{-1/2} v^{1/2} D_{Li}^{1/2}$$
(1)

where I_p is the peak current (A) from CV, n the charge transfer number, F the Faraday's constant, C_{Li} the Li-ion concentration, A the electrode surface area, R the gas constant, T the absolute temperature, v the CV scanning rate (V s⁻¹), and D_{Li} Li-ion chemical diffusion coefficient. A plot of I_p vs. v^{1/2}, shown in Fig. 11, shows a linear relation between the two

variables. The D_{Li} determined from this method is 2.4×10^{-11} cm²/s. A more detailed discussion on Li-ion diffusion coefficient will be given in later part concerning GITT and PITT.



Figure 11. The plot of I_p vs. $v^{1/2}$ from the CV results with different scan rates, a linear fit of the data points is also shown in the graph.

Charge-discharge profile between 2.5 and 4.3 V at 80 mA/g (corresponds to 0.5 C rate) is plotted in Fig. 11. The first two charging curves show very flat charging plateau at 3.83 V, which corresponds to the oxidation peak obtained from CV in Fig. 9. This charging plateau becomes less distinctive and its potential increases as cycling index goes up. The charge capacity loss is very large for the first three cycles but stabilizes thereafter. Similar performances are found in the discharging curves where the discharging plateau, occurring at 3.7 V for the first two cycles, is even less pronounced than the charging one. Since the Page 23 potential was held at 4.3 V for 2 hours before discharging to 2.5 V for each cycle, the larger discharge capacity can be attributed to the charging at constant voltage. Potential of discharging plateau decreases with an increasing cycle index, and it is clearly demonstrated in Fig. 11 that polarization increases as cycle index increases.



2.5-4.3 V; i = 80 mA/g

Figure 12. Voltage vs. capacity profiles for the cell, $\text{LiNi}_{0.36}\text{Mn}_{0.29}\text{Co}_{0.35}\text{O}_2$, between 2.5 and 4.3 V (hold for 2 hours) at 80 mA/g. Cycle indices are labeled against respective cycles.

The cycling performance at different charge-discharge rates is shown in Fig. 13. The irreversible capacity losses during the first cycle are 37.3 mAh/g for 0.5 C (80mA/g) and 51.2 mAh/g for 2 C (320 mA/g). However, subsequent cycles demonstrate much less or even no capacity loss. This irreversible capacity loss during the first cycle is attributed to the

formation of solid electrolyte interface (SEI) layers on the cathode-electrolyte interface[38]. The first discharge capacities are 153.6 mAh/g (at 0.5 C rate) and 143.3 mAh/g (at 2 C rate), and at the end of the 30th cycle their values decay to 136.9 mAh/g and 121.9 mAh/g, respectively; and the capacity retention after 30 cycles are 89% at 0.5 C and 86% at 2 C. Assume a linear decrease of the discharge capacity against cycling life, which bears a mathematical expression in the form of

$$C = C_0 (1 - An) \tag{1}$$

where C_0 is the initial discharge capacity, A the capacity loss rate, and n the cycle index. A linear fit of the discharge capacity in Fig. 13 gives a rate of 0.52% per cycle at both charge-discharge rates; and this number is higher than that reported by X. Zhang et al.[39] who claimed 0.15% per cycle at 1 C rate.



Figure 13. Cycling performance at different rates, 0.5 C and 2 C, between 2.5 and 4.3 V for 30 cycles. The cells were held at 4.3 V for 2 hours before discharging to 2.5 V.

Fig. 14 shows the GITT curves at room temperature (third cycle) for the cell as a function of time. Prior to the GITT measurement, the cell was subjected to two charge-discharge cycles at 80 mA/g in the voltage window 2.5 - 4.3 V. GITT measurement was performed at a constant current of I₀=32µA (C/25 rate) for a time interval τ of 1 hour, followed by an open circuit of 5 hours to allow relaxation to steady state. This procedure was repeated for the voltage window of 2.5 - 4.3 V. The equilibrium potentials (E_s) are plotted as a function of lithium extraction x in LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂, as shown in Fig. 15. The x versus E_s plot is similar to voltage profile in Fig. 11. A plateau is found for x < 0.3, corresponding to a capacity of 83.2 mAh/g, which suggests a two-phase reaction[1]. The E_s then increases Page 26

steeply to 4.2 V, corresponding to 146.8 mAh/g charge capacity. Similar phenomenon was also reported in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2[1]$. It is noted in Fig. 14 that further titration curves beyond 4.2 V barely relax to steady state for the time allowed. However, the saw-like curve above 4.2 V in this experiment might present a slightly flat curve above 4.2 V if relaxation is sufficiently long. Therefore, further investigation focusing on higher voltage using GITT with prolonged relaxation time is needed to study phase transition at deep lithium de-intercalation.



Figure 14. The GITT curves for the cell, $\text{Li}/\text{LiNi}_{0.36}\text{Mn}_{0.29}\text{Co}_{0.35}\text{O}_2$ for the third charge cycle at room temperature.



Figure 15. Equilibrium potential (E_s) for the cell at room temperature as a function of lithium extraction x in LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂.

Chemical diffusion coefficient of Li-ion can be determined from GITT using Eq. (2)[40,41,42] [42]

$$D_{Li} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \qquad (\tau \ll L^2 / D_{Li})$$
(2)

where V_m is the molar volume of the compound, $\text{LiNi}_{0.36}\text{Mn}_{0.29}\text{Co}_{0.35}\text{O}_2$, M_B and m_B are its molecular weight, 69.63 g/mol, and active mass employed, respectively, A is the total contact area between the electrolyte and the electrode, and L is the thickness of the electrode. The determination of ΔE_s and ΔE_τ can be found in the Appendix.

The diffusion coefficients of Li-ion, D_{Li} , at different equilibrium potentials were calculated using Eq. (2) and plotted as a function of cell voltage, in comparison with the values for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂[1], as shown in Fig. 16. The values of D_{Li} are found to vary from 10^{-11} to 10^{-12} cm²/s, which are in the same order of magnitude with other layered compounds[37,43] and conform to the finding from CV curves. The initial D_{Li} is 3.1×10^{-11} cm²/s at 3.68 V, then increases gradually to 7.5×10^{-11} cm²/s at 3.85 V, and remains at a steady

value for the potential up to 4.13 V before it plunges. Since equilibrium was not reached at higher potentials as discussed before, such a plunge in D_{Li} at potential above 4.13 V is not a reflection of its true intrinsic nature. The variation of D_{Li} as a function of cell potential is similar to that of reported in LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ [1]. The minimum D_{Li} was observed at 3.72 V bearing a value of 1.8×10^{-10} cm²/s, and the stable value of 3×10^{-10} cm²/s at 3.9 V, for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ at room temperature. As a result, D_{Li} determined from this work is one order of magnitude lower than that published for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂.



Figure 16. Lithium-ion diffusion coefficient determined from GITT, D_{Li} , as a function of cell voltage for the third cycle at room temperature (Red square). The result for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂[1] is redrawn for comparison (Blue circle).

PITT was also employed to determine the Li-ion chemical diffusion coefficient. For long time approximation, t>> L^2/D_{Li} , current can be expressed explicitly as a function of time[40]:

$$I(t) = \frac{2QD_{Li}}{L^2} \exp\left(-\frac{\pi^2 D_{Li} t}{4L^2}\right)$$
(3)

where Q is the total charge transfer during each voltage step, which can be determined by graphically evaluating the area under the I-t curve, and L is the thickness of the electrode. The chemical diffusion coefficient can be determined from the linear plot of lnI vs. t. Fig. 17 shows a typical lnI vs. t plot at the potential step of 3.74 V, and it is observed that a linear relation is established after a transient period at the onset of the single titration step.

 D_{Li} determined from PITT as a function of cell voltage is plotted in Fig. 18 in comparison with the result obtained previously from GITT. The variation of D_{Li} from GITT and PITT is similar: there is a trough at 3.74 V, and then D_{Li} increases and stabilizes above 3.8 V. The values of D_{Li} are in the range of $10^{-11} \sim 10^{-12}$ cm²/s, which are about one order of magnitude lower than D_{Li} obtained using GITT method. This difference in D_{Li} may attribute to the different nature of testing techniques and time domain conditions, i.e. t>>L²/ D_{Li} in PITT and t<< L²/ D_{Li} in GITT. In comparison, D_{Li} determined from CV curves, ~10⁻¹¹ cm²/s, lies in between the values obtained from GITT and PITT.

A relatively low D_{Li} has been concluded from both methods. Without another composition for comparison, it is unable to determine which element takes effect in influencing Li-ion diffusion. Therefore, a different composition is needed to gain an insight in this problem, and hence help optimize the composition.



Figure 17. lnI vs. t curve plotted for the PITT step at 3.80 V. A linear relation between lnI and t is well established at t > 3000s.



Figure 18. Li-ion diffusion coefficient, D_{Li} , determined from PITT (red square symbol) as a function of cell voltage, in comparison with result (up to 4.17 V) obtained from GITT (blue round symbol).

4.3 Structural change due to cycling

The structure of LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ after 30 charge-discharge cycles at different current densities was studied by X-ray diffractoin. XRD patterns of two samples after cycling test are shown in Fig. 19, in comparison with freshly made LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ powder. Parameters used in Section 4.1 to measure cation mixing and hexagonal ordering, $I_{(003)}/I_{(104)}$, R-factor, and *c/a*, are listed in Table 5. It is noted that the cycled LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ powders present greater cation mixing and lower hexagonal ordering, both of which will further deteriorate the material's electrochemical performance. This explains why the specific charge/discharge capacities of Li / LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ cell decreased with increasing cycle number. The *c/a* ratio did not change much after 30 cycles at 0.5 C but decreased a lot at 2 C rate. Therefore, deviation from hexagonal structure occurred more readily at higher charge-discharge rate.

The (110) intensity increases while the (018) intensity attenuates in the cycled samples. A disappearing (110)/(018) doublet might indicate changes in the layered structure. It is noted, however, that an increase in peak intensity ratio of (110) over (018) was observed upon de-intercalation of Li-ion from the LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ structure, and (018) peak totally vanished up to 85% lithium extraction (Li_{0.15}Ni_{1/3}Mn_{1/3}Co_{1/3}O₂) [44]. Therefore, such a change in (110)/(018) doublet in this material is probably attributed to irreversible Li loss upon cycling, which may also be accountable for the capacity fading. A sharp increase in (116)

intensity is observed in both cycled samples, and is also reported in [34]; however, no clear explanation has been proposed, and this structural change requires further investigation. The formation of a new peak at $\sim 74^{\circ}$ is observed in both cycled samples. The origin of this peak has not been identified, but it may result from the formation of oxides on the cathode powder surface.



Figure 19. (a) Comparison of XRD patterns before and after cycling at different rates. Magnified patterns showing (b) degradation of (101) and (c) (110)/(018) doubet.

	As-prepared	30 cycles at 0.5 C	30 cycles at 2 C
$I_{(003)}/I_{(104)}$	1.68	0.94	0.92
R	0.7	1.8	1.1
c/a	4.971	4.969	4.926

Table 5. Parameters $I_{(003)}/I_{(104)}$, R, and *c/a* before and after cycling.

Coating the cathode particles with different materials is popular in improving the thermal stability and electrochemical performance. This might be a possible solution to resist Li loss since the coated layer passivates the cathode's surface and hence reduces the side reaction between cathode compound and the electrolyte. An increasing amount of Mn might stabilize the structure because Mn^{4+} , the predominant oxidation state determined in Section 4.2, does not participate in the redox reaction.

5. Future Work

In order to establish an empirical formula relating composition and performance, at least two more samples of different composition are needed to generate convincing evidence. Samples of constant Co composition and varying Ni and Mn compositions are preferred to confirm whether Mn is able to improve the stability of the layered structure. And these samples will also be employed to study the Mn effect on D_{Li} .

6. Conclusions

LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ powder was successfully synthesized through co-precipitated hydroxide route. The synthesized particle possesses a polyhedral morphology with an average size of about 1 µm. Clearly separated (006)/(012) and (018)/(110) doublets from XRD pattern suggests the formation of a well-layered structure in this compound. The intensity ratio $I_{(003)}/I_{(104)}$ shows little cation mixing between Ni²⁺ and Li⁺, but a relatively large R factor indicates a less hexagonal-ordered structure. Only one redox couple in the voltage window of 3.0 - 4.3 V is observed, which corresponds to redox reactions of Ni²⁺/Ni⁴⁺ A lack of redox peak at ~ 3 V illustrates no oxidation from Mn^{3+} to Mn^{4+} , indicating major oxidation state of Mn ion is 4+. LiNi_{0.36}Mn_{0.29}Co_{0.35}O₂ cathode material presents a good electrochemical performance. It shows a first discharge capacity of 154 mAh/g at 0.5 C rate, and 143 mAh/g at 2 C rate; its capacity retention after 30 cycles are 89 % and 85 %, respectively. Li-ion chemical diffusion coefficients determined from GITT and PITT techniques are in the range of $10^{-11} - 10^{-10}$ cm²/s, comparable with other layered compounds, and consistent with D_{Li} determined using CV test at different scan rate. Finally, a brief investigation on cycling induced structural change was studied using XRD, which revealed severe cation mixing and low hexagonal ordering upon cycling. The intensity increase of (110) over (108) might indicate deterioration of the layered structure due to Li loss.

7. References

- [1] K Shaju, G Rao, B Chowdari. J.Electrochem.Soc. 151 (2004) A1324.
- [2] T Ohzuku, Y Makimura. Chem.Lett. (2001) 642.
- [3] H. Ikeda, T. Saito, H. Tamura, A. Kozawa, R.H. Brodd. 1 (1975)
- [4] MB Armand. (1980) 145.
- [5] M. B. Armand, J. M. Chabagno, & M. J. Duclot. in: P. Vashishta, J.-N. Mundy, G. K. Shenoy (Eds.), North-Holland, Amsterdam, 1979, pp. 131-136.
- [6] J- Tarascon, A. S. Gozda, C. Schmutz, F Shokoohi, PC Warren. Solid State ionics 86-8 (1996) 49-54.
- [7] J- Tarascon, M Armand. 414 (2001) 367.
- [8] K Brandt. Solid State Ionics 69 (1994) 173.
- [9] A Patil, V Patil, D Wook Shin, J Choi, D Paik, S Yoon. Mater. Res. Bull. 43 (2008) 1913.
- [10] P Novak, et al.
- [11] MS Whittingham. Chem.Rev. 104 (2004) 4271.
- [12] PG Balakrishnan, R Ramesh, T Prem Kumar. J.Power Sources 155 (2006) 401.
- [13] MM Thackeray, JT Vaughey, AJ Kahaian, KD Kepler, R Benedek. Electrochemistry Communications 1 (1999) 111.
- [14] IJ Davidson, RS McMillan, JJ Murray, JE Greedan. J.Power Sources 54 (1995) 232.
- [15] RJ Gummow, D Liles, M Thackeray. Mater. Res. Bull. 28 (1993) 1249.
- [16] A Yamada, SC Chung, K Hinokuma. journal of the electrochemistry society 148 (2001) A224.
- [17] AS Andersson, JO Thomas , B Kalska, L Haggstrom. Electrochemical and Solid-State Letters 3 (2002) 66.
- [18] S Chung, JT Bloking, Y Chiang. 1 (2002) 128.

- [19] JM Tarascon, D Guyomard, GL Baker. J.Power Sources 44 (1993) 689.
- [20] Z Liu, A Yu, J Lee. J.Power Sources 81 (1999) 416.
- [21] T OHZUKU, A UEDA, M NAGAYAMA, Y IWAKOSHI, H KOMORI. Electrochim.Acta 38 (1993) 1159.
- [22] T Ohzuku, A Ueda. J.Electrochem.Soc. 141 (1994) 2972.
- [23] Y Koyama, I Tanaka, H Adachi, Y Makimura, T Ohzuku. J.Power Sources 119-121 (2003) 644.
- [24] Y Koyama, N Yabuuchi, I Tanaka, H Adachi, T Ohzuku. 151 (2004) A1551.
- [25] S Ahmad. 15 (2009) 321.
- [26] RH Geiss. in: Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films, Butxetworch-Heinemann, 1992, pp. 120-134.
- [27] J Ngala, N Chernova, M Ma, M Mamak, P Zavalij, M Whittingham. Journal of materials chemistry 14 (2004) 214.
- [28] J Cho. J.Electrochem.Soc. 146 (1999) 3571.
- [29] A. Rougier, P. Gravereau, C. Delmas. J.Electrochem.Soc. 4 (1996) 1168-1175.
- [30] T Ohzuku, A Ueda, M Nagayama. J.Electrochem.Soc. 140 (1993) 1862.
- [31] JR Dahn, U von Sacken, CA Michal. Solid State Ionics 44 (1990) 87.
- [32] JN Reimers, E Rossen, CD Jones, JR Dahn. Solid State Ionics 61 (1993) 335.
- [33] X Luo, X Wang, L Liao, S Gamboa, P Sebastian. J.Power Sources 158 (2006) 654.
- [34] K Shaju, G Rao, B Chowdari. Electrochim. Acta 48 (2002) 145.
- [35] C Gan, X Hu, H Zhan, Y Zhou. Solid State Ionics 176 (2005) 687.
- [36] J Paulsen. J.Electrochem.Soc. 147 (2000) 861.
- [37] M Levi, G Salitra, B Markovsky, H Teller, D Aurbach, U Heider. J.Electrochem.Soc. 146 (1999) 1279.

- [38] J Choi, A Manthiram. Electrochemical and solid-state letters 8 (2005) C102.
- [39] X Zhang, W Jiang, A Mauger, F Gendron, C Julien. J.Power Sources 195 (2010) 1292.
- [40] C WEN, B BOUKAMP, R HUGGINS, W WEPPNER. J.Electrochem.Soc. 126 (1979) 2258.
- [41] W WEPPNER, R HUGGINS. J.Electrochem.Soc. 124 (1977) 1569.
- [42] J Zhang, S Buckingham, LG Johnson. 10207445
- [43] K Shaju, G Rao, B Chowdari. J.Electrochem.Soc. 150 (2003) A1.
- [44] S Yin, Y Rho, I Swainson, L Nazar. Chemistry of materials 18 (2006) 1901.

Appendix

A typical single step GITT curve should bear the form shown below. Corresponding parameters are labeled in this graph.

