

Review of Electrochemical Performance of LiNiO_2 and Their Derivatives as Cathode Material for Lithium-ion Batteries

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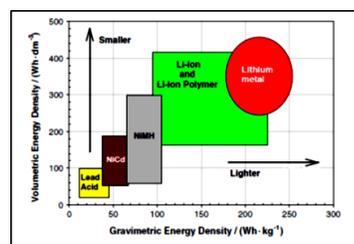
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Graphical abstract



Abstract

Lithium-ion battery which widely used as portable power sources with high energy density is greatly being increased due to the development and popularity of portable electronic device and vehicle. Lithium nickel oxide (LiNiO_2) and their derivatives are promising positive cathode materials for next generation of lithium-ion batteries. LiNiO_2 potentially offers a higher capacity at about 200 mAh/g. However it is more difficult to synthesized stoichiometric LiNiO_2 because of the loss of lithium from host structure during high temperature calcination due the high vapor pressure of lithium and capacity fade when charging up to a high voltage ($> 4.0\text{V}$ vs Li^+/Li) during deintercalation of lithium ion that affected cycling. The review is focused the electrochemical performance by substitution or effect doping of LiNiO_2 and their derivative by other metals as a cathode materials for lithium ion batteries.

Keywords: Lithium-ion batteries; lithium nickel oxide; cathode; doping

Abstrak

Bateri litium-ion digunakan secara meluas berikutan permintaan yang meningkat sebagai tenaga yang mudah alih dengan kepadatan tenaga yang tinggi disebabkan oleh pembangunan dan populariti peranti elektronik mudah alih. Litium nikel oksida dan terbitannya menjanjikan bahan katod positif bagi bateri litium ion untuk generasi masa akan datang. Ia mempunyai potensi berdasarkan kapasiti yang tinggi sebanyak 200 mAh/g. Walau bagaimanapun, LiNiO_2 stokiometrik sukar disintesis kerana litium hilang dari perumah disebabkan tekanan wap litium ketika proses rawatan haba tinggi dan kapasitinya pudar semasa pengecasan apabila pada voltan meningkat tinggi ($> 4.0\text{V}$ vs Li^+/Li) semasa ion litium bebas interlakasi menyebabkan kesan terhadap keupayaan kitaran. Ciri-ciri ini mungkin dapat dikawal oleh penggantian separa Ni dengan logam lain. Prestasi elektrokimia dikaji semula melalui penggantian atau kesan doping LiNiO_2 dan terbitannya dengan logam lain sebagai bahan katod bagi ion bateri litium.

Kata kunci: Bateri litium-ion; litium nikel oksida; katod; doping

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1.0 INTRODUCTION

The battery system was recognized that can offer of high value opportunity according of interest in energy storage for grid that attribute to multiple factors including the capital costs of managing peak demands, the investments needed for grid reliability and integration of renewable energy storage sources. Lithium-ion batteries also included in battery system whose development for commercial electronics and electric vehicles is being applied to grid storage [1].

New demands usually stimulate the development of new batteries and consequently accelerate the researches on new lithium insertion materials. Lead acid, nickel-metal hydride, and lithium

ion batteries are the most common rechargeable batteries. Lead acid battery technology is well proven and is more than a century old. However the lead acid battery shows low gravimetric and volumetric energy density. Nickel-metal hydride batteries provide reliable cyclability and are commonly used in hybrid vehicles. Their downside is a relatively low energy density and low cycle life and relatively high self-discharge rate up to 10% per month. That makes lithium ion systems an attractive alternative. Figure 1 shows crudely volumetric and gravimetric energy densities for some common batteries. Lithium ion cells provide a cell configuration that operates at over twice the potential of lead acid or NiMH cells. The reactivity of lithium has been problematic and the low cycle life has been a problem especially under high current densities.

However, modern lithium based electrodes provide much better power density and cycle life, and as a result lithium ion cells are being considered for use in larger applications like vehicles [2]. The Department of Energy's Office of Freedom Care and Vehicle technologies also was support the researchers in development high performance lithium ion batteries because it light weight and high energy density and that make them ideal candidate for transportation use such as electric vehicles (EVs), hybrid-electric vehicles (HEVs), plug-in hybrid-electric vehicles (PHEVs), and fuel-cell electric vehicles (FCEVs) [3][6].

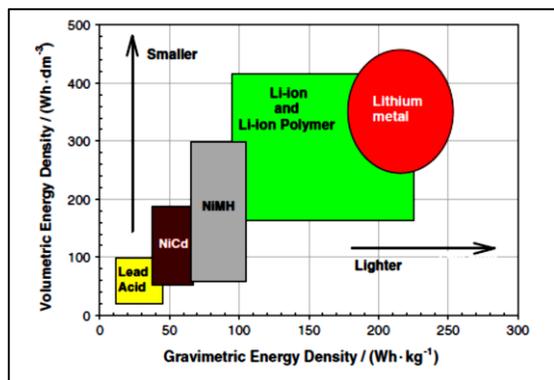


Figure 1 Plot of volumetric energy density against gravimetric energy density for common batteries [2]

In various aspects, this kind of lithium secondary battery has many advantages over the traditional rechargeable systems like lead acid and Ni–Cd, for example, a high energy density, a high average output voltage (3.6 or 3.7 V), a low self-discharge (<5% per month), no memory effect like that of Ni–Cd and Ni–MH, an excellent cycling behavior (its cycle number can be >1200), a high rate capability like 1C, a high coulomb efficiency (near to 100% except in the first cycle), a wide work temperature range (ranging from -25 to $+45$ °C, expected to be $+70$ °C), an easy measurement of the residual capacity, maintenance free and very few adverse effects on the environment (it can be called a green battery)[5][7-9].

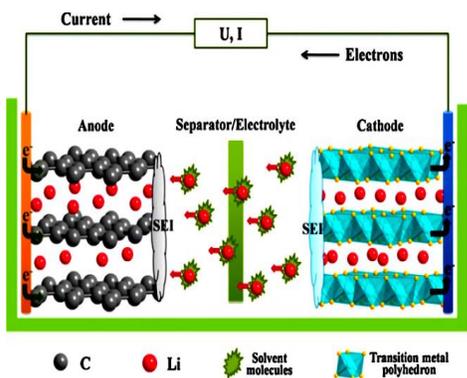


Figure 2 Working principles of LIB (charging) [4]

The basic working principles of lithium ion batteries are shown in Figure 2. A lithium ion battery can work as energy storage device by converting electric energy into electrochemical energy. There are three key components in lithium ion batteries system comprise cathode, anode and electrolyte. Nowadays, lithium ion batteries system both anode and cathode material are from

intercalation materials. Cathode materials are typically oxides of transition metal which consist of a largely unchangeable host with specific sites for Li ions to be intercalated in. All lithium ions are in the cathode sides initially. During charging, Li ions are extracted from cathode host, solvate into and move through the non-aqueous electrolyte, and intercalate into the anode host. Meanwhile, electrons also move from cathode to anode through the outside current collectors forming an electric circuit. The chemical potential of Li is higher in the anode than in the (electro) chemical energy. Such process is reversed when the battery is discharging where the electrochemical energy is released in the form of electric energy [4][10]. The cathode region and anode region are separated by separator, a micro-porous membrane that allows the electrolyte to penetrate and prevent shorting between the two electrodes. The electrolyte should be ionically conducting and electronically insulating in principle, however the actual properties of the electrolyte much more complicated. In current lithium ion batteries technology, the cell voltage and capacities are mainly determined by the cathode material that also the limiting factor for Li transportation rate [4].

2.0 CATHODE MATERIAL

The developments of cathode materials therefore become extremely crucial and receive more attention in recent decade [4]. Research and developments of cathode materials with improved electrochemical performance and/or low cost has always focus and methods such as sol-gel [5], non-classical ones including mechano-chemical, hydrothermal, template, pulse laser deposition, plasma-enhanced chemical vapor deposition, radio-frequency magnetron sputtering, mechano-chemical method, incorporation of heteroatom, composite technology, soft-chemistry route such as ion exchange and oxidation-reduction reaction, solid-state reaction and carbon combustion synthesis [11-12] have been widely applied [13]. Among the transition metal oxide LiNiO_2 , LiMn_2O_4 and LiCoO_2 are the most promising cathode material [15, 24]. Lithium cobalt oxide (LiCoO_2) is a most widely used cathode material on the market. However, LiCoO_2 compounds are expensive, toxic, and therefore not environmentally benign. Also, the capacity of LiCoO_2 is limited to about 140 mAh/g [14]. LiMn_2O_4 is quite inexpensive and does not bring about environmental pollution, but its cycling performance is not good. The cathode materials reviewed here include LiNiO_2 and their derivative.

Criteria for cathode material selection included [15]:

- (i) Electrochemical compatibility with the electrolyte solution over the required charge/discharge potential range
- (ii) Facile electrode kinetics
- (iii) A high degree of reversibility
- (iv) Air stability in the fully lithiated state.

Although LiNiO_2 has the lowest operating voltage of the three materials listed, it offers many advantages as a lithium-ion cathode material. These include:

- (i) Good high temperature stability
- (ii) Low self-discharge rate
- (iii) High specific capacity
- (iv) Compatibility with many electrolyte solutions
- (v) Environmentally friendly
- (vi) Moderately low in cost

2.1 Lithium Nickel Oxide

Lithium Nickel Oxide (LiNiO₂) has been considered as a promising positive electrode material for high energy rechargeable batteries [16-21]. LiNiO₂ has layered structure similar to LiCoO₂ and is cheaper than LiCoO₂ [10, 13, 23]. Although LiNiO₂ has high theoretical capacity, it is difficult to synthesis in its tendency of non-stoichiometric phase, and it is not easy to prepare on large scale, [13, 22] due to its lower thermodynamic stability compare LiCoO₂ and the presence of excess nickel on Li sites. These anti sites in LiNiO₂ strongly affect the electrochemical properties of batteries [23].

LiNiO₂ synthesized by the solid-state reaction method does not have a large discharge capacity and does not exhibit good cycling performance, probably because it has poor crystallinity, and a smaller fraction of the LiNiO₂ phase due to the presence of impurities. On the other hand, the homogeneous mixing of the starting materials can be accomplished by the combustion method. Song *et al.* studied use this method in an O₂ stream using urea and nitrate as a fuel. The electrochemical properties showed that the first discharge capacities were 135.5, 179.1, 164.2, and 167.1 mAh/g for the samples calcined for 6, 12, 24 and 36 h, respectively, with the sample calcined for 12 h having the highest first discharge capacity. The sample calcined for 36 h has the second highest first discharge capacity but shows the worst cycling performance. The sample calcined for 6 h has the lowest first discharge capacity but shows the best cycling performance. The sample calcined for 24 h has a relatively high first discharge capacity (164.2 mAh/g) and a good cycling performance [24].

At the similar method, Kwon *et al.* investigated the variation of the discharge capacities with C-rate for the synthesis LiNiO₂. LiNiO₂ has the largest discharge capacities at n = 10 (after stabilization of the cycling performance) at the 0.1, 0.2 and 0.5 C rates. This is considered to be related with the largest value of $I_{0.0} / I_{0.4}$ and the smallest value of R-factor (the least degree of cation mixing) among all the samples [25]. The variations, with the number of cycles, in the discharge capacities of LiNiO₂ synthesized by the combustion method (voltage range 2.7–4.4 V, 0.1 C rate) [73], the sol–gel method (voltage range 3.0–4.2 V, 0.05 C rate) [74], and the solid-state reaction method (voltage range 2.8–4.3 V, 0.1 C rate) [75] were compared. The LiNiO₂ synthesized by the combustion method had the highest first discharge capacity (189 mAh/g), followed, in order, by electrodes synthesized by the sol–gel method (169 mAh/g) and by the solid-state reaction method (145 mAh/g). From the fourth cycle, the LiNiO₂ synthesized by the sol–gel method had a higher discharge capacity than the sample fabricated by the combustion method. However, the two samples exhibited similar cycling performance, starting with the fourth cycle. The LiNiO₂ synthesized by the solid-state reaction method had a lower discharge capacity than that synthesized by the other methods. The solid-state sample also exhibited poor cycling performance. The small discharge capacity and the poor cycling performance of LiNiO₂ synthesized by the solid-state reaction method are believed to be the result of poor crystallinity and poor particle size uniformity. Since the voltage ranges and the C-rates are different, a direct comparison is not possible. Nevertheless noteworthy, the LiNiO₂ electrode synthesized by the combustion method has the highest first discharge capacity, a relatively high discharge capacity, and relatively good cycling performance.

In the case of partial substitution of Ni with other metals in LiNi_{1-y}M_yO₂ system there are still some possible improvement. Presently, some lithium nickel oxide derivatives are considered by the battery manufacturers to be very promising for application in 4 V lithium-ion batteries. With the aim of finding new positive electrode materials for lithium-ion batteries, many research and development effort has been devoted towards LiNiO₂ and LiNiO₂

substituted materials. For example, partial substitution of Ni with Co was later found to be effective at reducing the cationic disorder [26] and improve the cyclability [27] and substituted LiNi_{1-y}M_yO₂ (M : Ga [28], Mg and Ti [29] as well as the LiCo_{1-y}Mg_yO₂ system [28] were recently shown exhibit very good reversible cycling behavior [30] Li(Ni,Mg,Ti)O₂ materials present a good thermal stability and power rate [28], the Mg²⁺ ions stabilize the structure since they are not involved in the redox process and thus low volume change is observed during cycling. In order to inhibit the reduction of Ni⁴⁺ during cycling, doping with heteroatoms such as Al, Co or Li can also be employed to stabilize LiNiO₂ and to improve the electrochemical performance.

2.2 Lithium Nickel Cobalt Oxide

Interestingly LiCoO₂ and LiNiO₂ from complete solid solutions to give rise to a family of rhombohedral layered structured LiNi_(1-y)Co_yO₂ compounds where both Ni and Co are in their oxidation state of III. Thus, the substitution of nickel by cobalt in the 0.2 <y< 1.0 range inhibits the formation of Ni (II) impurities, this stabilizing the two dimensional character of the layered structure of LiNiO₂ [30]. This feature has promoted that LiNi_{1-y}Co_yO₂ system is one of the most promising candidate cathode materials of advanced lithium ion batteries because of its low cost, better rate capability and higher capacity compare with LiCoO₂ as well as its superior thermal stability compared to LiNiO₂ (following the tendency for LiCoO₂ to show good thermal stability). The good electrochemical performance of these compound relies on a well layered structure in which Li and (Co/Ni) cations do not mix by occupy alternating fcc (1 1 1) planes [31]. Delmas group [32-36] determined the structural details and physical properties of the LiNi_{1-y}Co_yO₂ system and showed that there is an increased ordering as the cobalt concentration increases. Thus cobalt suppresses the migration of nickel to the lithium site in the Li nickel/manganese/cobalt oxides. The most commonly used electrode material related LiNi_{1-y}Co_yO₂ is a LiNi_{0.8}Co_{0.2}O₂ and these compounds are able to offer a stable cyclability on the 180 mAh/g range. The large replacement of cobalt in the high Ni, y= 0.2 range improves the environmental compatibility and this is an additional bonus for the practical interest of the LiNi_{0.8}Co_{0.2}O₂ electrodes [30]. Chowdari and their coworker studies shown that, LiNi_{0.8}Co_{0.2}O₂ has 190 mAhg⁻¹ discharge capacity for the first cycle [39]. The stoichiometry of LiNi_{0.8}Co_{0.2}O₂ was found to be ideal stoichiometry [40]. The composition that reveals the best electronic transport parameter is LiNi_{0.75}Co_{0.25}O₂ [41]. LiNi_{0.7}Co_{0.3}O₂ showed better capacity retention than LiNi_{0.8}Co_{0.2}O₂ as a result of enhanced layering characteristics as the Co content increased [42]. Cobalt substitution enhances the 2D nature of the crystal lattice by reducing the cation mixing (i.e. reduced occupancy of Ni-ions in the Li-layer) [43]. Wang *et al.* reported that, rechargeability of LiNi_{0.5}Co_{0.5}O₂ and LiNi_{0.25}Co_{0.75}O₂ electrodes is still good with a capacity fading rate of 0.3-0.18 mAhg⁻¹ per cycle [44].

The mechanism for the capacity fade of LiNi_xCo_{1-x}O₂ electrodes on cycling could be due to the following factor:

- The structural change due to lithium insertion/extraction causes the contraction and expansion of the unit cell which may lead to the formation of fractures in the particles of the active material.
- In the change state MO₂ react with the organic electrolyte and induces the dissolution of M ions into the solution

LiNiO₂ has been identified to experience several topotactic phase transformation during lithium insertion and extraction processes.

Substituted aluminium in nickel cobalt oxides, such as $\text{LiNi}_{1-y}\text{Co}_y\text{Al}_z\text{O}_2$, are prime candidates for the cathode advanced lithium batteries for use in large system as required for hybrid electric vehicles [45]. The presence of Al in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ improves both the thermal and electrochemical properties. The high specific capacity and good power capability of this material make it attractive for vehicular applications although it is still not considered as inherently safe as other candidates such as LFP [26]. Cho *et al.*, reported that $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ with initial discharge capacities larger than 160 mAh/g were successfully prepared [46]. Chen *et al.*, show that a small amount of the aluminium doping in $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x$ ($0 < x < 0.1$) cathodes significantly stabilizes the cell impedance and hence improves their power performance [47].

Substituted or doping Mg into $\text{LiNi}_{1-y}\text{CoO}_2$ system enhances the electrochemical performance of the cathode materials. In particular, Mg has been known to be a good candidate as a dopant since it can increase the electronic conductivity of LiCoO_2 , which was reported by Carewska *et al.* Tukamoto and West's work showed that the electronic conductivity increases at the higher Mg contents, which may due to the Mg^{2+} substitutes onto Co^{3+} sites, leading to the creation of an equal number of Co^{4+} ions for charge balance and thus increasing the conductivity [30]. Xiang *et al.*, in their studies show that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and Mg-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ have a high degree of ordered hexagonal structure. In the first cycle, the Mg-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode delivers an initial discharge capacity of 177 mAhg^{-1} and maintains good cycling behavior after 50 cycles (161 mAhg^{-1}). The capacity loss is 9%. In comparison, the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode delivers an initial discharge capacity of 180 mAhg^{-1} with the capacity loss of 32% after 50 cycles (123 mAhg^{-1}). Mg doping significantly improves the cycling stability as well as the reversible capacity. Rate capability is one of the most important electrochemical characteristics of lithium secondary battery required for power storage application. The Mg-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode delivers an initial discharge capacity of 188 mAhg^{-1} and maintains good cycling behavior with only a little capacity loss (9%) after 50 cycles. For undoped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode, the capacity loss is 23, 32, 18 and 27% at 0.5, 1, 3 and 5C after 50 cycles, respectively. Impressively, the Mg-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode has less capacity loss of 9, 9, 7 and 8% at 0.5, 1, 3 and 5C, respectively. Mg-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ presents much better cycling performance than the undoped one at different current densities, even at high rate up to 5C [49]. Albrecht *et al.* studied shows that $\text{Li}(\text{Ni}_{1-y}\text{Co}_y)\text{O}_2$ has been successfully applied to aluminium and magnesium-doped lithium nickel cobalt mixed oxides $\text{Li}(\text{Ni}_{1-y}\text{Co}_y\text{M}_z)$ ($\text{M} = \text{Al}, \text{Mg}$). The additional element stabilize the layered structure and enhance the cycling stability. The size of the latter can be controlled by the synthesis temperature. Cobalt, aluminium and magnesium all stabilize the layered structure. The lithium nickel disorder strongly, though refinement need to be considered carefully. Both, aluminium and magnesium doping enhance the cycling stability of lithium nickel cobalt mixed oxides. The decomposition temperature of charged electrodes without electrolyte is rather a function of the delithiation state of aluminium or magnesium content. Therefore, aluminium and magnesium enhance the thermal stability of the delithiated phase mainly by intrinsic limitation of the delithiation [50].

2.3 Lithium Nickel Manganese Oxide

Lithium nickel manganese oxide layer-structured compound $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, has promise as an alternative material because its electrochemical and safety characteristic are comparable or superior to LiCoO_2 . $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ can offer high theoretical specific capacity about 280 mAh/g and significantly enhanced structural stability because Mn ion maintain an oxidation state of +4 during electrochemical cycles [51]. Figure 3 shows the typical

electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The charge/discharge voltages of this material are around 3.6–4.3 V where $\text{Ni}^{2+}/\text{Ni}^{4+}$ act as the redox couple as confirmed from in situ X-ray absorption spectroscopy (XAS) study. Various methods including X-ray and neutron diffraction, nuclear magnetic resonance (NMR) spectroscopy, transmission electron microscope (TEM) and first-principles calculations have been performed to investigate the structural change and local cation distribution of this material. The results showed that different from classic layered material composed of pure Li layer and pure MO_2 slab, 8–10% Ni ions are usually found in the Li layer of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by solid state or sol-gel synthesis methods [4].

$\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$ phase system was studied by the Dahn group [52]. They reported a solid solution for $y \leq 0.5$ but deterioration of the electrochemical behaviour with increasing manganese content. Spahr *et al.* [53] repeated the work, also showing a maximum solubility of 0.5 Mn. They however found optimum electrochemical behaviour for the composition $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. They reported XPS and magnetic data that are consistent with the present interpretation of Ni^{2+} and Mn^{4+} ions rather than Ni^{3+} and Mn^{3+} and showed electrochemical cycling curves very reminiscent of LiNiO_2 . Ohzuku [54] was reported that the compound (0.5Ni, 0.5Mn, 0.0Co) as shown good electrochemical data and this was reconfirmed almost by the Dahn group [55]. Considering the Li-Ni disorder being major factor affecting the material rate capability, attempts to create new compounds of $\text{LiCo}_x\text{Ni}_y\text{Mn}_{1-x-y}$ are motivated. With additional Co ions existing in the structure, the Li-Ni interlayer mixing can be reduced to 1–6% [4].

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is reported well electrochemical by Ohzuku *et al.* in 2001 [54] and show relatively good performance at elevated temperature (80% capacity can be retained at 55°C and half capacity at 95°C) [56]. The $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ layer compound can be regarded as the solid solution of LiCoO_2 , LiNiO_2 and LiMnO_2 . $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ deliver similar reversible capacity with $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. Their voltage profile are also similar in shape, but the operation voltage window of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ can be extended to 3.6–4.7 V. While the introduction of Co ions into $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ could improve the material stability [4].

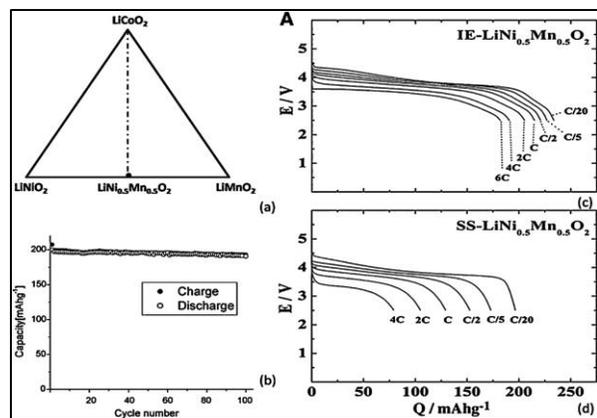


Figure 3 Performance of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$: (a) compositional phase diagram, (b) cycling performance, (c) rate performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by ion exchange method, and (d) rate performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized by solid state method [4]

Other transition metals such Ti doping in $\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$ phase system. Layered $\text{LiNi}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_2$ was prepared by an emulsion drying method. Solid solution of $\text{LiNi}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_2$ ($R-3m$, space group) was formed to $x \leq 0.3$, and when $x > 0.3$, the layered structure transformed to the simple cubic structure. A small amount

of Ti doping into $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ structure resulted in reduced cation mixing in the Li layer, and the stronger Ti-O bond relative to the Mn-O one would stabilize the crystal structure. Consequently, charge-discharge capacity and Li^+ chemical diffusion of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5-y}\text{Ti}_y\text{O}_2$ cells were enhanced by the improvement of physical properties in the oxide matrix and good thermal safety characteristics at a highly oxidized state [57]. Doping non transition metal fluorine, F process was a useful and efficient approach to reduce the cation mixing and improve the poor rate performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ material. The structure, morphology and electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are influenced by F doping effect and the reversible capacity of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_{1.96}\text{F}_{0.04}$ is 155.0 mAh g^{-1} after 50 cycles at 0.2 C, 0.5 C and 1.0 C ratios between 2.8 and 4.6 V [58].

2.4 Lithium Nickel Aluminium Oxide

Among the electrochemically inactive ions, Al has been preferred due to light in weight, abundant, less expensive and environmental benignity. The Al-substituted lithium nickel oxide is expected to be cathode material with higher energy density and lower cost with less toxic [59]. In addition, it has been found that Al substitution leads to an increase in the electrode potential where the reversible Li intercalation take place. Al-substitution oxide have been reported to display better thermal stability in delithiated state as compared to pure LiNiO_2 and lithium nickelate in its charged state [60][61]. However the capacity decrease as the aluminium content increases, which is to be expected given that aluminium is not electrochemically active. Guilnard *et al.* [62] investigated the electrochemical performances of $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ ($0.10 \leq Y \leq 0.50$) specimens synthesized by a co-precipitation method. Charge-discharge cycling of $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ as positive electrode material in lithium cells has shown that aluminium substitution suppresses all the phase transitions observed for LiNiO_2 system [63].

From several experiment, it has been found that the synthesis condition have a strong effect on the composition and crystal structure of lithium nickelates. The local cationic distribution in $\text{Al}_y\text{Ni}_{1-y}\text{O}_6$ depends on the synthesis temperature. At atmospheric pressure, higher synthesis temperature promotes the reaction of cation mixing between the layers [64].

Castro-Gracia *et al.* group studied $\text{LiNi}_{0.5-y}\text{Al}_y\text{Co}_{0.5}\text{O}_2$ ($0 \leq y \leq 0.3$) solid solutions have been synthesized by a sol-gel method using succinic acid as chelating agent. X-ray diffraction patterns show that all the samples are single phase and have the layered α - NaFeO_2 structure. The regular variation of the lattice parameters and the IR frequency modes indicate the formation of the solid solutions. Aluminium doping increases the interval of thermal stability favoring the formation of well-crystallized $\text{LiNi}_{0.5-y}\text{Al}_y\text{Co}_{0.5}\text{O}_2$ powders at lower temperatures and preventing the loss of lithium from the structure. The grain size decreases upon doping and this fact can favor the lithium diffusion. The initial charge and discharge capacities decrease as the aluminum content gets higher. However, more stable charge-discharge cycling performances have been obtained as compared to those displayed by the native oxides diffusion coefficients increase with Al^{3+} doping due to the increase in the interlayer distance and the decrease of the size of the particles [65].

2.6 Other Lithium Nickel Oxide Derivative

$\text{LiNi}_{1-y}\text{Fe}_y\text{O}_2$ system can be single structural to LiNiO_2 which could be obtained in the range of $0 \leq y \leq 0.3$ and that the iron substitution led to a decrease in the electrochemical activity [65-67]. Prado *et al.* [72] reported that the substitution of Fe for Ni in LiNiO_2 degrades the electrochemical properties by making the lattice size larger and, thus, making the Ni^{2+} ions more stable than Ni^{3+} .

According Song *et al.* [76] $\text{LiNi}_{1-y}\text{Fe}_y\text{O}_2$ with $y = 0.025$ and 0.050 had higher first discharge capacities than LiNiO_2 and better or similar cycling performance at a 0.1 C rate in the voltage range of 2.7–4.2 V. The $\text{LiNi}_{0.975}\text{Fe}_{0.025}\text{O}_2$ sample had the highest first discharge capacity of 176.5 mAh/g and a discharge capacity of 121.0 mAh/g at $n = 100$.

Ti ions were used to substitute the Ni ions in LiNiO_2 since there are advantages in terms of lower atomic weight and clear reduced (III)-oxidized (IV) states in the Li- intercalation reaction. Jahn-Teller distortion in $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$ is reduced with decreasing Ni^{3+} ions due to the substitution of Ti^{3+} ions. [67,68] (Sethuprakash,2005). Ha *et al.* reported that $\text{LiNi}_{0.9}\text{Ti}_{0.1}$ has a better thermal stability than LiNiO_2 and $\text{LiNi}_{0.975}\text{Ti}_{0.025}\text{O}_2$ show that initial discharge capacity of 171 mAh/g and excellent capacity retention over 30 cycles [69]. Song *et al.* studied $\text{LiNi}_{0.995}\text{Ti}_{0.005}\text{O}_2$, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ were synthesized by wet milling and solid-state reaction. All the synthesized samples possessed the α - NaFeO_2 structure of the rhombohedral system (space group; $R\bar{3}m$) with no evidence of any impurities. Among all the specimens, $\text{LiNi}_{0.990}\text{Al}_{0.005}\text{Ti}_{0.005}\text{O}_2$ has the largest first discharge capacity 196.3mAh/g at a rate of 0.1C [70].

Another derivative of LiNiO_2 is a $\text{LiNi}_{1-x}\text{Sb}_x\text{O}_2$ system. Cui *et al.* [71] reported $\text{LiNi}_{1-x}\text{Sb}_x\text{O}_2$ ($x = 0.0, 0.1, 0.15, 0.20, 0.25$) showed the cell with Sb-doped LiNiO_2 deliver charge capacities of 159.2, 145.3, 138 and 98.78 mAh/g for the Sb content corresponding to 0.1, 0.15, 0.20 and 0.25 respectively. The coulombic efficiencies are higher than that of LiNiO_2 material, meaning that oxygen loss has been effectively suppressed in the charge state. The substituting Sb^{5+} ions, being inactive, reduce the ideal specific capacity of substituted compounds. $\text{LiNi}_{0.8}\text{Sb}_{0.2}\text{O}_2$ deliver the biggest discharge capacity of 117 mAh/g and coulombic efficiency of 84.8% in the first cycle. After 20 cycle the discharge capacity fade by 12.4%. It exhibits excellent capacity retention due its reinforced structural stability and discharge capacity of 102.4 mAh/g still obtained after 20 cycles in the voltage range of 2.5–4.5V. Oxygen loss has been effectively suppressed by introducing Sb^{5+} ion in LiNiO_2 . Higher thermal decomposition temperature in the charge state further confirm that $\text{LiNi}_{0.8}\text{Sb}_{0.2}\text{O}_2$ is more stable than LiNiO_2 .

Gallium-doping to LiNiO_2 was investigated, and it is effective to improve the cycling behavior of LiNiO_2 [28]. Gallium was selected because it forms a trivalent Ga^{3+} ion, and its ionic radius (0.76 Å) is close to that of the Ni^{3+} ion (0.74 Å). The gallium-doping to LiNiO_2 stabilizes the crystal structure during the charging process, i.e., single hexagonal structure is retained all over the charging state without monoclinic phase and without two-hexagonal-phase region. Consequently, the crystal lattice parameters change continuously and gradually improving the cycling behavior at high capacity. Ga content of $y = 0.02$ shows high rechargeable capacity of ~ 190 mAh/g and retention of more than 95% after 100 cycles. The gallium-doped LiNiO_2 also demonstrates an excellent over-charge resistance. The thermal stability of the specimen is now under investigation. According Song *et al.* [70] $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ has a α - NaFeO_2 structure of rhombohedral system. It showed discharge capacity of 174.4 mAh/g at first cycle and maintain at 117.4 mAh/g after 20 cycle. Kwon *et al.* studied the variation, with C-rate, of discharge capacity vs. number of cycles curve for the $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ cathode. It has the largest first discharge capacity of 149 mAh/g at 0.1 C rate. The first discharge capacity decreases as the C- rate increased. The $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ cathode exhibits good cycling performances at 0.2 and 0.5 C rates from $n = 1$, and it has similar cycling performances at all the C-rates after $n = 10$. It shows very low discharge capacity degradation rates of 0.17 and 0.04 mAh/g/cycle, respectively, at 0.2 and 0.5 C rates. At 0.1 C rate, the $\text{LiNi}_{0.975}\text{Ga}_{0.025}\text{O}_2$ cathode exhibits the discharge capacity of 114 mAh/g at $n = 50$.

3.0 CONCLUSION

The development of improved cathode materials is a challenge for meeting current and future energy storage requirements. Several transition metal based cathode materials can provide high voltages and good capacities. Substitutions of certain cation for nickel in LiNiO_2 and their derivative such as cobalt, aluminium, magnesium and other can modify the characterization, electrochemical performance and properties of the positive electrode to fulfill characteristic for best cathode for lithium ion batteries. The synthesis and temperature condition also influence the structure performance of the cathode.

References

- [1] B. Dunn, H. Kamath, J.-M. Tarascon. 2011. Review: Electrical Energy Storage for the Grid: A Battery of Choices. *Science*. 334: 928–935. DOI: 10.1126/science.1212741.
- [2] A. Väyrynen & J. Salminen. 2012. Lithium Ion Battery Production. *J. Chem Thermodynamics*. 46: 80–85.
- [3] A. Chen. 2007. Batteries of the Future II. Building Better Batteries Through Advanced Diagnostics. Retrieved from Science @ Berkeley Lab website <http://www2.lbl.gov/Science-Articles/Archive/sabl/2007/Feb/future-batteries-II.html>.
- [4] B. Xu, D. Qian, Z. Wang, Y.S. Meng. 2012. Recent Progress in Cathode Materials Research for Advanced Lithium Ion Batteries. *Mater. Sci. Eng. R* 73: 51–65.
- [5] L. J. Fu, H. Liu, C. Li, Y.P. Wu, E. Rahm, R. Holze, H. Q. Wu. 2005. Electrode Material for Lithium Secondary Batteries Prepared by Sol-gel Method. *Prog. Mater. Sci.* 50: 881–928.
- [6] M. Wohlfahrt-Mehrens, C. Vogler, J. Garche. 2004. Aging Mechanism of Lithium Cathode Materials. *J. Power Sources*. 127: 58–64.
- [7] Y. Nishi. 1997. *Something About Lithium Ion Batteries*. Tokyo: Shokabo Press.
- [8] J. O. Besenhard. 1999. *Handbook of Battery Materials*. Weinheim: Wiley-VCH.
- [9] Y. P. Wu, C. Wan, C. Jiang, S. B. Fang. 2002. *Lithium Ion Secondary Batteries*. Beijing: Chemical Industry Press.
- [10] J. W. Fergus. 2010. Recent Developments in Cathode Materials for Lithium Ion Batteries. *J. Power Sources*. 195: 939–954.
- [11] Y. Gan, L. Zhang, Y. Wen, F. Wang, H. Su. 2008. Carbon Combustion Synthesis of Lithium Cobalt Oxide as Cathode Material for Lithium ion Battery. *Particuology*. 6: 81–84.
- [12] L. Zhang, X. Lv, X. Wen, F. Wang, H. Su. 2009. Carbon combustion Synthesis of $\text{LiNi}_0.5\text{Mn}_1.5\text{O}_4$ and Its Use as a Cathode Material for Lithium Ion Batteries. *J. Alloy Compds*. 480: 802–805.
- [13] C. Li, H.P. Zhang, L. J. Fu, Y. P. Wu, E. Rahm, R. Holze, H. Q. Wu. 2006. Cathode Materials Modified by Surface Coating for Lithium Ion Batteries. *Electrochimica Acta*. 5: 3872–3883.
- [14] G. X. Wang, S. Bewlay, Y. Yao, Y. Chen, Z. P. Guo, H. K. Liu, S. X. Dou. 2003. Multiple-ion-doped Lithium Nickel Oxides as Cathode Materials for Lithium-Ion Batteries. *J. Power Sources*. 119–12: 189–194.
- [15] S. Megahed, W. Ebner. 1995. Lithium-ion Battery for Electronic Applications. *J. Power Sources*. 54: 155–162.
- [16] M. G. S. R. Thomas, W. I. F. David, J. B. Goodenough, P. Grove. 1985. Synthesis and Structural Characterization of the Normal Spinel $\text{Li}[\text{Ni}_2]\text{O}_4$. *Mater. Research Bull.* 20: 1137.
- [17] M. Broussely, F. Perton, J. Labat, R.J. Staniewicz, A. Romero. 1993. $\text{Li}/\text{Li}_x\text{NO}_2$ and $\text{Li}/\text{Li}_x\text{CoO}_2$ Rechargeable Systems: Comparative Study and Performance of Practical Cells. *J. Power Sources*. 43: 209–216.
- [18] M. Broussely, F. Perton, P. Biensen, J. M. Bodet, J. Labat, A. Lacerf, C. Delmas, A. Rougier, J. P. Peres. 1995. Li_xNiO_2 A Promising Cathode for Rechargeable Lithium Batteries. *J. Power Sources*. 54: 109–114.
- [19] J. R. Dahn, U. V Sacken, M. W. Juzkow, H. Al-Janaby. 1991. Rechargeable LiNiO_2 /carbon Cells. *J. Electrochem. Soc.* 138: 2207.
- [20] T. Ohzuku, & A. Ueda. 1994. Why Transition Metal (Di)Oxides are the Most Attractive Materials for Batteries. *Solid State Ionic*. 69: 201–211.
- [21] R. Sathiyamoorthi, P. Manisankar, P. Shakkthivel, M. S. Lee, T. Vasudevan. 2008. Synthesis Characterization and Electrochemical Studies of $\text{LiNi}_{0.8}\text{Mn}_{0.2}\text{O}_2$ Cathode Material for Rechargeable Lithium Batteries. *Bull. Mater. Sc.* 31: 441–447.
- [22] Y. D. Zhong, X. B. Zhao, G. S. Cao. 2005. Characterization of Solid-state Synthesized Pure and Doped Lithium Nickel Cathode Oxide. *Mater. Sci. Eng.* B121: 248–254.
- [23] K. Chang, B. Hallstedt, D. Music. 2012. Thermodynamic Description of the LiNiO_2 - NiO_2 Pseudo-binary System and Extrapolation to the $\text{Li}(\text{Co}, \text{Ni})\text{O}_2$ - $(\text{Co}, \text{Ni})\text{O}_2$ System. *Music CALPHAD: Computer Coupling of Phase Diagram and Thermochemistry*. 37: 100–107.
- [24] M. Y. Song, I. H. Kwan, H. R. Park, D. R. Munn. 2012. Electrochemical Properties of Lithium Nickel Oxide Synthesized by the Combustion Method in an O_2 Stream. *Ceramics International*. 38: 2443–2448.
- [25] S. N. Kwon, S.-D. Yoon, H. R. Park, M. Y. Song. 2010. Variation of Discharge Capacities with C-rate for $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ ($\text{M} = \text{Ni}, \text{Ga}, \text{Al}$ and/or Ti) Cathodes Synthesized by the Combustion Method. *Ceramics International*. 36: 893–898.
- [26] M. M. Doeff. 2013. Battery Cathodes. In: R.J Brodd (Ed.). *Batteries for Sustainability*. New York, NY: Springer. 5–49.
- [27] C. Poullierie, F. Perton, P. H Biensan, J. P. Peres, M. Broussely, C. Delmas. 2001. Effect of Magnesium Substitution on the Cycling Behavior of Lithium Nickel Cobalt Oxide. *J. Power Sources*. 96: 293.
- [28] Y. Nishida, K. Nakane, T. Satoh. 1997. Synthesis and Properties of Gallium-doped LiNiO_2 as the Cathode Material for Lithium Secondary Batteries. *J. Power Sources*. 68: 561–564.
- [29] Y. Gao, V. Yakovleva, V. Ebner. 1998. Novel $\text{LiNi}_{1-x}\text{Ti}_x\text{Mg}_{x/2}\text{O}_2$ Compounds as Cathode Materials for Safer Lithium-Ion Batteries. *Electrochem. Solid State Lett.* 1: 117–119.
- [30] H. Tukamoto, & A. R. J. West. 1997. Electronic Conductivity of LiCoO_2 and its Enhancement by Magnesium Doping. *J. Electrochem. Soc.* 144: A3164–A3168.
- [31] C. Poullierie, L. Croguennec, C. Delmas. 2000. The $\text{Li}_x\text{Ni}_{1-y}\text{M}_y\text{O}_2$ ($y=0.05, 0.10$) System: Structural Modifications Observed upon Cycling. *Solid State Ionics*. 132: 15–29.
- [32] B. Scrosati. 2000. Recent Advances in Lithium Ion Battery Materials. *Electrochimica Acta*. 45: 2461–2466.
- [33] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakosho, H. Komori. 1993. Comparative Study LiCoO_2 , $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ and LiNiO_2 for 4 volt Secondary Lithium Cells. 38: 1159.
- [34] A. Rougier, I. Saadoun, P. Gravereau, P. Willman, C. Delmas. 1996. Effect of Cobalt Substitution on Cationic Distribution in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ Electrode Materials. *Solid State Ionics*. 90: 8–90.
- [35] I. Saadoun, & C. Delmas. 1996. $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ Positive Electrode Materials: Relationships between the Structure, Physical Properties and Electrochemical Behaviour. *J. Mater. Chem.* 6: 193–199.
- [36] I. Saadoun, & C. Delmas. 1998. On the $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ System. *J. Solid State Chem.* 136: 8–15.
- [37] I. Saadoun, M. Menetrier, C. Delmas, C. 1997. Redox Processes in $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ Cobalt-rich Phases. *J. Mater. Chem.* 7: 2505–2511.
- [38] E. Zhecheva, & R. Stoyanova. 1993. Stabilization of the Layered Crystal Structure of LiNiO_2 by Co-substitution. *Solid State Ionics*. 66: 143–149.
- [39] B. V. R. Chowdari, G. V. Subba Rao, S. Y. Chow. 2001. Cathodic Behaviour of (Co, Ti, Mg)-doped LiNiO_2 . *Solid State Ionics*. 140: 55–62.
- [40] G. T. K Fey, R. F. Shiu, V. Subramaniam, J. G. Chen, C. L. Chen. 2002. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Cathode Materials Synthesized by the Maleic Acid Assisted Sol-Gel Method for Lithium Batteries. *J. Power Sources*. 103: 265–272.
- [41] P. Wilk, J. Marzec, J. Molenda. 2003. Structural and Electrical Properties of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$. *Solid State Ionics*. 157: 109–114.
- [42] J. Cho, H. Jung, Y. Park, G. Kim, H.S. Lim. 2000. Electrochemical Properties and Thermal Stability of $\text{Li}_x\text{Ni}_{1-x}\text{Co}_x\text{O}_2$ Cathode Materials. *J. Electrochem. Soc.* 147: 15–20.
- [43] S. Madhavi, G. V. Subba Rao, B. V. R. Chowdari, S. F. Y Li. 2002. Cathodic Properties of (Al, Mg) Co-doped $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$. *Solid State Ionics*. 152–153: 199–205.
- [44] G. X. Wang, J. Horvat, D. H. Bradhurst, H. K. Liu, S. X. Dou. 2000. Structural, Physical and Electrochemical Characterisation of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ Solid Solutions. *J. Power Sources*. 85: 279–28.
- [45] I. Nakai, & T. Nakagome. 1998. In Situ Transmission X-Ray Absorption Fine Structure Analysis of the Li Deintercalation Process in $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.5})\text{O}_2$. *Electrochem. Solid State Lett.* 1: 259–261.
- [46] H. Chao, B. Xia, B., Xu, N., Zhang, C. 2004. Structural and Electrochemical characteristics of Co and Al co-doped Lithium Nickelate Cathode Materials for Lithium-ion Batteries. *J. Alloy. Compd.* 376: 282–286.
- [47] C. H. Chen, J. Liu, M. E. Stoll, G. Henriksen, D. R. Vissers, K. Amine. 2004. Aluminium Doped Lithium Nickel Cobalt Oxide Electrodes for High-power Lithium Ion Batteries. *J. Power Sources*. 128: 278–285.
- [48] M. Carewska, S. Scaccia, F. Croce, A. Arumugam, Y. A. Wang, Y. Greenbaum. 1997. Electrical Conductivity and ^6Li NMR Studies of $\text{Li}_{1+y}\text{CoO}$. *Solid State Ionic*. 93: 227–238.
- [49] J. Xiang, C. Chang, F. Zhang, J. Sun. 2009. Effect of Mg Doping on the Electrochemical Properties of $\text{LiNi}_{0.8}\text{Co}_{0.2}$ Cathode Material. *J. Alloy. Compd.* 475: 483–487.
- [50] S. Albrecht., J. Kumpers, M. Kruff, S. Malcus, C. Vogler, M. Wahl, M. Wohlfahrt-Mehrens. 2009. Electrochemical and Thermal Behavior of

- Aluminium-and Magnesium-doped Spherical Lithium Nickel Cobalt Mixed Oxides $\text{Li}_{1-x}(\text{Ni}_{1-y}\text{Co}_y\text{M}_x)\text{O}_2$ (M=Al, Mg). *J. Power Sources*. 119–121: 178–183.
- [51] H. Li, Q. Xu, X-X. Shi, D. W. Song, Q-L. Zhang. 2013. Electrochemical Performances of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with Different Synthesis Methods. *Rare Metals*. DOI 10.1007/S12598-013-0088-2.
- [52] E. Rossen, C. D. W. Jones, J. R. Dahn. 1992. Structure and Electrochemistry of $\text{Li}_x\text{MnyNi}_{1-y}\text{O}_2$. *Solid State Ionics*. 57: 311.
- [53] M. E. Sphar, P. Novak, B. Schnyer, O. Haas, R. Nesper. 1998. Characterization of Layered Lithium Nickel Manganese Oxides Synthesized by a Novel Oxidative Coprecipitation Method and Their Electrochemical Performance as Lithium Insertion Electrode Material. *J. Electrochem. Soc.* 145(4): 1113–1121.
- [54] T. Ohzuku, & Y. Makimura. 2001. Layered Lithium Insertion Material of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$: A Possible Alternative to LiCoO_2 for Advanced Lithium-ion Batteries. *Chem Lett*. 30: 744–745.
- [55] Z. Lu, D. D. MacNeil, J. R. Dahn. 2001. Layered Cathode Materials $\text{Li}[\text{NixLi}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ for Lithium-Ion Batteries. *Electrochemical and Solid State Letter*. 4: A191–A194.
- [56] N. Yabuuchi, & T. Ohzuku. 2005. Electrochemical Behaviors of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in Lithium Batteries at Elevated Temperatures. *J. Power Sources*. 146: 636–639.
- [57] N. Kumagai, S-T. Myung, S. Komaba, K. Hosoya, K. Kurihara. 2006. Effect of Ti on Structure and Electrochemical Properties of $\text{LiNi}_{0.5}\text{Mn}_{0.5-x}\text{Ti}_x\text{O}_2$ Synthesized by Emulsion Drying Method. 208th ECS Meeting: Abstract 11.
- [58] C. Hu, J. Gua, Y. Peng, Y. Chen. 2013. Preparation and Electrochemical Performance of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_{2-x}\text{F}_x$ ($0 \leq x \leq 0.04$) Cathode Material Synthesized with Hydroxide Co-precipitation for Lithium Ion Batteries. *J. Alloy Comps.* 581: 121–127.
- [59] D. Song, H. Ikuta, T. Uchida, M. Wakira. 1999. The Spinel Phases $\text{LiAl}_y\text{Mn}_{2-y}\text{O}_4$ ($y=0, 1/12, 1/9, 1/6, 1/3$) and $\text{Li}(\text{Al,M})_{1/6}\text{Mn}_{11/6}\text{O}_4$ (M=Cr, Co) as the Cathode for Rechargeable Lithium Batteries. *Solid State Ionics*. 117: 151–156.
- [60] E. Shinova, H. Zecheva, R. Stoyanova. 2006. Formation of $\text{LiAl}_y\text{Ni}_{1-y}\text{O}_2$ Solid Solutions Under High and Atmospheric Pressure. *J. Solid State Chem.* 179: 3151–3158.
- [61] T. Ohzuku, T. Yanagawa, M. Kouguchi, A. Ueda. 1997. Innovative Insertion Material of $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$ (R-m) for Lithium-ion (shuttlecock) Batteries. *J. Power Sources*. 68: 131–134.
- [62] M. Guilmard, A. Rougier, M. Grune, L. Croguennec, C. Delmas. 2003. Effects of Aluminum on the Structural and Electrochemical Properties of LiNiO_2 . *J Power Sources*. 115: 305–314.
- [63] M. Guilmard, C. Poullerie, L. Croguennec, C. Delmas. 2003. Structural and Electrochemical Properties of $\text{LiNi}_{0.70}\text{Co}_{0.15}\text{Al}_{0.15}\text{O}_2$. *Solid State Ionics*. 160: 39–50.
- [64] J. Kim, B. H. Kim, Y. H. Baik, P. K. Chang, H. S. Park, K. Amine. 2006. Effect of (Al, Mg) Substitution in LiNiO_2 Electrode for Lithium Batteries. *J. Power Sources*. 158: 641–645.
- [65] S. Castro-Gracia, A. Castro-Cauceiro, M. A. Senaris-Rodrigues, F. Soulette, C., Julien. 2003. Influence of Aluminium Doping on the Properties of LiCoO_2 and $\text{LiNiCo}_{0.5}\text{O}_2$ Oxides. *Solid State Ionics*. 156: 15–26.
- [66] C. Delmas, G. Prado, A. Rougier, E. Suard, L. Fournes. 2000. Effect of Iron on the Electrochemical Behavior of Lithium Nickelate: from LiNiO_2 to 2D- LiFeO . *Solid State Ionics*. 135: 71–79.
- [67] V. Sethuprakash. 2005. Structural and Electrochemical Studies of Lithium Nickel Oxide Derivatives Doped with Transition and Non-Transition Metals Prepared by Solid-State Reaction Method. University of Malaya, Kuala Lumpur.
- [68] J. W. Jeong, & S-G. Kang. 2003. Structural and Electrochemical Properties of $\text{LiNi}_y\text{Ti}_{1-y}\text{O}_2$ Prepared by a Wet Process. *Journal of Power Sources*. 123: 75–78.
- [69] H.-W. Ha, K. H. Jeong, K. Kim. 2006. Effect of Titanium Substitution in Layered LiNO_2 Cathode Materials Prepared by Molten-salt Synthesis. *J. Power Sources*. 161: 606–611.
- [70] M. Y. Song, C. K. Park, S. D. Yoon, H. R. Park, D. R. Munn. 2009. Electrochemical Properties $\text{LiNi}_{1-y}\text{M}_y\text{O}_2$ (M= Ni, Ga, Al and/or Ti) Cathode. *Ceramics International*. 35: 1145–1150.
- [71] P. Cui, Z. Jia, L. Li, T. He. 2011. Preparation and Characteristic of Sb-doped LiNiO_2 Cathode Materials for Li-ion Batteries. *Journal of Physics and Chemistry of Solid*. 72: 899–903.
- [72] G. Prado, A. Rougier, L. Fournes, C. Delmas. 2000. *J. Electrochem. Soc.* 147(8): 2880.
- [73] M. Y. Song, I. H. Kwon, H. U. Kim, S. Shim, D. R. Mumm. 2006. *J. Appl. Electrochem.* 36: 801.
- [74] M. Y. Song, R. Lee. 2002. Synthesis by Sol-gel Method and Electrochemical Properties of LiNiO_2 Cathode Material for Lithium Secondary Battery. *J. Power Sources*. 111: 97–103.
- [75] D. S. Lee. 2004. A Study on the Synthesis and the Electrochemical Properties of $\text{LiNi}_1\text{yMyO}_2$ (M= Zn^{2+} , Al^{3+} and Ti^{4+}) Cathode Materials for Lithium Secondary Battery. Master Thesis, Chonbuk National University, Republic of Korea.
- [76] M. Y. Song, I. H. Kwon, S. Shim, J. H. Song. 2010. Electrochemical Characterizations of Fe-substituted LiNiO_2 synthesized in air by combustion method. *Ceramics International*. 36: 1225–1231.