Synthesis of $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathodes with deficient and excess lithium using an ultrasonic sound-assisted co-precipitation method for Li-ion batteries

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Abstract. The possible improvements in structural stability and capacity of nickel–cobalt–aluminium cathode material were investigated by synthesizing this compound with various lithium amounts ($\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ where $x = 0.90, 0.95, 1.00$ and 1.05). An ultrasound-assisted co-precipitation method was performed to produce spherical, nanosized powders with a narrow size distribution which satisfies a homogeneous and dense film during calendaring. Layered $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ ($x = 0.90, 0.95, 1.00$ and 1.05) cathode active materials were successfully synthesized with this method and chemical compositions of the powders synthesized were determined by inductively coupled plasma-mass spectroscopy. Structural characterization was carried out via X-ray diffraction and scanning electron microscopy techniques. The electrochemical properties of the cathode materials were investigated by electrochemical impedance spectroscopy, galvanostatic charge/discharge and cyclic voltammetry methods. Among the cathode compositions in the current study, $\text{Li}_{1.05}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ exhibited the highest capacity, 138 mAh g^{-1} with 95% capacity retention upon 22 cycles.

Keywords. Co-precipitation; ultrasound; cathode material; Li-ion battery; sonochemistry.

1. Introduction

In recent years, commercial consumption of Li-ion batteries has become more prevalent due to their wide spread use in mobile devices, such as mobile phones, tablets and portable computers [1]. It is known that the choice of cathode materials significantly affects the performance and the overall cost of Li-ion batteries [2]. Among the cathode materials, layered structured compounds, which are the earliest form of intercalation cathodes, find their way in many applications. Studies show that layered LiNiO_2 has a higher energy density with lower cost compared to LiCoO_2 and their commercial counterparts [3–5]. However, there have been some difficulties during LiNiO_2 synthesis and it also has a poor thermal stability in the charged state causing safety problems [6]. To improve the thermal stability of LiNiO_2 and to reduce high cost of LiCoO_2 due to Co content, Ni–Co mixed-layered compounds were developed [7]. Belharouak *et al* [8] showed that alloying Ni–Co mixed-layered compounds with Al is an efficient way for further improvement in the stability of this compound. Recently, a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) electrode material has become a commercial product as a cathode material. However, some possible improvements can still be conducted for this compound to have better structural stability, capacity and reversibility during cycling.

One of the important challenges in Ni-oxide based cathodes is to prevent cation disordering of Ni ions in the lithium site. This disordering leads to lithium deficient stoichiometry with the chemical formula $(\text{Li}_{1-x}\text{Ni}_x^{2+})(\text{Ni}_x^{2+}\text{Ni}_{1-2x}^{3+})\text{O}_2$. Li-ion intercalation became difficult during charging/discharging and it results in a polarization loss due to structural distortion caused by the Ni ion in the Li site [9]. This emphasizes the fact that the amount of lithium in the $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ compounds is critical since lithium greatly affects the structural stability and the electrochemical performance of batteries.

The cation disordering on the octahedral sites has a great influence on reversibility. Among non-stoichiometric LiNiO_2 studies, $\text{Li}_{0.966}\text{Ni}_{1.004}\text{O}_2$ exhibited significant reversibility and a specific capacity of about 150 mAh g^{-1} [10]. Even a small deviation from ideal stoichiometry results in striking improvements in the electrochemical performance.

An effective surface area of active materials is another key point affecting the performance of the batteries in terms of capacity and rate capability. An increase in the effective surface area provides more active sites for surface reactions, a lower diffusion distance to Li^+ ions and higher electrode–electrolyte contact areas [11]. Moreover, during electrode preparation, having a homogeneous and dense film on the current collector greatly depends on the size and shape of

the active material particles. Having spherical-shaped fine particles with a narrow size distribution provides dense slurry and homogeneous coating of this slurry to the current collector. In this way, capacity loss during cycling can be minimized. An ultrasound-assisted co-precipitation method can provide spherical, nanosized particles with a narrow size distribution [12,13].

Ultrasonic sound theory is based on bubble formation, growth and collapse. Once these bubbles are formed, they grow with the diffusion of vapour solutes through these bubbles. The growth of bubbles is continuous until they reach critical sizes in the range of ten microns to a few hundred microns. When bubbles reach the critical size, they collapse and this leads to an increase in the temperature up to 5000 K and pressure up to 1000 bar locally. As a result of the local increase in temperature and pressure, chemical bonds are broken [14]. Moreover, bubbles formed by ultrasound act as nucleation sites for newer particles to form in the solution [15]. This nucleation dominant process results in spherical nanosized particles with a narrow size distribution.

In the current study, the ultrasound-assisted co-precipitation method was used to synthesize $\text{Li}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ compounds. Moreover, structural and electrochemical performances of layered $\text{Li}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ($x = 0.90, 0.95, 1.00$ and 1.05) cathode active materials were examined to comprehend the effect of the lithium amount on these properties.

2. Experimental

$\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}$ oxide powders were synthesized by the ultrasonic sound-assisted co-precipitation method using nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$) as precursor materials. Citric acid was used as a chelating agent to allow simultaneous precipitation of these transition metals. Each metallic salt was separately dissolved in distilled water with a metallic salt to a citric acid molar ratio of 4:1. The aqueous aluminium solution was pumped to a feeding unit, which is a closed circuit continuous circulation system attached to the UIP2000hdT generator (Hielscher Ultrasound Technology) with a rate of 50 ml min^{-1} . This step was followed by simultaneous addition of NH_4OH solution and cobalt–citric acid solution with rates of 5 and 50 ml min^{-1} , respectively. Citric acid containing nickel solution was added in the same way as cobalt. Fifteen minute circulation was used to expose the powders to the ultrasonic irradiation, after each aqueous solution was fed into the reactor. During the mixing of aqueous solutions, NH_4OH (28% NH_3) was added into the solution to maintain the pH at 10.5 ± 0.1 . The pH level was then raised to 13.5 by adding 6 M NaOH solution following the 15 min circulation. The solution was then exposed to ultrasonic irradiation for additional 30 min as a final step until the given energy to

the system reaches 350 Wh. The prepared jelly-like solution was dried at 110°C and then pre-calcined at 300°C for 12 h. After pre-calcination, the Al- and Co-doped NiO phase was obtained. Pre-calcined samples were washed several times with distilled water using a rod-type sonicator. The samples were then filtered and dried. Lithium carbonate and the synthesized powder were mixed in a mixer mill with various Li to NCA ratios, such as 0.90, 0.95, 1.00 and 1.05. The powder mixtures were then calcined at 800°C for 24 h to obtain $x\text{Li-NCA}$ samples.

The crystal structure of samples was analysed using an X-ray diffractometer (XRD, Bruker D8 Advance, $\text{CuK}\alpha$). Lattice parameters of structures and the weight ratio of phases were determined using MAUD Rietveld refinement software [16]. The particle size distribution of the powders was analysed by a particle size analyser (Mastersizer 2000). The morphology of the powders was investigated using scanning electron microscopy (SEM, Nova NanoSEM 430) and high-resolution transmission electron microscopy (HRTEM) (JEOL JEM 2100F HREM). The chemical composition of the powders was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) (Perkin Elmer DRC II model, ICP-MS).

Electrodes were prepared in the form of a slurry by mixing the produced powders which are cathode-active materials, polyvinylidene difluoride binders and carbon black with a ratio of 90:5:5, respectively. The slurry was coated on an aluminium foil using a doctor blade with a $230 \mu\text{m}$ gap. After the pre-drying step, electrodes were cut into 18 mm diameter discs and were kept under vacuum at 120°C for 12 h. This procedure yields, loading of an $\sim 7.9 \text{ mg cm}^{-2}$ active material in the electrode. Cells were assembled, using lithium foil as the counter electrode, 1 M LiPF₆ in a 50:50 EC:DEC solution as the electrolyte and glass micro fibre paper as the separator, in a glove box filled with argon gas. First discharge capacity was performed at a C/18 rate, whereas the electrochemical cells were cycled at a C/12 rate for 22 cycles ($1 \text{ C} = 180 \text{ mAh g}^{-1}$) in the range of 2.8–4.2 V. Cyclic voltammetry (CV) measurements were carried out within the voltage range of 2.8–4.2 V with a scan rate of 0.02 mV s^{-1} . CV, charge/discharge and voltage profiles were recorded using a potentiostat/galvanostat (SOLATRON 1480 Multistat). Electrochemical impedance spectroscopy (EIS) measurements for each sample at the discharged state were carried out after first and last cycles by VersaSTAT 3 within the frequency range of 300 kHz to 3 mHz with an AC amplitude of $\pm 10 \text{ mV}$. The $(R(\text{QR})\text{QR})$ equivalent circuit model was used for interpretation of EIS measurements using ZSimpWin software.

3. Results

Figure 1 represents the XRD pattern of the cubic Co–Al co-doped NiO phase (space group $Fm\bar{3}m$), which was obtained after pre-calcination, recorded in the 2θ range of $25\text{--}85^\circ$.

Figure 1. Rietveld refinement of the cubic NiO (Al- and Co-doped) phase.

Figure 2. XRD spectra of layered x Li-NCA samples ($x = 0.90, 0.95, 1.00$ and 1.05).

As a result of Rietveld refinement, the 3.36% R_w value was obtained showing that diffraction peak positions match well with those of the NiO phase. The lattice parameter, a of the NiO phase increased from its pure state (un-doped NiO phase) with the value of $4.117 \text{ \AA}$ [17] to $4.181 \text{ \AA}$. This 1.56% increase in the lattice parameter, a , indicates that aluminium and cobalt atoms were incorporated into the structure without forming a secondary phase.

Figure 2 shows the XRD spectra of single-phase layered x Li-NCA samples ($x = 0.90, 0.95, 1.00$ and 1.05) recorded within the 2θ range of $15\text{--}85^\circ$. This figure shows that all peaks match well with the standard layered structure of $\alpha\text{-NaFeO}_2$ (space group $R\bar{3}m$). Moreover, splitting of (006)/(102) and (108)/(110) doublets, belonging to these planes in the XRD spectrum, is an indication of the successful layered structure formation [18,19]. Lattice parameters, a and c , were obtained by Rietveld refinement and calculated compositions of x Li-NCA samples are listed in tables 1 and 2, respectively. As the lithium amount increases, lattice parameters, a and c , gradually decrease which results in constant trigonal distortion, c/a . No change in the c/a ratio shows that the trigonal characteristic was not affected from the increased amount of lithium. Likewise, Majumder

et al [9] and Park *et al* [20] reported the c/a ratio as 4.95 for the $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ compound in their study. In addition to this, the intensity ratio, $I_{(003)}/I_{(104)}$ shows the absence of cation disorder, if its value is higher than 1.2 in the case of doped-layered systems [21]. The current study showed that this ratio is affected from lithium stoichiometry. Although for all layered x Li-NCA samples ($x = 0.90, 0.95, 1.00$ and 1.05) with a $I_{(003)}/I_{(104)}$ ratio larger than the critical value, this ratio increases as the amount of lithium in the structure increases. To support this finding, site occupancies of Ni and Li atoms were also refined supposing that some amounts of Ni^{2+} could occupy the Li site, in exchange of the same amount of Li^+ occupying the Ni site. Per cent occupancy of Ni^{2+} ions in the Li site is listed in table 1. Occupancy refinement showed that the amount of Ni^{2+} ions in the Li site gradually decreased from 5.419 to 1.197% as the lithium content increases. This means that an increase in the lithium content prevented occupancy of divalent nickel ions in the lithium sites.

Oxygen atom positions are also given in table 1. These oxygen parameters were taken advantage of the calculation of the Li-gap together with the lattice parameter, c . The calculated Li-gap shows the distance between oxygen atoms, where lithium intercalates/de-intercalates in the structure. Li-gap calculation was carried out using equation (1), where z is the oxygen parameter and c is the lattice parameter [22] using the hexagonal setting of the $R\bar{3}m$ space group, with Li and transition metal atoms to be at $3b$ and $3a$ sites, respectively:

$$\text{Li-gap} = \frac{c}{3} - \left(\frac{2}{3} - 2 \cdot z \right) \cdot c. \quad (1)$$

In layered oxides with a hexagonal structure, both lithium and transition metals are in between oxygen atoms with an alternating settling. This alternating settling repeats itself three times forming a hexagonal unit cell with the lattice parameter, c . This means that the sum of the transition metal layer thickness and Li-gap value is one third of the lattice parameter, c . The more the Ni^{2+} ions are located in Li sites, the larger the transition metal layer thickness (the distance between oxygen atoms having transition metals between them) and smaller the Li-gap. As can be seen in table 1, a decrease in the metal layer thickness nullifies the rise in the Li-gap more and consequently, a decrease in the lattice parameter c , was observed. The reason is the difference in the ionic radius of these ions. The ionic radii of Li^+ , Ni^{2+} and Ni^{3+} ions are 0.076, 0.069 and 0.056 nm, respectively. As the nickel atom leaves its own site as Ni^{2+} ion to occupy the lithium site, the Li-gap decreases since Ni^{2+} ions are smaller than the Li^+ ions. On the other hand, Li^+ ions are larger than the Ni^{3+} ions causing an increase in the metal layer thickness. The difference between the ionic radius of Li^+ and Ni^{3+} ions is larger than the difference between the ionic radius of Li^+ and Ni^{2+} . For this reason, the expansion of the metal layer thickness will dominate the overall change causing an increase in the

Table 1. Structural parameters of x Li-NCA samples obtained by Rietveld refinement.

Sample	a (Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$	Ni in Li site (%)	Oxygen parameter, z	Transition metal layer thickness (Å)	Li-gap (Å)	R_w (%)
0.90Li-NCA	2.871	14.210	4.95	1.773	5.419	0.2588	2.117	2.619	4.145
0.95Li-NCA	2.870	14.206	4.95	1.876	5.389	0.2591	2.109	2.627	3.715
1.00Li-NCA	2.870	14.203	4.95	1.893	3.944	0.2587	2.119	2.615	3.802
1.05Li-NCA	2.869	14.196	4.95	1.923	1.997	0.2595	2.096	2.636	4.931

Table 2. Chemical analysis results of layered x Li-NCA samples obtained by ICP-MS analysis.

Sample	Concentration (wt%)				Calculated formula
	Li	Ni	Co	Al	
0.90Li-NCA	6.91	54	9.32	1.22	$\text{Li}_{0.89}(\text{Ni}_{0.82}\text{Co}_{0.14}\text{Al}_{0.04})\text{O}_{2\pm\sigma}$
0.95Li-NCA	7.29	54	9.28	1.26	$\text{Li}_{0.93}(\text{Ni}_{0.82}\text{Co}_{0.14}\text{Al}_{0.04})\text{O}_{2\pm\sigma}$
1.00Li-NCA	7.37	52	8.99	1.23	$\text{Li}_{0.98}(\text{Ni}_{0.82}\text{Co}_{0.14}\text{Al}_{0.04})\text{O}_{2\pm\sigma}$
1.05Li-NCA	7.56	51	8.93	1.19	$\text{Li}_{1.02}(\text{Ni}_{0.82}\text{Co}_{0.14}\text{Al}_{0.04})\text{O}_{2\pm\sigma}$
1.10Li-NCA	7.63	52	8.90	1.23	$\text{Li}_{1.02}(\text{Ni}_{0.82}\text{Co}_{0.14}\text{Al}_{0.04})\text{O}_{2\pm\sigma}$

lattice parameter, c , as the lithium content decreases. Likewise, Kanno *et al* [10] reported that as the lithium content decreases, the lattice parameter, c , increases. Among x Li-NCA samples, 1.05Li-NCA has the highest Li-gap value which is 2.636 Å. As this value becomes higher, lithium ion diffusion should be faster.

Composition of the compounds was determined using the concentrations measured by ICP-MS. The results given in table 2 are in good agreement with the targeted compositions. The 1.10Li-NCA sample was also synthesized to investigate the effect of a further increase in the Li content on the structural and electrochemical properties. As can be seen from table 2, the 1.10Li-NCA sample contains the same amount of lithium as the 1.05Li-NCA sample. The reason could be the saturation of Li sites so that a further increase in the Li content made no change in the composition. Therefore, the 1.10Li-NCA sample was not investigated further in terms of morphology and electrochemistry. For all compositions, the lithium amount is lower than the amount added at the beginning which might be attributed to lithium volatility. In the literature, it is a common approach to add excess lithium to obtain stoichiometric composition or to synthesize intentionally Li-rich cathode materials for a better performance [23–26].

The nanosized crystallites in the NiO phase were investigated by HRTEM which is shown in figure 3. This analysis showed that crystallites' sizes are around 20 nm. Figure 4 shows the SEM images of NiO and x Li-NCA samples. The mean particle size, on the other hand, was measured for 20 particles and averaged as 7.4 μm from SEM images. After heat treatment at 800°C for 24 h, the mean particle size of layered x Li-NCA samples rises up to 25 μm , while crystallites

Figure 3. HRTEM image of the Co and Al co-doped cubic NiO phase.

turn into a sub-micron sizes. The morphology of these powders also turns into an irregular morphology from spherical crystallites.

Figure 5 shows the particle size distributions of the synthesized powders as $d(0.1)$, $d(0.5)$ and $d(0.9)$ which imply that 10, 50 and 90 volume percentages of the particles are below the given values in micrometres, respectively. The width at the half height of the peak point inserted as the full-width at half maximum column in the figure. This value gives information about the measure of the particle size distribution for comparison purposes. Ultrasonic sound-assisted synthesis provided a narrow particle size distribution, even after the calcination.

Capacity and capacity retention values of layered x Li-NCA samples are given in table 3. Having the least degree of cation

Figure 4. SEM images of (a) cubic NiO and layered, (b) 0.90Li-NCA, (c) 0.95Li-NCA, (d) 1.00Li-NCA and (e) 1.05Li-NCA samples.

Figure 5. Particle size distribution of (a) cubic NiO phase and (b) layered x Li-NCA samples ($x = 0.90, 0.95, 1.00$ and 1.05).

mixing and the largest Li-gap, the 1.05Li-NCA sample has the highest capacity retention value of 95%, as can be seen in table 3. Figure 6 shows the voltage profiles at C/18 and C/12 rates, respectively. Of all the compositions, 1.05Li-NCA

gave the highest nominal voltage and capacity. Having better structural properties may be the reason for better electrochemical properties. Moreover, excess lithium probably provides the saturation of lithium ion sites. Therefore, migration of

Table 3. Capacity and capacity retention values of layered x Li-NCA samples.

Sample	First discharge capacity at C/18 (mAh g ⁻¹)	Discharge capacity after 1 cycle at C/12 (mAh g ⁻¹)	Discharge capacity after 22 cycles at C/12 (mAh g ⁻¹)	Capacity retention after 22 cycles at C/12 (%)
0.90Li-NCA	122	103	79	76.8
0.95Li-NCA	132	111	87	77.8
1.00Li-NCA	132	108	82	76.7
1.05Li-NCA	138	134	127	94.6

Figure 6. Voltage profiles of x Li-NCA samples at (a) C/18 and (b) C/12.

nickel ions to lithium ion sites is prevented. This saturation was also contributed to the capacity retention providing the better cycling performance.

Figure 7 shows the cyclic discharge capacity and coulombic efficiency plots of all x Li-NCA samples. It can be said that coulombic efficiency is not much affected from the change in lithium content. In other words, as the lithium content increases both charge and discharge capacities increase with coulombic efficiency above 96%. However, up to 7th cycle, 0.90Li-NCA, 0.95Li-NCA and 1.00Li-NCA samples lost 22.8, 16.6 and 17.6% of their discharge capacity, respectively. Capacity loss of these samples after 22 cycles was 23.2, 22.2 and 23.3%, respectively. It can be said that these samples have lost the majority of their capacity as they reached 7th cycle. This loss can be associated with the passivation layer (surface film) formation due to chemical decomposition of the electrolyte which causes the lithium loss leading to the capacity loss [27]. After 6th cycle, discharge capacity of 0.90Li-NCA, 0.95Li-NCA and 1.00Li-NCA samples stayed almost stationary. Of all the compositions, 1.05Li-NCA has the highest first discharge capacity (138 mAh g⁻¹) and gave the best cyclic reversibility, i.e., saved its 95% of capacity after 22 cycles.

Capacity conservation behaviour of x Li-NCA samples was further investigated by CV shown in figure 8 to determine

whether cyclic reversibility was affected from the change in lithium content. It is known that $\Delta E_p = 0.059/n$ for a reversible electrochemical process, where ΔE_p is the difference between anodic and cathodic peak voltages and n ($n = 1$ in our case) is the number of electrons involved in the electrochemical reaction [28]. Therefore, reversibility is directly related to the ΔE_p in our system. ΔE_p values showed that the 1.05Li-NCA sample has the highest reversibility with a $\Delta E_p = 0.079$. The other three samples have nearly the same ΔE_p values around 0.15 with a lower reversibility as compared to 1.05Li-NCA. Broad peaks around 4.1 and 3.9 V were observed for all samples caused by a phase transition especially during intercalation. It was reported that [29] charging/discharging nickel-based-layered oxides give rise to the formation of four different phases (three hexagonal phases, H1, H2 and H3 and one monoclinic phase, M). The reduction peak around 4.1 V corresponds to the H2 + H3 phase, while the M + H2 phase formation is observed around 3.9 V. Han *et al* [30] claim that an increase in inactive Al content in the structure prevents phase transition. They observed a single peak formation during CV, as inactive Al content in the structure reaches 5%. When Al content was 3%, there were still additional peaks caused by the phase transition. Since, the synthesized powders in this study contain 4% inactive Al, this amount may not be sufficient to prevent phase

Figure 7. (a) Cyclic discharge capacity and (b) coulombic efficiency plots of layered $x\text{Li-NCA}$ samples at the C/12 rate for 22 cycles.

Figure 8. CV of $x\text{Li-NCA}$ samples.

Figure 9. EIS graphs of x Li-NCA samples at 0% SOC: (a) after first discharge and (b) after 22 cycles.

Table 4. EIS results of x Li-NCA samples after first discharge and 22nd cycles.

Sample	After first discharge				After 22 cycles			
	R_{el} (Ω)	R_{sf} (Ω)	R_{ct} (Ω)	χ^2	R_{el} (Ω)	R_{sf} (Ω)	R_{ct} (Ω)	χ^2
0.90Li-NCA	6.7	112.6	1182	2.35×10^{-3}	6.6	269.3	790.3	2.49×10^{-3}
0.95Li-NCA	5.9	121.8	1188	1.66×10^{-3}	5.4	215.3	1140	1.19×10^{-3}
1.00Li-NCA	5.4	385.7	3208	2.21×10^{-3}	4.9	691.3	1579	6.01×10^{-3}
1.05Li-NCA	4.8	130.1	386.5	3.67×10^{-3}	4.6	125.7	494.8	4.51×10^{-3}

transition. However, no significant effect of lithium content on suppression of phase transition was observed in our case. Further improvement can be achieved by synthesizing 5% Al containing NCA composition. Nobili *et al* [31] stated that the sharper the CV peaks, the faster the kinetics of the electrochemical reaction. Since, the 1.05Li-NCA sample has the sharpest peaks in both anodic and cathodic reaction processes, it has the highest charge transfer rate.

Figure 9 and table 4 show the EIS results of x Li-NCA samples. R_{el} , R_{sf} and R_{ct} are attributed to the electrolyte resistance, passivation layer resistance (surface film) and charge transfer resistance, respectively. These resistances are significant while determining the electrochemical performance of the active materials.

Of all the compositions, 1.05Li-NCA showed the best performance in terms of EIS measurements. Only 1.05Li-NCA

composition gave optimum charge transfer and surface film resistances.

Wang *et al* [32] reported that an increase in the surface film resistance is due to the increase in the thickness of the surface film over increasing number of cycles. The thickness of the surface film increases as a consequence of irreversible decomposition of the electrolyte (as well as lithium consumption). In this study, R_{sf} values of all samples increased except that of the 1.05Li-NCA sample. There is almost no change in the R_{sf} value of this sample which can be explained by the stability of the surface film over cycling. Since the R_{sf} value of the 1.05Li-NCA sample is almost constant, it can be said that the amount of lithium consumed does not change much over cycling. The obtained highest capacity retention for this sample supports the previous statement. A small increase in the resistance values after 22 cycles can also be explained by the

ageing of batteries. Among five compositions, however, the 1.00Li-NCA sample only had the largest R_{ct} and R_{sf} values even after first discharge as can be seen in figure 9.

Further improvements in cyclic stability may also be achieved by doping this compound to stabilize nickel ions and to prevent phase transitions during charging/discharging. Capacity retention has increased from 83 to 91% by applying $\text{Li}(\text{Ni}_{0.75}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mg}_{0.05})\text{O}_2$ as a positive electrode [33]. Capacity retention improvements by doping the NCA compound with fluorine, titanium, sodium and many more was also achieved in the previous literature [34–36]. The composition study of dopants can also be widen the perspective when a better electrochemical performance is aimed. Moreover, it was reported that surface coating of this compound [37,38] has increased both discharge capacity and cyclability even at high C-rates. Therefore, surface treatments and/or doping of this compound may also not only provide higher cyclic reversibility, but also improvement in discharge capacity.

4. Conclusion

We investigated the effect of the lithium amount on the structural stability, capacity and rate capability of Li-NCA cathode materials. In the current study, a set of $x\text{Li-NCA}$ samples ($x = 0.90, 0.95, 1.00$ and 1.05) were synthesized using an ultrasonic sound-assisted co-precipitation method. The particle size analysis results showed that the pristine Co and Al co-doped NiO phase was successfully synthesized as nanoparticles with a narrow size distribution with the help of ultrasound. XRD analysis indicated that single phase-layered $\text{Li}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ could be produced for all the cases, $0.90 \leq x \leq 1.05$. First discharge capacities were measured as 122, 132, 132 and 138 mAh g⁻¹ for 0.90Li-NCA, 0.95Li-NCA, 1.00Li-NCA and 1.05Li-NCA samples, respectively. Among the compositions produced, 1.05Li-NCA exhibited the best structural stability, $I_{(003)}/I_{(104)}=1.923$ and Li-gap=2.636 Å and the highest discharge capacity of 138 mAh g⁻¹ with 94.6% capacity retention. Moreover, 1.05Li-NCA exhibited the lowest surface film (130.1 Ω after first discharge and 125.7 Ω after 22 cycles) and charge transfer resistances (386.5 Ω after first discharge and 494.8 Ω after 22 cycles) among the other compositions. The current study showed that the Li amount in the layered structure significantly affects the electrodes' structural stability and also its electrochemical performance. 1.05Li-NCA was determined as a promising composition in terms of structural and electrochemical performances for future studies.

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