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Characterization of Electronic and Ionic Transport in Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 (NCA)

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Despite the extensive commercial use of Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 (NCA) as the positive electrode in Li-ion batteries, and its long research history, its fundamental transport properties are poorly understood. These properties are crucial for designing high energy density and high power Li-ion batteries. Here, the transport properties of NCA are investigated using impedance spectroscopy and dc polarization and depolarization techniques. The electronic conductivity is found to increase with decreasing Li-content from \( \sim 10^{-4} \text{ S cm}^{-1} \) to \( \sim 10^{-2} \text{ S cm}^{-1} \) over \( x = 0.0 \) to 0.75. A surprising result is that the lithium ionic diffusivity vs. \( x \) shows a v-shaped curve with a minimum at \( x = 0.5 \), while the unit cell parameters show the opposite trend. This suggests that cation ordering has greater influence on the composition dependence than the Li layer separation, unlike other layered oxides. From temperature-dependent measurements in electron-blocking cells, the activation energy for lithium ion conductivity (diffusivity) is found to be 1.25 eV (1.20 eV). Chemical diffusion during electrochemical use is limited by lithium transport, but is fast enough over the entire state-of-charge range to allow charge/discharge of micron-scale particles at practical C-rates.

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Cathodes having high energy and power density, adequate safety, excellent cycle life, and low cost are crucial for Li-ion batteries that can enable the commercialization of electric transportation. Towards this end, much research has previously focused on the development of the LiNi_{1/2}Co_{1/2}O_2 (NC) cathode due to its high capacity (\( \sim 275 \text{ mAh g}^{-1} \)) and favorable operating cell voltage (4.3 V vs. Li/Li\(^+\)).

The sintered pellets were polished lightly on both sides to a thickness of 0.30 to 0.80 mm. One side of the polished pellets was coated with a thin layer of graphite to form good electrical contact with the metal current collectors in the cells. Delithiation was performed in a Swagelok-type electrochemical cell using lithium metal foil as the counter electrode, the NCA pellet as the working electrode, and a liquid electrolyte mixture containing 1 M LiPF\(_6\) in 1:1 by mole ratio. Delithiation was performed continuously or intermittently (applied for one hour intervals followed by a half-hour rest). After electrochemical delithiation to the desired composition, the cells were disassembled and the pellets were washed with acetone and pure EC/DEC solvent, and heated at 120 °C in an inert atmosphere for at least 24 h in order to homogenize the lithium distribution. The pellets were again polished lightly on both sides to remove any surface lithium salt.

Electronic conductivity measurement.— The as-sintered lithiumated and partially delithiated pellets were painted with silver paste on both sides forming the cell configuration Ag[NCA]Ag. The pellets were subsequently heat set at 120 °C overnight in order to remove the organic solvent. The Ag[NCA]Ag cells were placed in battery coin cell holders with support of stainless steel disks on both sides of the pellet. Direct current polarization technique (DC) as well as electrochemical impedance spectroscopy (EIS) were employed to measure the electronic conductivity of the samples using Bio-logic SA France Model: VMP3 (Clairx, France) in the frequency range 200 kHz−0.5 Hz. The measurements were performed at temperatures from 25−100 °C using...
measurements.

The final powder was dried in the glove box at 80°C with additional acetonitrile to remove salt and other impurity phases. The powder was washed with deionized water after each analyzed by PXD of the exposed surface. No impurity phases were observed for the latter sample, while for the former sample a relatively large amount of Li2CO3 was observed (Figure 1). Therefore, all sample handling and measurements were performed under inert conditions.

In order to measure ion diffusivity as a function of lithium content, dc polarization/depolarization measurements were made on thin sintered NCA pellets (0.26–0.30 mm thickness and 0.219–0.158 cm2 surface area) of known weight, using Swagelok-type cells. The same cell preparation procedure and components as described above for electrochemical delithiation were used. A charging current equivalent to C/400 rate were applied for 25 h, after which the cell was relaxed at open circuit voltage (OCV) conditions for at least 75 h to reach the steady state OCV. Lithium ionic diffusivity was derived from the voltage relaxation vs time (depolarization process). Here we considered the diffusion length to be one half the sample thickness.

X-ray diffraction and rietveld refinements.— Powder X-ray diffraction (PXD) measurements were performed in Bragg-Brentano reflection geometry using a Rigaku/Max/b 185 mm radius goniometer X-Ray Powder Diffractometer equipped with a 13 kW RU300 Cr-source rotating anode X-ray generator (Cr Kα radiation), diffracted beam monochromator and a scintillation point detector. All PXD data were collected from 26 to 120° 20 with a step size of 0.02° and a step speed of 0.5°/min.

To investigate sample stability during exposure, a sample exposed to ambient air and one stored under inert (glove box) conditions were each analyzed by PXD of the exposed surface. No impurity phases were observed for the latter sample, while for the former sample a relatively large amount of Li2CO3 was observed (Figure 1). Therefore, all sample handling and measurements were performed under inert conditions.

To elucidate the change in unit cell parameter in Li1−xNi0.8Co0.15Al0.05O2 as a function of x, a series of samples was chemically delithiated by reaction with nitroniumtetrafluoroborate (Sigma Aldrich) in dry acetonitrile (Alfa Aesar). The reaction mixture was kept in an argon filled glove box for three days in order to complete the reaction. The partially delithiated NCA powder was separated from the solution by centrifugation (Eppendorf Centrifuge, Model 5804R, Hauppauge, NY, USA)). The powder was washed with additional acetonitrile to remove salt and other impurity phases. The final powder was dried in the glove box at 80°C before PXD measurements.

Rietveld refinements were performed using the program FullProf.25 The backgrounds were described by linear interpolation between selected points, while pseudo-Voigt profile functions were used to fit the diffraction peaks. In general the unit cell parameters, sample displacement, profile parameters and the overall temperature factors, Biso were refined. The structural model for Li1−xNi0.8Co0.15Al0.05O2 (space group: R-3m, a = 2.86 and c = 14.199 Å) published by Guilmard et al.26 was used as starting model for the refinements of Li1−xNi0.8Co0.15Al0.05O2. The occupancies of Ni and Al were changed to match the material composition while that of Li was changed to accommodate the relevant degree of delithiation. At high degrees of delithiation a second NCA phase was observed, which was satisfactorily modeled using a second R-3m Li1−xNi0.8Co0.15Al0.05O2 with slightly different cell parameters.

Results and Discussion

Electronic conductivity.— The impedance spectra of as-sintered lithiated NCA measured at selected temperatures on the symmetric cell configuration, Ag[NCA]Ag are shown in Figure 2a. Nearly perfect semicircles are obtained in the temperature range 25–100°C and in the frequency range 2 × 10−5–5 × 10−2 Hz. The absence of a second semicircle is an indication of absence of other resistive processes and also suggests minor or negligible ionic conductivity. Similar impedance spectra were observed for the partially delithiated samples. The impedance spectra were evaluated with the ideal equivalent circuit shown in Figure 2b. For temperature-dependent measurements, impedances were measured during both heating and cooling processes and also suggests minor or negligible ionic conductivity.

Table I. Summary of techniques and cell configurations used to elucidate electronic and ionic conductivity, and the ion diffusivity, as a function of temperature and/or Li-content.

<table>
<thead>
<tr>
<th>Probed</th>
<th>Technique</th>
<th>Cell configuration</th>
<th>Transport properties as a function of :</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic conductivity</td>
<td>EIS - AC</td>
<td>Ag/NCA/Ag</td>
<td>Temperature, Li- content</td>
</tr>
<tr>
<td></td>
<td>EIS - DC</td>
<td>Ag/NCA/Ag</td>
<td>Temperature, Li- content</td>
</tr>
<tr>
<td>Ionic conductivity &amp; diffusivity measurements</td>
<td>EIS - AC</td>
<td>Li/PEO/NCA/PEO/Li</td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>EIS - DC</td>
<td>Li/PEO/NCA/PEO/Li</td>
<td>Temperature</td>
</tr>
<tr>
<td>Ion diffusivity</td>
<td>EIS - AC and DC</td>
<td>Li/PEO/NCA/PEO/Li</td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>Depolarization</td>
<td>Li/Separator (w. electrolyte)/NCA/current collector</td>
<td>Li- content</td>
</tr>
</tbody>
</table>

Abbreviations: EIS: Electrochemical Impedance Spectroscopy, AC: Alternating Current, DC: Direct Current, GITT: Galvanostatic Intermittent Titration Technique, NCA: Li1−xNi0.8Co0.15Al0.05O2, PEO: polyethylene oxide.
cooling. The capacitance ($C$) values can be calculated from the fitting parameters $Q$ and $n$ according to $C = (R^n Q)^{1/n}$ where $Q$ is a constant phase element and $n$ is essentially a measure of the degree of depression of an arc (here $n$ is usually in the range of 0.98–0.92 depending on the temperature and degree of delithiation). Derived capacitance values are $\sim 10^{-10}$F and thus confirm that the observed impedance responses originate from the bulk (grains) of the samples, i.e. not the grain boundaries. Derived capacitance values are $\sim 10^{-10}$F and thus confirm that the observed impedance responses originate from the bulk (grains) of the samples, i.e. not the grain boundaries. The absence of any additional polarization process (i.e. second semicircle) at low frequencies for all samples indicates that this conduction is predominantly due to electronic carriers. In order to substantiate this observation, DC polarization and depolarization measurements were performed for lithiated and partially delithiated NCA samples using the same cell configuration as for the impedance spectroscopy. Figure 2c is representative of a typical DC measurement on a NCA sample. During application of a constant voltage the current increases in a step-function manner to a stationary value with the applied load. The conductivities of the lithiated and partially delithiated NCA samples measured for lithium diffusion $D^{+}_{\text{Li}}$ are expected.28–30

The electronic conductivities of the lithiated and partially delithiated NCA are plotted in Figure 3a as a function of inverse temperature. The conductivities of the partially delithiated samples measured at a given temperature increase monotonically with increasing delithiation (Figure 3b, for measurements at 30°C). Over the measured compositional range, the electrical conductivity shows thermally-activated behavior. The values of activation energy, calculated using an Arrhenius law, vary from 0.22–0.14 eV (±0.04 eV) as shown in Figure 3a, and is consistent with the value reported by Saadoune and Delmas22 for Li$_x$Ni$_{0.9}$Co$_{0.1}$O$_2$. These are typical values for the migration process of a small polaron generally observed in mixed-valence systems.31 It is reported that Co is less prone to oxidize from the trivalent to tetravalent state in the presence of Ni.22 The electronic configurations of Co$^{3+},$ Ni$^{3+}$ and Ni$^{4+}$ have the $t_2$ orbital filled in each case. As a result, electron delocalization is unlikely. The increase in electronic conductivity is associated with the presence of mixed Ni$^{3+}/$Ni$^{4+}$ valence states resulting from delithiation, which leads to hole formation in the narrow (Ni$^{3+}/$Ni$^{4+}$) band. It is seen from the Figure 3a and 3b that beyond 60% delithiation (i.e. $x=0.60$) the sample exhibits a sharp rise in electronic conductivity. This may be due to oxidation of cobalt from the trivalent to tetravalent state at this delithiation level. The degree of cobalt oxidation is evidently small, since a high degree of oxidation would lead to metallic behavior due to the presence of holes in the broad $t_2$ band. We were not able to measure the electronic

Figure 2. (a) Impedance spectra of as-sintered fully lithiated NCA at two different temperatures measured using the symmetrical cell configuration Ag/NCA/Ag, (b) equivalent circuit used to evaluate the impedance spectra, and (c) time dependent current in polarization measurements performed at various temperatures in the same cell configuration under constant applied voltage.

Figure 3. (a) The electronic conductivity of lithiated and partially delithiated NCA ($\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) (as a function of inverse temperature obtain from DC measurement and calculated activation energy using the Arrhenius equation. AC impedance also exhibit the same magnitude of conductivity. (b) The electronic conductivity of NCA ($\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) as a function of $x$ in the $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at 30°C obtained from DC measurement.
conductivity beyond 60% delithiation, as the samples were too fragile for reliable assembly of cells. Comparing to literature, Sethuprakash and Basirun reported metallic-like electronic conductivity of lithiated Li$_{1-x}$Ni$_{0.5}$Co$_{0.2}$Al$_{0.3}$O$_2$. This is surprising if their samples are truly lithiated to a high extent (low Co$^{3+}$/Co$^{4+}$ ratio).

Ionic conductivity and diffusivity by AC impedance.— Results with electron-blocking cells must take into account the temperature dependent ionic conductivity of the PEO blocking layer. Figure 4a shows the impedance spectra of lithiated NCA measured at 58°C in the cell configuration Li/PEO/NCA/PEO/Li. In contrast to the ion-blocking cells above, these impedance spectra consist of two semicircles at high frequencies (inset of Figure 4a) followed by a Warburg response at low frequencies. The high frequency semicircle represents the total resistance to electronic and ionic motion including contributions from the bulk conductivity of PEO. The Warburg response is indicative of stoichiometric polarization owing to blocking of electrons. In order to obtain the ionic conductivity and diffusivity, the impedance spectra were fitted with the equivalent circuit as shown in Figure 4b. Good agreement is obtained between the simulated and experimental data.

Fitting results are presented in Figure 4c and 4d. The ionic conductivity according to above equation, as is observed in Figure 4c and 4d.

Ionic conductivity and diffusivity by steady state polarization/depolarization.— DC polarization/depolarization measurements were also performed using electronically blocking cell arrangements over a range of temperatures in order to substantiate the result obtained from the impedance measurements. These measurements were not performed at low temperature due to the excessively long times required to reach steady state (also observed in AC impedance). Figure 5 shows the time dependence of the polarization voltage (galvanostatic mode). The voltage immediately jumps from zero to $V_{\text{polarization}} = kT \ln \left( \frac{R_{\text{cell}}}{R_{\text{ionic}}} \right)$ where $R_{\text{cell}}$ and $R_{\text{ionic}}$ refer to the contributions due to trapping of ionic and electronic carriers and $c_{\text{ion}}$, $c_{\text{eon}}$ denote to the ionic and electronic carrier concentrations. It is discernable from Figure 4c and 4d that both the ionic conductivity and diffusivity display single slope behavior which indicates the absence of charge carrier trapping effect ($c_{\text{ion}}$ and $c_{\text{eon}}$). That is, charge carrier association-dissociation is not prominent in the measured temperature range. In the intrinsic dilute defect, $c_{\text{ion}} \gg 1$, the ionic diffusivity should be higher than the ionic conductivity according to above equation, as is observed in Figure 4c and 4d.
Figure 5. Time dependent DC polarization voltage at ~60°C obtained from the electron blocking cell Li/PEO/NCA/PEO/Li. Results are fitted with Eq. 1 in order to obtain ionic conductivity and diffusivity (inset).

Figure 6. (a) Time dependent cell voltage measured on the NCA (Li$_{1-x}$Ni$_x$Co$_{1-x}$Al$_{0.15}$O$_2$) plate by titrating a fixed amount of lithium and holding at open circuit conditions. (b) Fit of the depolarization cell voltage to Eq. 1 in order to extract the chemical diffusivity of lithium ion at $x = 0.25$.

The two slopes can be fitted separately by Eq. 1 and clearly shows the two regimes, as shown in Figure 7. The change in the depolarization voltage vs. time during the stepwise galvanostatic titration of fixed cell dimensions at the same composition. This is surprising, and is everywhere at least 10$^5$ lower than the experiment. Using Eq. 1 in order to extract the chemical diffusivity. Two slopes are clearly fitted.

To investigate this observation further, we prepared a series of chemically delithiated NCA powders and performed X-ray diffraction measurements, for which results appear in Figure 8. For $x = 0.0$ and 0.1, only one NCA phase was observed (denoted NCA1), while for samples of $x \leq 0.25$ a second NCA phase (denoted NCA2) was also observed. As the lithium content is decreased ($x = 0.25$ to 0.5), the fraction of NCA2 increases from 5 to 14 mol%, while further decrease ($x = 0.75$) results in only a slight increase in the amount of NCA2 to 15 mol%. Thus the amount of NCA2 reaches a plateau value. The R-3m symmetry of NCA1 is preserved in NCA2, but the cell parameters are different for NCA2, and suggest a significantly different Li-content in this phase. A notable feature for both phases is the appearance of a maximum in unit cell dimensions at $x = 0.5$, which suggests a change in cation ordering at that composition. Yoon et al. have previously reported similar structure observations for NCA using in situ electrochemical cells, wherein after initial delithiation a second NCA phase appears exhibits a maximum in $a$-axis and minimum in $c$-axis with increasing $x$. However, there are significant differences between the present results and theirs, in the relative amounts of the two phases as a function of $x$, the concentrations at which the maximum in $c$ and minimum in $a$ occur, and the fact that in our case, both phases exhibit the same variation in $c$ and $a$ dimensions with $x$, whereas in their work one of the phases exhibits nearly invariant $c$ and $a$. The room-temperature lithium ion diffusivity obtained from depolarization measurements are plotted in Figure 9 as a function of lithium content. Firstly, that the ionic conductivity varies by about an order of magnitude with $x$, and is everywhere at least 10$^5$ lower than the electronic conductivity (Figure 3b). Secondly, the ionic conductivity shows an inverse relationship to the unit cell parameters in Figure 8b, whereby diffusivity decreases as unit cell dimensions increase. The minimum in diffusivity at $x = 0.5$ corresponds to a maximum in unit cell dimensions at the same composition. This is surprising, and is
counter to the expectation that a c-axis expansion corresponding to an increase in the Li slab distance lowers the activation energy for migration and should therefore increase the Li diffusion coefficient.\textsuperscript{6,37} Recalling that the depolarization data (Figure 6b) indicate a change in mechanism and/or rate-controlling phase around \( x = 0.5 \), we considered alternative explanations. We examined the diffraction data for evidence for changes in cation ordering. Rietveld refinement did not indicate significant mixing between Li and the transition metals. Possible changes in cation ordering within the transition metal layers need to be investigated further. No superstructure peaks indicative of ordering were detected. The dependence of ion diffusivity on Li vacancy concentration \( x \) is consistent with a defect chemical model where between \( x = 0 \) and \( x = 0.5 \), diffusivity is dependent on interstitial concentration and therefore decreases with increasing vacancy concentration through a Frenkel equilibrium. The increase in diffusivity for \( x > 0.5 \) is consistent with a dependence on vacancy concentration. However, changes in cation ordering which are more subtle than can be detected in the present diffraction data, and related changes in migration energy, may be the dominant influence.

We know of no other published diffusion data for NCA to compare with the present results. For NC, however, Montoro et al.\textsuperscript{21} reported a M-shaped relation between the chemical diffusion coefficient of \( \text{Li}_{1-x}\text{Ni}_{x}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 \) and lithium content, based on GITT measurements of composite electrodes. The diffusivity data reported by Montoro ranged from \( \sim 10^{-10} \) to \( \sim 5 \times 10^{-9} \) cm\( ^2 \)s\(^{-1} \) over the entire Li-compositional window. In contrast, Cho et al.\textsuperscript{20} reported an almost constant lithium diffusion coefficient of \( \text{Li}_{1-x}\text{Ni}_{x}\text{Co}_{0.2}\text{O}_2 \) as a function of lithium content. However, their data showed a much higher diffusivity (\( \sim 10^{-8} \) cm\( ^2 \)s\(^{-1} \)). We believe that extrinsic factors may be present in these previous results due to the nature of the samples, and that neither may represent the pure single phase transport behavior. Table II compares the diffusivity data obtained in the present work with literature results.

Table II. Diffusivity of NCA at 30°C measured by different techniques and comparison with the available literature data of NC.

<table>
<thead>
<tr>
<th>Technique Used</th>
<th>Composition</th>
<th>Diffusivity (cm(^2)s(^{-1} ))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>( \text{LiNi}<em>{0.8}\text{Co}</em>{0.15}\text{Al}_{0.05}\text{O}_2 ) (NCA)</td>
<td>( \sim 3 \times 10^{-10} )</td>
<td>This study</td>
</tr>
<tr>
<td>DC</td>
<td>( \text{LiNi}<em>{0.8}\text{Co}</em>{0.15}\text{Al}_{0.05}\text{O}_2 ) (NCA)</td>
<td>( \sim 2 \times 10^{-10} )</td>
<td>This study</td>
</tr>
<tr>
<td>Depolarization</td>
<td>( \text{Li}<em>{0.9}\text{Ni}</em>{0.8}\text{Co}<em>{0.15}\text{Al}</em>{0.05}\text{O}_2 ) (NCA)</td>
<td>( \sim 4 \times 10^{-10} )</td>
<td>This study</td>
</tr>
<tr>
<td>GITT</td>
<td>( \text{Li}<em>{0.9}\text{Ni}</em>{0.8}\text{Co}<em>{0.15}\text{Al}</em>{0.05}\text{O}_2 ) (NC)</td>
<td>( \sim 10^{-10} )</td>
<td>22</td>
</tr>
<tr>
<td>GITT</td>
<td>( \text{Li}<em>{0.9}\text{Ni}</em>{0.8}\text{Co}<em>{0.15}\text{Al}</em>{0.05}\text{O}_2 ) (NC)</td>
<td>( \sim 10^{-8} )</td>
<td>21</td>
</tr>
</tbody>
</table>

Conclusions

Electronic and lithium ionic transport in NCA have been measured using ion and electron blocking cell configurations and both ac and dc techniques. NCA exhibits semiconducting behavior over the entire range of lithium concentrations measured (\( x = 0.0 \) to 0.7). Starting from the fully lithiated state, the electronic conductivity gradually increases with increasing delithiation, and rises more sharply beyond about 60% delithiation. We suggest that the latter increase is due to the onset of Co\(^{2+}/\text{Co}^{3+}\) multivalency. Regarding lithium ionic conductivity (and diffusivity), in fully lithiated NCA the activation energy is 1.25 eV. No evidence for charge carrier association or dissociation was seen in the measured temperature range. However, the ion diffusivity as a function of lithium concentration shows V-shaped behavior.

Figure 8. Left: PXD data for chemical delithiated Li\(_{1-x}\)Ni\(_x\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\). The inset shows the 2theta region around the (003) reflection. Note the appearance the (003) peak of the second NCA phase (denoted NCA2) at \( x = 0.25 \). Right: Unit cell parameters (\( a \)- and \( c \)-axis) of the two observed NCA phases (NCA1: black squares, NCA2: red triangles). The mol% of the two phases for each \( x \) is noted in plot. Error bars for NCA1 fall within symbols.

Figure 9. Diffusivity of NCA (Li\(_{1-x}\)Ni\(_x\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\)) as a function of lithium content at room temperature obtained from depolarization experiments shown in Figure 6a.
with a minimum at about \( x = 0.5 \). The unit cell parameters show the opposite trend with a maximum at \( x = 0.5 \). This behavior is counter to expectations for ion migration energy as a function of \( c \)-axis dimensions, and suggests more subtle cation ordering effects that remain to be resolved. From the magnitude of the electronic and ionic transport parameters across the measured range of Li concentration, it can also be concluded that chemical diffusion is always limited by lithium ion transport rather than electronic conductivity, and that bulk transport is rapid enough to allow charging and discharging of micron size particles at practical C-rates regardless of state-of-charge.

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