Characterization of Electronic and Ionic Transport in Li$_{1-x}$Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC$_{333}$) and Li$_{1-x}$Ni$_{0.50}$Mn$_{0.20}$Co$_{0.30}$O$_2$ (NMC$_{523}$) as a Function of Li Content

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Characterization of Electronic and Ionic Transport in Li$_{1-x}$Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC$_{333}$) and Li$_{1-x}$Ni$_{0.50}$Mn$_{0.20}$Co$_{0.30}$O$_2$ (NMC$_{523}$) as a Function of Li Content

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Despite the extensive commercial use of Li$_{1-x}$Ni$_{1+y}$Mn$_x$Co$_2$O$_4$ (NMC) 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 NMC$_{333}$ and NMC$_{523}$ are investigated using impedance spectroscopy and DC polarization and depolarization techniques. The electronic conductivity is found to increase with decreasing Li-content (increasing state-of-charge) from $\sim 10^{-7}$ S cm$^{-1}$ to $\sim 10^{-2}$ S cm$^{-1}$ over Li concentrations $x = 0.00$ to $0.75$, corresponding to an upper charge voltage of 4.8 V with respect to Li/Li$^+$. The lithium ion diffusivity is at least one order of magnitude lower, and decreases with increasing $x$ to $x = -0.5$. The ionic conductivity and diffusivity obtained from the two measurements techniques (EIS and DC) are in good agreement, and chemical diffusion is limited by lithium transport over a wide state-of-charge range.

Cathodes having high energy and power density, adequate safety, excellent cycle life, and low cost are a critical need for Li-ion batteries to enable the commercialization of electric transportation and stationary storage. Towards this end, much previous research focused on the development of LiNi$_{1-x}$Co$_x$O$_2$ (NC) cathode due to its high capacity ($\sim 275$ mAh/g) and favorable operating cell voltage (4.3 V vs. Li/Li$^+$), which is within the voltage stability window of current liquid electrolytes, and lower cost than LiCoO$_2$. Despite extensive optimization, e.g., with respect to the Ni/Co ratio, electronic conductivity, we know of no published measurements for NMC$_{333}$ and NMC$_{523}$, which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.0131608jes] All rights reserved.

Electrochemical delithiation.—The sintered pellets were polished to thicknesses of 0.30 to 0.80 mm. Delithiation was performed in a Swagelok-type electrochemical cell using lithium metal foil as the counter electrode, the NMC pellet as the working electrode, the electrolyte mixture containing 1 M LiPF$_6$ in 1:1 by mole of ethylene carbonate/diethyl carbonate (EC/DEC). The NMC was sintered at 900°C for 1 h in ambient atmosphere, preceded by heating at 5°C/min, and followed by cooling at the same rate. This procedure yielded samples of 96–98% relative density, sufficiently high that the measured conductivity represents the bulk value. Corrections for porosity are small because for solids of high density, porosity reduces the effective cross-sectional area in direct proportion to the pore volume fraction, and the conductivity is therefore proportional to density.

Thus our objective in this work is to systematically characterize and interpret the transport properties of NMC$_{333}$ and NMC$_{523}$. We use additive-free, single phase sintered samples in which the extrinsic effects due to binders, conductive additives, and particle microstructures that may be present in composite electrodes are avoided. Using electron blocking and ionic blocking cell configurations, respectively, and electrochemical impedance spectroscopy and DC polarization and depolarization techniques (see Table I), we deconvolute the electronic and ionic conductivities of NMC$_{333}$ and NMC$_{523}$ as a function of temperature and Li content, up to a lithium deficiency of $x = 0.75$, which corresponds to high charge voltages of 4.7 V and 4.8 V for NMC$_{333}$ and NMC$_{523}$ respectively. Our sample configuration permits measurement of single-phase properties up to delithiation levels (state-of-charge) where electrochemically-induced microfracture intrudes. Electronic conductivity was not apparently affected by these effects, whereas ionic transport shows an apparent increase beyond $x = 0.50$ which we attribute to fast transport paths created by microfracture.

**Experimental**

NMC powder of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC$_{333}$) and LiNi$_{0.50}$Mn$_{0.20}$Co$_{0.30}$O$_2$ (NMC$_{523}$) compositions were obtained from TODA America Inc. (Battle Creek, MI, USA). Compacted pellets were prepared from the powder by pressing at 340 MPa, forming cylindrical samples of 14 mm diameter. The pellets were sintered at 900°C for 12 h in ambient atmosphere, preceded by heating at 5°C/min, and followed by cooling at the same rate. This procedure yielded samples of 96–98% relative density, sufficiently high that the measured conductivity represents the bulk value. Corrections for porosity are small because for solids of high density, porosity reduces the effective cross-sectional area in direct proportion to the pore volume fraction, and the conductivity is therefore proportional to density.

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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>Transport properties as a function of</th>
<th>Cell configuration</th>
<th>Technique</th>
<th>Probed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, Li-content</td>
<td>Ag/NMC/Ag</td>
<td>EIS - AC</td>
<td>Electronic conductivity</td>
</tr>
<tr>
<td>Temperature</td>
<td>Ag/NMC/Ag</td>
<td>EIS - DC</td>
<td>Ionic conductivity</td>
</tr>
<tr>
<td>Temperature</td>
<td>Li/PEO/NMC/PEO/Li</td>
<td>EIS - AC</td>
<td>Ion diffusivity</td>
</tr>
<tr>
<td>Temperature</td>
<td>Li/PEO/NMC/PEO/Li</td>
<td>EIS - DC</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Li/separator/electrolyte/</td>
<td>Depolarization</td>
<td></td>
</tr>
<tr>
<td>Li-content</td>
<td>NMC/current collector</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: EIS: Electrochemical Impedance Spectroscopy, AC: Alternating Current, DC: Direct Current, GITT: Galvanostatic Intermittent Titration Technique, NMC: LiNi0.33Mn0.33Co0.33O2 or LiNi0.33Mn0.33Co0.33O2; PEO: polyethylene oxide.

**Results and Discussion**

**Electronic conductivity.**—The impedance spectra of as-sintered lithiated NMC523 measured at selected temperatures in the symmetric Ag/NMC/Ag configuration, Ag/NMC/Ag shown in Figure 1a. Nearly perfect semicircles are obtained in the temperature range 25–100°C and in the frequency range 2 × 10^6–5 × 10^−1 Hz. Similar impedance spectra were observed for the partially delithiated NMC523 and NMC333. The impedance spectra were evaluated with the ideal equivalent circuit shown in Figure 1b. For temperature-dependent measurements, impedances were measured during both heating and cooling. The capacitance (C) values can be calculated from the fitting parameters (here is usually in the range of 0.96–0.90 depending on the temperature and degree of delithiation). Derived capacitance values are ~5 × 10^−11 F and thus confirm that the observed impedance responses originate from the bulk (grains) of the samples (i.e., the values are continuously or intermittently using a Bio-logic SA France Model VMP3 instrument (Claux, France). After electrochemical delithiation to the desired compositions, the cells were allowed to relax at open circuit voltage conditions, 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 lithiated and partially delithiated pellets were painted with silver paste on both surfaces forming the symmetric cell configuration Ag/NMC/Ag. The pellets were subsequently heated at 120°C overnight in order to remove the organic solvent in the silver paint. The Ag/NMC/Ag cells were placed in battery coin cell holders with supporting stainless steel disks on both sides of the pellet. Direct current polarization technique (DC) as well as electrochemical impedance spectroscopy (EIS) was employed to measure the electrical conductivity of the samples, using the Bio-logic VMP3 instrument, in the frequency range 200 kHz–0.5 Hz. The measurements were performed at temperatures from 25–100°C using a VWR temperature controller. The sample temperature was measured using a thermocouple.

**Ionic transport measurements.**—The ionic diffusivity and conductivity of the fully lithiated, starting NMC was measured by direct current (DC) polarization and by electrochemical impedance spectroscopy (EIS). EIS was measured over the frequency range 200 kHz–10 μHz at AC amplitude of 10 mV, and as a function of temperature. Doped polyethylene oxide (PEO) was used as an electron-blocking, lithium-conducting electrode layer. The measurements were performed in the symmetric cell configuration Li[PEO[NMC][PEO][Li in a Swagelok-type cell. The PEO membrane was fabricated by mixing PEO powder (from Scientific Polymer Products, Inc., Mw 4,000,000) and LiI (from Aldrich, 99.99%) in a 6:1 molar ratio in dry acetonitrile. Details of preparation can be found elsewhere.24

In order to measure ion diffusivity as a function of lithium content, DC polarization/depolarization measurements were performed on thin sintered NMC pellets (0.26–0.30 mm thickness and 0.219–0.158 cm² surface area), 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/200 and/or C/400 rate were applied for 10 h, after which the cell was relaxed at open circuit voltage (OCV) conditions for at least 25 h to reach the steady state OCV. Lithium ionic diffusivity was derived from the voltage relaxation vs time (depolarization process). The diffusion length was assumed throughout to be one half the sample thickness.

Figure 1. (a) Impedance spectra of as-sintered fully lithiated NMC523 (LiNi0.33Mn0.33Co0.33O2) at two different temperatures measured using the symmetrical cell configuration Ag/NMC/Ag, (b) equivalent circuit used to evaluate the impedance spectra, and (c) time dependent voltage in polarization measurements performed at partially delithiated NMC333 (LiNi0.33Mn0.33Co0.33O2) in the same cell configuration under constant applied current.
several orders of magnitude smaller than expected for grain boundary impedance.25 The absence of any additional polarization process (i.e., a 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 NMC samples using the same cell configuration as for impedance spectroscopy. Figure 1c is representative of a typical DC measurement on a NMC533 sample. During application of a constant current the voltage increases in a step-function manner to a constant value, and decays as a step-function upon switching off the applied current. Such behavior is indicative of an electronically dominated conduction process since in the case of significant contributions from ionic motion, slower relaxation of voltage upon polarization and depolarization with rate constants determined by lithium diffusion DLi are expected.26–29

The electronic conductivities of the lithiated and partially delithiated NMC523 and NMC333 are plotted in Figures 2a and 2b as a function of inverse temperature. The conductivities of the partially delithiated samples measured at a given temperature increase monotonically with increasing delithiation (Figure 2c, 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, range from 0.42–0.05 eV (±0.03 eV) as shown in Figures 2a and 2b, and are similar in magnitude to the values reported by Saadoune and Delmas28 for Li1Ni0.50Mn0.20Co0.30O2. These are typical values for the migration of a small polaron, as is generally observed in mixed-valence systems.31 It has been reported that Co is less prone to oxidize from the trivalent to tetravalent state in the presence of Ni.33 The electronic configurations of Co3+, Ni2+ and Ni4+ have the (t2) orbital filled in each case. As a result, electron delocalization is unlikely. The increase in electronic conductivity is associated with the presence of mixed Ni3+/Ni4+ valence states resulting from delithiation, which leads to hole formation in the narrow (Ni4+/Ni3+) band. It is seen from Figures 2a–2c that upon initial delithiation, the sample exhibits a sharp rise in electronic conductivity. Then the slope decreases, although another slight upward inflection appears between x = 0.5 and 0.75. In our previous study of transport in NCA, we observed a sharp rise of conductivity beyond 60% delithiation.34 This was explained as the oxidization of a small amount of cobalt from the trivalent to tetravalent state at this delithiation level.35 It seems that there may also be a small degree of cobalt oxidation in NMC since the conductivity pattern is similar to NCA. We were not able to measure the electronic conductivity beyond 75% delithiation in the NMC samples, as the samples became too fragile to assemble into cells, due to the intercalation-induced dimensional changes at the crystallite level. It is also seen in Figure 2 that the starting NMC523 exhibits higher electronic conductivity than the starting NMC333, although after 30% delithiation both have similar electronic conductivity. The initial higher conductivity of the NMC523 may be due to the higher Ni content, since Ni is considered an active conduction site which may facilitate electron hopping.

Ionic conductivity by AC impedance.—Interpretation of results for the electron-blocking cells must take into account the temperature dependent ionic conductivity of the PEO blocking layer. Figure 3a shows the impedance spectra of lithiated NMC333 measured at 61 °C in the cell configuration Li/PEO/NMC/PEO/Li. In contrast to the ion-blocking cells above, these impedance spectra consist of one semicircle at high frequencies (inset of Figure 3a) 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 3b using Zview software. The lower frequency Warburg response provides the ionic resistance, and the relaxation frequency of the Warburg response provides the relaxation time, from which we obtained ionic diffusivity

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Electronic conductivity of lithiated and partially delithiated (a) NMC523 (LiNi0.50Mn0.20Co0.30O2) and (b) NMC333 (LiNi0.33Mn0.33Co0.33O2) (as a function of inverse temperature obtain from DC measurement and calculated activation energy using the Arrhenius equation. AC impedance also exhibit same magnitude of conductivity). (c) The electronic conductivity of NMC (Li1-xNMC) as a function of x value in Li1-xNMC at 30 °C obtained from DC measurement. After electrochemical delithiation to the desired compositions, the cells were allowed to relax under open circuit voltage conditions.

![Figure 3a](https://example.com/figure3a.png)

**Figure 3a.** Qualitatively similar impedance spectra were observed for NMC523; however, at temperatures below 60 °C the frequency range is not sufficiently wide to obtain the relaxation frequency. Hence, for the lower temperatures, the model fit to lower frequencies was extrapolated to reach the relaxation frequency. We were not able to measure at temperatures higher than 60 °C due to melting of the PEO film, which tended to short circuit the cell. The activation energy for ionic conductivity and diffusivity could not be reliably extracted due to the narrow measurement temperature range. The ionic conductivity and diffusivity of NMC333 and NMC533 are compared in Table II at two different temperatures between 50–60 °C for each composition. This is to our knowledge the first measurement of these ion transport parameters in any pure phase NMC samples. It is seen from Table II that ionic diffusivity is higher than ionic conductivity at the same temperature. Given the predominant elec
tronic conductivity, the Li$^+$ diffusivity ($D_{Li}$) should have the form $D_{Li} \propto \sigma_{ion}(\frac{x_{ion}}{x_{elec}} + \frac{x_{elec}}{x_{ion}})$ where $x_{ion}$ and $x_{elec}$ refer to the contributions due to trapping of ionic and electronic carriers (values of $x_{ion}$ and $x_{elec}$ being between zero and one) and $\sigma_{ion}$, $\sigma_{elec}$ denote the ionic and electronic carrier concentrations. Since the measurement was performed at relatively high temperature, there should be minimal charge carrier trapping. That is, charge carrier association-dissociation is not prominent in the measured temperature range, and $x_{ion}$ and $x_{elec}$ both reach their limiting value of unity. In the intrinsic dilute defect limit, $c_{ion} \gg 1$, the ionic diffusivity should be higher than the ionic conductivity according to above equation, as is observed in Table II.

### Ionic diffusivity by steady state polarization/depolarization.

DC polarization/depolarization measurements were also performed using electronically blocking cell arrangements in order to substantiate the results obtained from the impedance measurements. These measurements were not performed at low temperature due to the ex cessively long times required to reach steady state (also observed in AC impedance). Figure 4a shows the time dependence of the polarization/depolarization voltage. The voltage immediately jumps from zero to $IR_{ion/R_{ion}}(R_{ion} + R_{elec})$ where $R_{ion}$ and $R_{elec}$ are the resistances due to Li ion and electronic carriers. With increasing time, the partial current of the blocked electrons decreases and eventually vanishes. A steady state is then observed (voltage being $IR_{ion}$) during which the total current is carried only by the unblocked ions. The ionic conductivity can be obtained from this ionic resistance. The relaxation time of the polarization process is $\tau$, which provides the chemical diffusion coefficients $D_{Li}$ (via $t^\pi = L^2/(\pi^2 D_{Li})$). It should be noted that owing to the internal concentration profiles, $\sigma_{ion}$ and $D_{Li}$ are averaged over a Li composition range, corresponding to a polarization voltage of 250 mV. The behavior of the depolarization was analogous to that during polarization. Owing to the relatively high diffusion coefficients, a steady state cell voltage was reached during polarization at $\sim$50°C.

### Lithium ion diffusivity as a function of lithium concentration from depolarization measurements.

Figure 5a shows an example of the cell voltage vs. time during the stepwise galvanostatic titration of fixed amounts of lithium from the NMC sample. A lithium concentration gradient is developed across the sample during titration. After each delithiation step, the cell is allowed to relax in the OCV condition, and the cell voltage slowly reaches steady state, corresponding to removal of the lithium concentration gradient. Lithium ion diffusivity data derived from the relaxation of the cell voltage, i.e. the depolarization process, using Eq. 1 is shown in Figure 5b. It is seen that the depolarization cell voltage can be fitted very well with Eq. 1.
The room-temperature lithium ion diffusivity for NMC333 and NMC523 obtained from these measurements are plotted in Figure 6 as a function of lithium content. Although data for both compositions have similar trends, NMC523 exhibits the higher diffusivity throughout as a function of lithium content. Although data for both compositions have similar trends, NMC523 exhibits the higher diffusivity throughout as a function of lithium content. Although data for both compositions have similar trends, NMC523 exhibits the higher diffusivity throughout as a function of lithium content.

Table III. Comparison of lithium ion diffusivity of NMC333 and NMC523 from the present work with available literature data.

<table>
<thead>
<tr>
<th>Technique Used</th>
<th>T°C</th>
<th>Composition</th>
<th>Diffusivity (cm²/s)</th>
<th>Reference</th>
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<tr>
<td>AC</td>
<td>60</td>
<td>LiNi₀.₅₀Mn₀.₂₀Co₀.₃₀O₂ (NMC323)</td>
<td>4.5 × 10⁻⁸</td>
<td>This study</td>
</tr>
<tr>
<td>AC</td>
<td>61</td>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>5.5 × 10⁻⁸</td>
<td>This study</td>
</tr>
<tr>
<td>DC</td>
<td>50</td>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>7.6 × 10⁻⁹</td>
<td>This study</td>
</tr>
<tr>
<td>Depolarization</td>
<td>25</td>
<td>Li₀.₀₆Ni₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>4.1 × 10⁻¹⁰</td>
<td>This study</td>
</tr>
<tr>
<td>Depolarization</td>
<td>25</td>
<td>Li₀.₂₃Ni₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>1.3 × 10⁻¹⁰</td>
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<tr>
<td>Depolarization</td>
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<td>Li₀.₀₆Ni₀.₅₀Mn₀.₂₀Co₀.₃₀O₂ (NMC223)</td>
<td>4.6 × 10⁻¹⁰</td>
<td>This study</td>
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<tr>
<td>Depolarization</td>
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<td>Li₀.₀₆Ni₀.₅₀Mn₀.₂₀Co₀.₃₀O₂ (NMC223)</td>
<td>2.5 × 10⁻¹⁰</td>
<td>This study</td>
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<tr>
<td>GITT</td>
<td>25</td>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>~10⁻¹²</td>
<td>19</td>
</tr>
<tr>
<td>GITT</td>
<td>25</td>
<td>Li₀.₂₃Ni₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>~10⁻¹⁰</td>
<td>19</td>
</tr>
<tr>
<td>CV</td>
<td>25</td>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>~5 × 10⁻¹⁴</td>
<td>21</td>
</tr>
<tr>
<td>CV</td>
<td>25</td>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333)</td>
<td>~3 × 10⁻¹⁰</td>
<td>23</td>
</tr>
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</table>
Conclusions

Electronic and lithium ionic transport in NMC have been measured using ion and electron blocking cell configurations and AC and DC techniques. NMC exhibits semiconducting electronic conductivity over the range of lithium concentrations from $x = 0.0$ to $0.75$. Starting from the fully lithiated state, the electronic conductivity increases with increasing delithiation, which is attributed to Ni$^{3+}$/Ni$^{4+}$ multivalency, and rises especially sharply over the initial 10% of delithiation. There is a second upward inflection at about 75% delithiation, which may be due to the onset of Co$^{3+}$/Co$^{4+}$ multivalency. The ionic diffusivity as a function of lithium concentration decreases with delithiation up to at least $x = 0.5$. Since the unit cell parameters in published literature show the opposite trend with a maximum at $x = 0.5$, the observed diffusivity 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.

Electronic and ionic transport parameters across the measured range of Li concentration, it is concluded that chemical diffusion is always limited by lithium ion transport rather than electronic conductivity. From the reported ion transport coefficients, kinetic requirements such as the particle size necessary for particular charge/discharge times can be readily calculated.

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References

Erratum: Characterization of Electronic and Ionic Transport in Li$_{1-x}$/Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC333) and Li$_{1-x}$/Ni$_{0.50}$Mn$_{0.20}$Co$_{0.30}$O$_2$ (NMC523) as a Function of Li Content [J. Electrochem. Soc., 163, A1512 (2016)]

Ruhul Amin$^{a,b}$ and Yet-Ming Chiang$^a$

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Throughout this paper, Li$_{1-x}$/Ni$_{0.50}$Mn$_{0.20}$Co$_{0.30}$O$_2$ should be Li$_{1-x}$/Ni$_{0.30}$Mn$_{0.30}$Co$_{0.20}$O$_2$ and NMC523 should be NMC532.