Electrochemical Activity of Li in the Transition-Metal Sites of O3 Li[Li1−2x/3Mn2/3−xNi1/3]O2

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A combination of first principles calculations and lithium NMR spectroscopy was used to examine the effect of electrochemical cycling on lithium ions located in the transition metal layers in layered lithium nickel manganese. These lithium ions participate in the electrochemical process with NMR results showing that they are removed from the octahedral sites on charging, but return on discharging. Calculations indicate that the lithium ions become increasingly unstable, as the concentration of vacancies in the lithium layers increases. A lithium ion nearby three vacancies in the lithium layers drops immediately, with no activation barrier, into the adjacent tetrahedral site in the lithium layers; charging to higher potentials is then required to remove this lithium ion.

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Recently, Li[Li1−2x/3Mn2/3−xNi1/3]O2 has emerged as a promising class of positive electrode materials for rechargeable lithium batteries.\(^1,2\) In these materials, Li removal leads to the oxidation of Ni\(^{3+}\) to Ni\(^{4+}\),\(^3\) while the valence of Mn remains approximately at +4 for all Li compositions. The remarkable stability of these materials against transformation to thermodynamically more stable phases is related to the valence states of the ions in this material. Both Mn\(^{4+}\) and Ni\(^{4+}\) ions strongly favor octahedral coordination and the activation energy for conversion from octahedral to tetrahedral coordination is high. Passing through the tetrahedral site is a prerequisite for any transition-metal ion diffusion to take place in these layered structures as different octahedral sites are connected by face-sharing tetrahedral sites. Ni\(^{4+}\), which requires less energy to go tetrahedral, is only present at high lithium contents where the occupation of tetrahedral sites is precluded as they share faces with the octahedral sites occupied by lithium.

Even for the nominally stoichiometric material Li[Ni\(_{1/3}\)Mn\(_{2/3}\)]O\(_2\), some antisite disorder between the Li and transition metal (TM) layers is always present.\(^4\) Neutron and X-ray diffraction (XRD) studies\(^5-7\) have been used to determine Ni\(^{3+}\) occupancies in the Li\(^{+}\) layers of between 7 and 12%. Li NMR studies may be used to determine directly the Li occupancy in the TM layers, these studies finding 7% occupancy for some materials,\(^8\) but also showing that the Li occupancies may vary slightly from sample to sample, even for materials with the same nominal composition. Extrinsic Li doping of the TM layer may be achieved by substituting 3Ni\(^{3+}\) by 1Mn\(^{4+}\) and 2Li\(^{2+}\), leading to the series Li[Li\(_{1−2x/3}\)Mn\(_{2−x}\)Ni\(_{x}\)]O\(_2\). Complete substitution of Ni leads to the end member Li[Li\(_{1}Mn\(_{2}\)Ni\(_{1}\)]O\(_2\) (or Li[Li\(_{1}Mn\(_{0}\)])\). Typically, it is assumed that the Li ion in the TM layer is a passive component and does not participate in the intercalation and deintercalation reactions. In this article, we use NMR and first principles computations to demonstrate that this premise is incorrect and that the Li is reversibly removed from its octahedral site in the TM layer upon charging the electrode. Both NMR and first principles computations are particularly suited to investigate this approach as they offer a detailed picture of the local structure and energetics around the Li ion. Structural changes such as the ones discussed in this article are difficult to observe by XRD.

LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) and Li[Li\(_{1}Mn\(_{0.5}\)Ni\(_{0.5}\)]O\(_2\) were synthesized using stoichiometric quantities of coprecipitated manganese and nickel double hydroxides. The methods used to prepare and characterize these samples, and to fabricate the electrodes, are identical to those described elsewhere.\(^4,5\) Different cells were charged to a potential of 4.8 V (vs. Li) at C/47, and then discharged to 2.5 V. One cell was cycled between these two potentials for 20 cycles. Cells were stopped at different potentials, taken apart, and samples were extracted for the NMR experiments.\(^6\) Li magic-angle spinning (MAS) NMR experiments were performed at 29.47 MHz on a CMX-200 spectrometer as described in Ref. 4. Rotor synchronized spin-echoes (90°-\(\tau\)-180°-\(\tau\)-acq) were used to acquire the spectra (i.e., \(\tau\) = 1spinning frequency). The first principles approach is similar to that used in previous investigations on Li-insertion electrodes.\(^9-12\) Ultrasoft pseudopotentials as implemented in the Vienna \textit{ab initio} Simulation Package,\(^13\) with an exchange-correlation correction in the Generalized Gradient Approximation, were employed.

Figure 1a shows the \(^{6}\)Li MAS NMR spectra of Li[Li\(_{1−2x/3}\)Mn\(_{2−x}\)Ni\(_{x}\)]O\(_2\), with \(x = 1/3\) as function of state of charge. Two major clusters of resonances are observed, one at approximately 1300-1500 ppm and one at approximately 700 ppm. The first set of resonances have been assigned to Li in the TM layers, while the lower frequency resonances are assigned to Li local environments in the TM layers, based on our earlier work,\(^8,9\) and on the shifts observed for Li[Mn\(_{x}\)O\(_{2}\)].\(^14\) The resonances at 1498 and 1324 ppm are assigned to Li local environments in the TM layers surrounded by 6Mn\(^{4+}\) and (5Mn\(^{4+}\) + 1Ni\(^{3+}\)) transition metals in the first cation coordination shell, respectively.\(^8\) As the sample was charged, the intensity under these peaks decreased, indicating that Li was removed from sites in both the TM and Li layers. Li removal from the TM layers occurred even in the early stages of charging. Qualitatively similar spectra are seen for the \(x = 1/2\) sample, Li being removed from both sets of local environments.

The NMR spectrum of Li[Li\(_{1}Mn\(_{0.5}\)Ni\(_{0.5}\)]O\(_2\) following charging to 4.8 V and subsequent discharging to 2.5 V, is compared with the spectrum for the pristine material in Fig 1b. The resonances due Li in the TM layers clearly return at the end of a charge/discharge cycle, illustrating that the Li removal from the TM layers is reversible. The concentration of the local environment containing 6Mn\(^{4+}\) ions (1498 ppm) has decreased slightly relative to that due to 5Mn\(^{4+}\) and 1Ni\(^{3+}\), suggesting that local environments near more Mn\(^{4+}\) may participate less readily in the reversible deintercalation/insertion processes. This local environment is present in much lower concentrations for random Li/Ni/Mn arrangements in the TM layers.\(^5\) Thus, any TM diffusion at high potentials, involving migration into the now vacant Li octahedral sites, likely reduces the concentrations of the vacant sites in the TM layers nearby 6Mn\(^{4+}\) ions, and increases the concentrations of vacant sites nearby both Ni and Mn, consistent with the reduction of 1498 ppm \(^{6}\)Li resonance, and the observation of a weak resonance at approx. 1150 ppm seen on discharge (marked by an arrow on Figure 1b), which is assigned to the local environment Li[ONi\(_{1/3}\)OMn\(_{1/3}\)]. Diffusion in the TM layers

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following extended cycling, facilitated by the vacancies formed at high potentials, represents one possible mechanism for increasing the disorder in these layers. Consistent with this, the breadth of the resonance due to the Li in the Li layers increased dramatically following 20 charge/discharge cycles and is now similar in width to the corresponding resonance in the more disordered Li$_{\text{Ni}}$Ni$_{0.5}$Mn$_{0.5}$O$_2$ material.

The concentration of Li ions in the TM layers also decreases dramatically, which is likely due, at least in part, to a reduction of environments for Li near 6 or 5Mn$^{4+}$ ions in the more disordered material. The increased disorder seen by NMR is consistent with the changes seen in the cyclic voltametry and in the differential capacity plots of similar cathode materials on cycling, which are particularly pronounced in the first one to five cycles.

The potential at which Li is removed from a TM site may be computed by setting up a supercell with Li occupying one or more TM sites (Li$_{\text{TM}}$) and calculating the energy required to remove this ion (referenced to Li metal anode)

$$V = -[E_{\text{cell}}(\text{with Li}_\text{TM}) - E_{\text{cell}}(\text{Li}_\text{TM} \text{ removed}) - E(\text{Li on anode})]$$

In principle, the energy of these cells must be minimized not only with respect to the relaxation degrees of freedom, but also with respect to the configuration of Li and vacancies in the Li layer (in case they are partially charged). In this study, we limit ourselves to estimating the potential at with Li$_{\text{TM}}$ is removed, for a few relevant configurations of Li and vacancies in the Li layer of a cell with 12 formula units (24 oxygen ions). Removing Li$_{\text{TM}}$ from a completely discharged material (all sites in the Li layer filled) requires between 3.23 and 3.27 V (calculated). This must be compared to removing a single Li in the Li layer from this cell which requires between 2.84 and 2.98 V (depending on the local TM environment for that Li). These computed voltages are typically significantly underestimated with respect to the experimental potentials. Comparing the calculated average voltage for removing Li from Li$_{\text{Ni}}$Ni$_{0.5}$Mn$_{0.5}$O$_2$ ($=3.2$ V) with the experimental average voltage of about 3.9 V indicates that the underestimation will be about 0.7 V. Because the potential for extracting Li$_{\text{TM}}$ falls near the average potential, it is likely that Li is extracted from the TM layer during charging.

Because the previous result indicates only that it is thermodynamically possible to remove Li$_{\text{TM}}$, we have further investigated the mechanism by which it may be removed. To migrate from a site in the TM layer into the Li layer, Li must pass through a tetrahedral site. Typically Li occupies only this tetrahedral site when the four octahedral sites that share faces with it (three in the Li layer and one in the TM layer) are unoccupied. We find that when a trivacancy forms in the Li layer above Li$_{\text{TM}}$, this Li ion moves into the tetrahedral site without an activation barrier (Fig. 2b). This indicates that Li spontaneously leaves the TM layer upon removal of a Li near a Li divacancy. Figure 2a shows such a configuration. Li divacancy sits above the Li$_{\text{TM}}$ site. When one more Li is removed to form a trivacancy, Li migrates into the tetrahedral site. We calculated this col-

![Figure 1](image-url)
with a vacant environment containing Mn$^{4+}$ in the ordered spinels \((\text{Li}_{0.5} \text{Zn}_{0.5})_{\text{tet}} (\text{Li}_{0.5} \text{Mn}_{1.5})_{\text{oct}} \text{O}_4\) and Ni$^{2+}$ tetrahedral sites are coordinated to 9Mn$^{4+}$. A292

The presence of Li in tetrahedral sites during part of the charge/discharge cycle may have negative effects on the mobility of Li. Occupation of a tetrahedral site blocks three octahedral sites from being occupied, thereby limiting the number of sites that participate in Li diffusion. The creation of vacancies in the TM layer could also enhance interdiffusion of the transition metal ions, resulting in the increased disorder of these materials, which is observed experimentally after prolonged cycling.

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