LITHIATED OXIDES FOR LITHIUM-ION BATTERIES

by

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ABSTRACT
Rechargeable lithium batteries that can be assembled in the discharged state with lithiated metal oxide cathodes and carbon anodes are being developed to minimize the safety hazards associated with batteries that use pure metallic lithium anodes. This paper highlights the progress that has been made to develop lithiated transition metal oxide cathodes that have a layered structure, Li$_x$MO$_2$, and those that have a spinel-type structure, Li$_x$M$_2$O$_4$, ($M = \text{Co, Ni, Mn, V}$). Emphasis is placed on the structural properties of insertion electrodes that control their stability during electrochemical cycling. The use of lithiated spinel oxide instead of lithiated carbon (LiC$_6$) as the anode is briefly discussed.

INTRODUCTION
Insertion compounds have been widely studied over the last two decades as electrodes for lithium batteries. Early work was carried out on cathode materials such as TiS$_2$, WO$_3$, V$_2$O$_5$, and MnO$_2$, which were evaluated in cells with metallic lithium anodes [1]. Recently, the focus of lithium battery technology has shifted to rechargeable systems—in particular, "lithium-ion" systems in which lithium ions are shuttled between an anode host structure and a cathode host structure during charge and discharge. Much of today's research is spent on developing cells with lithium-carbon anodes (Li$_x$C$_6$, $0 < x < 1$) [2] and high-voltage cathodes, such as Li$_{1-x}$CoO$_2$ [3-5], Li$_{1-x}$NiO$_2$ [5-7], and Li$_{1-x}$Mn$_2$O$_4$ [8-12] ($0 < x < 1.0$). Lithium insertion into carbon takes place between 1 and 0 V with respect to a lithium reference electrode, whereas lithium extraction from LiCoO$_2$, LiNiO$_2$, and LiMn$_2$O$_4$ occurs at approximately 4 V. In practice, therefore, lithium-ion cells with carbon anodes and these high-voltage cathodes charge and discharge between 4 V and 3 V.

The structural stability of a host electrode to the repeated insertion and extraction of lithium is undoubtedly one of the key properties for ensuring that a lithium-ion cell operates with good electrochemical efficiency. In transition-metal oxides, both stability of the
oxygen-ion array and minimum displacements of the transition metal cations in the host are required to ensure good reversibility. Structures with a cubic-close-packed (ccp) oxygen array are more stable to lithium insertion/extraction than hexagonal-close-packed (hcp) structures. For example, the oxygen array in hcp structures such as α-Fe₂O₃ [13], β-MnO₂ [14], and MnO₂ (ramsdellite) [15] shears toward cubic close packing on lithium insertion in response to electrostatic interactions between the incoming lithium ions and transition metal cations in face-shared octahedral sites. The shear process is often accompanied by displacements of the transition metal cations within the oxygen lattice. These structural modifications tend to degrade the integrity of an insertion electrode, particularly when it is subjected to repeated charge and discharge.

Structures of transition metal oxide insertion electrodes are, in general, not tolerant to overcharge or overdischarge. It is, therefore, critically important to carefully control fabrication conditions so that the composition of the electrode corresponds to that of the most stable host structure of the metal oxide system. Furthermore, cell operating conditions, such as voltage limits and current drain, must be carefully controlled to ensure that the structural integrity of the electrodes is not destroyed on cycling.

The results in this paper illustrate the importance of limiting the structural changes within an insertion electrode during electrochemical cycling to the absolute minimum. The discussion is focused primarily on the advantages of the high-voltage cathodes of current interest, namely, LiCoO₂, LiNiO₂, and LiMn₂O₄. Examples of electrodes that, from a structural viewpoint, are not tolerant to lithium insertion and extraction are also provided for comparison. The use of the low-voltage spinel Li₄Ti₅O₁₂, which discharges at approximately 1.5 V against lithium, as an anode in lithium-ion cells is briefly addressed.

CATHODE MATERIALS

(i) Layered Structures, LiMO₂ (M = Co, Ni, Mn, V).

a) LiCoO₂ and LiNiO₂. The ideal layered LiMO₂ structure (M = Co, Ni, V) has a close-packed oxygen array which is slightly distorted from ideal cubic close packing (Fig. 1). The structure has trigonal (R₃m) symmetry; the unit cell parameters are usually defined in terms of the hexagonal setting. Both LiCoO₂ and LiNiO₂ are of particular interest for lithium battery applications [3-7]. They are synthesized by solid state reaction of the appropriate precursors (for example, CoCO₃, NiO, and LiOH) at temperatures that typically range from 700°C to 850°C. At present, LiCoO₂ is the material of choice, despite its high cost, because it is relatively easy to prepare a high-quality electrode with essentially the ideal layered structure. The ideal layered LiNiO₂ structure is more difficult to synthesize; in this case, the product often contains a small proportion of nickel within the lithium layers, which can seriously damage electrode performance. An optimized LiNiO₂ electrode is, however,
more forgiving than LiCoO$_2$ and is more stable to charge, particularly at low lithium loadings; rechargeable capacities of more than 150 mAh/g of cathode have been reported [5,6].

![Image](image_url)

**Fig. 1.** Schematic representation of layered LiMO$_2$ compounds (M = V, Co, Ni). M atoms are located within the layers of shaded octahedra; Li atoms are in alternate layers of unshaded octahedra.

Both Li$_{1-x}$CoO$_2$ and Li$_{1-x}$NiO$_2$ undergo reversible phase transitions, which have been attributed to changes in crystal symmetry from trigonal to monoclinic [6,7]. The transitions are attributed to order-disorder phenomena associated with the lithium ions. An important feature of these transitions is that they occur with only relatively small changes of the unit cell parameters [7]. Because the oxygen array of the CoO$_2$ and NiO$_2$ framework structures is not substantially distorted by the transitions, and the metal cations of the host do not enter the interstitial space of the MO$_2$ framework, these two electrode systems exhibit the good reversibility. Table 1 shows the change in the lattice parameters of a Li$_{1-x}$NiO$_2$ electrode on delithiation.

**Table 1.** Changes in lattice parameters and crystal symmetry of Li$_{1-x}$NiO$_2$ (after Dahn et al [7]).

<table>
<thead>
<tr>
<th>x in Li$_{1-x}$NiO$_2$</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Crystal Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.883</td>
<td>2.883</td>
<td>14.215</td>
<td></td>
<td>Trigonal</td>
</tr>
<tr>
<td>0.06</td>
<td>2.878</td>
<td>2.878</td>
<td>14.217</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.11</td>
<td>2.872</td>
<td>2.872</td>
<td>14.234</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>2.869</td>
<td>2.869</td>
<td>14.241</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>5.002</td>
<td>2.841</td>
<td>14.303</td>
<td>90.45</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>0.31</td>
<td>4.996</td>
<td>2.832</td>
<td>14.340</td>
<td>90.56</td>
<td></td>
</tr>
<tr>
<td>0.41</td>
<td>4.955</td>
<td>2.831</td>
<td>14.416</td>
<td>90.45</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>4.944</td>
<td>2.820</td>
<td>14.469</td>
<td>90.45</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>2.826</td>
<td>2.826</td>
<td>14.445</td>
<td></td>
<td>Trigonal</td>
</tr>
<tr>
<td>0.61</td>
<td>2.826</td>
<td>2.826</td>
<td>14.397</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.71</td>
<td>2.823</td>
<td>2.823</td>
<td>14.400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.82</td>
<td>2.825</td>
<td>2.825</td>
<td>14.427</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.82</td>
<td>2.821</td>
<td>2.821</td>
<td>14.434</td>
<td></td>
<td>Trigonal</td>
</tr>
</tbody>
</table>
Note that the $b$ and $c$ parameters of the monoclinic unit cell relate directly to the $a$ and $c$ parameters of the trigonal unit cell, and that $a_{\text{monoclinic}} = 2a_{\text{trigonal}} \sin 60^\circ$; all parameters vary gradually as lithium is extracted from the structure. The unit cell volume of Li$_{1-x}$NiO$_2$ decreases marginally, by 2.7%, between $x = 0$ and $x = 0.6$, the range over which the electrode is usually cycled. The interlayer spacing increases slightly on delithiation, in response to a decrease in the binding energy within the lithium-depleted layers, which allows rapid lithium-ion diffusion. These layered structures are therefore able to cope well with lithium insertion/extraction reactions; structural integrity of the electrodes is maintained provided that Li/Li$_{1-x}$CoO$_2$ and Li/Li$_{1-x}$NiO$_2$ cells operate between carefully controlled compositional (voltage) limits. At low lithium loadings ($x<0.5$), the high oxidation potential of these cathodes threatens their structural stability, and chemical decay (for example, by reaction with the organic electrolyte) becomes a factor that can limit the life of the lithium-ion cells.

b) \textit{LiVO$_2$}. Unlike LiCoO$_2$ and LiNiO$_2$, the layered structure of LiVO$_2$ is destabilized by lithium extraction; at $x=0.3$ in Li$_{1-x}$VO$_2$, approximately one-third of the vanadium ions migrate from the vanadium layer to the lithium-depleted layer [16]. This process destroys the two-dimensional space for lithium-ion diffusion. The product has a defect rock-salt structure that offers limited electrochemical activity [17]. Reinsertion of lithium does not regenerate the layered structure. The structural degradation of the layered VO$_2$ host is clearly evident from the X-ray diffraction patterns of the original material and the delithiated product (Fig. 2). In particular, the significant decrease in the intensity of the [003] peak at approximately 18°20′ (which can be used as a yardstick to measure the degree of layering within cubic-close-packed oxygen arrays) indicates the movement of vanadium ions into adjacent layers.

c) \textit{LiMnO$_2$}. A layered LiMnO$_2$ compound that is isostructural with LiCoO$_2$, LiNiO$_2$, and LiVO$_2$ has not yet been synthesized. However, a recent report has indicated that a layered compound with approximate composition LiMnO$_2$ can be prepared, by leaching Li$_2$O from the layered rock-salt compound Li$_2$MnO$_3$ (Li$_2$O•MnO$_2$) with acid and, thereafter, relithiating the resulting manganese oxide with lithium [18]. This technique results in a layered lithium manganese oxide product, Li$_{1.09}$Mn$_{0.91}$O$_2$, with a structure that closely resembles that of LiCoO$_2$ and LiNiO$_2$; it has a small amount (9%) of lithium in the manganese layers (Fig. 3a). However, unlike LiCoO$_2$ and LiNiO$_2$, Li$_{1.09}$Mn$_{0.91}$O$_2$ is a 3 V, not a 4 V, electrode. The oxygen array of this layered structure is unstable to lithium extraction; delithiation causes a shearing of the oxygen planes, which keeps the manganese ions octahedrally coordinated but places the lithium ions in trigonal prismatic coordination (Fig. 3b). The instability of the oxygen array to lithium insertion/extraction limits the use of this compound as a rechargeable electrode in lithium cells; further work is required to improve its cycling behavior.
Fig. 2. The X-ray diffraction patterns of a) LiVO₂, b) Li₀.₅VO₂, and c) Li₀.₂VO₂ showing the large decrease in intensity of the [003] peak at approximately 18°2θ in response to a migration of the V atoms into the lithium layers (taken from reference [21]).

Fig. 3. The layered structures of a) Li₁₀₉Mn₀₉₁O₂ and b) Li₀₃₆Mn₀₉₁O₂ (taken from reference [18]).

(ii) Spinel Materials Li[M₂]O₄.

The [M₂]O₄ framework of a Li[M₂]O₄ spinel is an attractive host structure for lithium insertion/extraction reactions because it provides a three-dimensional network of face-sharing tetrahedra and octahedra for lithium-ion diffusion (Fig. 4). In the [M₂]O₄ spinel framework which has cubic symmetry Fd3m, 75% of the metal cations occupy alternate layers between the cubic-close-packed oxygen planes; the remaining 25% of the metal cations are located in the adjacent layers. Therefore, sufficient M cations exist in every layer to provide, on delithiation, a sufficiently high binding energy to maintain an ideal cubic-close-packed oxygen array. In most cases, spinel structures expand and contract isotropically
during lithium insertion and extraction. Such cubic electrodes are more stable to electrochemical cycling than those in which there is a large anisotropic expansion or contraction of the lattice parameters. For example, the spinels Li$_4$M$_3$O$_{12}$ (or alternatively, Li[M$_{1.67}$Li$_{0.33}$]O$_4$, $M = \text{Mn, Ti}$) are extremely tolerant to cycling because the cubic unit cell expands and contracts by less than 1% within controlled compositional limits [19,20]. By contrast, the orthorhombic unit cell of a MnO$_2$ (ramsdellite) electrode expands anisotropically when lithiated to a composition Li$_{0.9}$MnO$_2$; the unit cell parameters $a$, $b$ and $c$ change by $+5.7\%$, $+16.5\%$, and $-1.4\%$, respectively, which represents a 21.5% increase in the unit cell volume. In this case, the strain that is imposed on the host structure is far too severe for the electrode to survive repeated cycling.

![Image](image_url)

**Fig. 4.** The [M$_2$]O$_4$ framework of a Li[M$_2$]O$_4$ spinel.

(a) $\text{LiMn}_2\text{O}_4$. Of the lithium spinels, the system Li$_x$Mn$_2$O$_4$ is the most attractive for lithium-ion batteries; it offers the highest voltage (4 V) against lithium and provides a stable cubic [Mn$_x$]O$_4$ framework over the whole 4 V compositional range $0<x<1$ [8,9]. But Li$_x$[Mn$_2$]O$_4$ has two main disadvantages. Firstly, it is difficult to extract, electrochemically, all the lithium from the structure at practical voltages. This limits the rechargeable capacity at 4 V to about 120 mAh/g. Secondly, at the end of discharge, when, under non-equilibrium conditions, the overall composition of the electrode reaches LiMn$_2$O$_4$, the surface of some particles is more extensively lithiated than the bulk and can reach a $\text{Li}_{1+\delta}\text{Mn}_2\text{O}_4$ composition in which the average Mn oxidation state falls below 3.5. For $\delta>0$, a Jahn-Teller distortion occurs at the particle surface and reduces the symmetry of the spinel from cubic to tetragonal ($c/a = 1.16$). The large anisotropic expansion of the unit cell that is reflected by the 16% increase in the $c$ parameter is too severe for the cubic and tetragonal phases to remain as one intergrown structure. The incompatibility between the oxygen arrays of the cubic and tetragonal phases causes the electrode to fracture at the particle surface. This effect destroys structural integrity and particle-to-particle contacts, which are essential for maintaining the electronic conductivity of the electrode. Gummow et al. [12] have proposed that the structural damage is a reason for the slow loss of capacity that occurs on cycling Li/Li$_{1-x}$Mn$_2$O$_4$ cells (Fig. 5a). This damaging effect can be reduced by suppressing the onset of the Jahn-Teller distortion by modifying the composition of the spinel electrode.
to keep the average Mn oxidation state slightly above 3.5 at the end of the 4 V plateau [12]. This has been accomplished by using electrodes of general formula Li$_{1+\delta}$Mn$_{2-\delta}$O$_4$ or Li$_{1-\delta}$Mn$_{2+\delta}$O$_4$ with small values of $\delta$, for example, $\delta = 0.05$. In general, materials with Mn$^{n+}$ slightly greater than 3.5 are found within the darkened triangle of the Li-Mn-O phase diagram (Fig. 6). Although these modified spinel electrodes offer slightly inferior electrode capacities to Li[Mn$_2$]O$_4$, they do exhibit very stable cycling behavior and deliver rechargeable capacities in excess of 100 mAh/g (Fig. 5b). In principle, other cations can be used to "stabilize" Li[Mn$_2$]O$_4$, for example, LiM$_{5/2}$Mn$_{2-\delta}$O$_4$ (M = Mg or Zn).

**Fig. 5.** Cycling behavior for the first 10 cycles of a) Li/LiMn$_2$O$_4$ and b) Li/Li$_{1.03}$Mn$_{1.97}$O$_4$ cells, showing the improved capacity retention in b) (taken from reference [12]).

**Fig. 6.** An expanded view of the Li-Mn-O phase diagram. The darkened area shows the composition of spinel electrodes of interest in which the oxidation state of the manganese ions is slightly greater than 3.5 (taken from reference [12]).

b) LiV$_2$O$_4$. Like LiVO$_2$, LiV$_2$O$_4$ is destabilized by lithium extraction, which limits its use as an insertion electrode [17,21]. Removal of lithium from the Li$_{1-x}$V$_2$O$_4$ spinel structure is accompanied, at $x=0.33$, by the displacement of approximately one-ninth of the vanadium ions in the vanadium-rich layer into adjacent layers. This destroys the [V$_2$]O$_4$ spinel framework and the ordered three-dimensional interstitial space for lithium-ion
diffusion. The product has a defect rock-salt structure, similar to that formed when lithium is extracted from layered LiVO₂ [16].

c) \( \text{LiCo}_2\text{O}_4 \). When LiCoO₂ is prepared at 400°C (often referred to as LT-LiCoO₂), the structural and electrochemical properties of the material are significantly different from those of LiCoO₂ prepared at 850°C (referred to as HT-LiCoO₂) [22-24]. The LT-Li₁₋ₓCoO₂ has a cubic-close packed oxygen lattice that remains unaffected by lithium extraction, whereas HT-Li₁₋ₓCoO₂ has trigonal symmetry with a \( c/a \) ratio that increases from 4.99 at \( x = 1 \) to 5.12 at \( x = 0.5 \). The LT-Li₁₋ₓCoO₂ electrodes discharge at approximately 0.5 V lower than HT-Li₁₋ₓCoO₂ but, in comparison to HT-Li₁₋ₓCoO₂, do not cycle well. Despite a structural anomaly that makes it impossible to distinguish, by powder X-ray or neutron diffraction techniques, a layered LiCoO₂ structure with an ideal cubic-close packed oxygen array from a cubic, lithiated spinel Li₂[Co₃]O₄ (both of which have \( c/a = 4.899 \)), high-resolution neutron diffraction data have shown recently that the oxygen array in LT-LiCoO₂ is not quite ideally cubic close packed \( (c/a = 4.914) \) [25]. The model for LT-LiCoO₂ that best fits the neutron diffraction data is one that can be described as having a structure with a cation distribution which is intermediate between an ideal layered and an ideal lithiated spinel structure. This interpretation, along with the poor electrochemical performance of LT-LiCoO₂, is consistent with the performance of LiNiO₂ electrodes that contain a significant amount of nickel in the lithium layers. Note, however, that removing lithium from LT-LiCoO₂ in acid generates an almost ideal spinel Li[Co₃]O₄ compound [25], according to the reaction:

\[
3\text{LT-LiCo}_2\text{O}_2 \rightarrow \text{Li[Co}_3\text{]}\text{O}_4 + \text{CoO} + \text{Li}_2\text{O}
\]  

[1]

Acid-leached spinel samples derived from nickel-doped LT-LiCo₁₋ₓNiₓO₂ compounds \( (0 \leq x \leq 0.2) \) show a significantly improved cycling ability over LT-LiCoO₂ products (Fig. 7) [26]; the resulting spinel structure expands/contracts by only 0.2% on lithium insertion/extraction.

![Graph](image1.png)

**Fig. 7.** Cycling behavior of a) Li/LT-LiCo₀.₅Ni₀.₁O₂ and b) Li/LT-Li₀.₄Co₀.₈Ni₀.₁O₂ (acid-leached) cells, showing the improved capacity retention in b) (taken from reference [26]).
Although further work is necessary to fabricate the perfect $[\text{Co}_2]\text{O}_4$ framework, it can be concluded from the studies undertaken thus far that this framework should be stable to lithium insertion/extraction. Because $\text{LiCoO}_2$ and $\text{LiNiO}_2$ compounds, with a cation distribution that is intermediate between a layered and a spinel structure, are not tolerant to electrochemical cycling, fabrication conditions must be carefully controlled to ensure that deviations from the desired stoichiometry and structure of an electrode are minimal.

**ANODE MATERIALS**

**Spinel Oxides**

Transition metal oxides that offer a low voltage against pure lithium, for example, $\text{WO}_2$ [26], $\text{MoO}_2$ [27], and $\text{LiFe}_2\text{O}_3$ [28,29], have been investigated in the past as anode materials for lithium-ion cells. Those materials that have rutile or corundum-type structures with hexagonally-close-packed oxygen arrays are not sufficiently stable to lithium insertion/extraction to be practical in rechargeable lithium cells. However, because the $[\text{B}_2]\text{X}_4$ framework of an $\text{A}\,[\text{B}_2]\text{X}_4$ spinel is stable to lithium insertion and extraction, and the voltage of the electrode can be tailored by changing the metal cation on the B sites of the framework, this family of spinels is an attractive candidate for finding a stable anode for lithium-ion cells [30,31]. One such material is $\text{Li}_4\text{Ti}_5\text{O}_{12}$, in spinel notation $\text{Li}[(\text{Ti}_{0.67}\text{Li}_{0.33})\text{O}_4]$; it offers a stable operating voltage of approximately 1.5 V vs. lithium. In principle, therefore, this material can be coupled with a 4 V electrode such as $\text{LiCoO}_2$, $\text{LiNiO}_2$, or $\text{LiMn}_2\text{O}_4$ to provide a cell with an operating voltage of approximately 2.5 V, which is twice that of a nickel-cadmium or nickel-metal hydride cell. Lithium reacts with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ according to the reaction:

$$3\text{Li} + \text{Li}_4\text{Ti}_5\text{O}_{12} \rightarrow \text{Li}_7\text{Ti}_5\text{O}_{12} \quad [2]$$

Because lithium insertion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel displaces tetrahedrally coordinated lithium ions into octahedral sites with the formation of a rock-salt-type $\text{Li}_7\text{Ti}_5\text{O}_{12}$ product, the electrode is two-phase and, therefore, provides a flat voltage response to lithium insertion. The theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 175 mAh/g. The exceptional stability of this electrode to electrochemical cycling has been demonstrated by Rossen et al. [24] and can be attributed to the stability of the $[\text{Ti}_{1.67}\text{Li}_{0.33}]\text{O}_4$ framework and to the minimal dilation (<1%) of the cubic unit cell that occurs on lithium insertion.

The principle of using two spinel oxides as anode and cathode in a lithium-ion cell has recently been demonstrated by using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode and a stabilized spinel, $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$ or $\text{LiZn}_{0.05}\text{Mn}_{1.95}\text{O}_4$, as cathode [31]. In a balanced cell, with a $\text{LiZn}_{0.025}\text{Mn}_{1.95}\text{O}_4$ cathode, the reaction is:
These cells are assembled in the discharged state from spinel products, which are fairly easy to prepare by solid-state reaction techniques. During the first charge cycle, lithium is inserted into Li$_4$Ti$_5$O$_{12}$ with a concomitant reduction of the titanium cations, and it is extracted from LiZn$_{0.025}$Mn$_{1.95}$O$_4$ with a concomitant oxidation of the manganese cations. The theoretical cell capacity and energy density (based on an average discharge voltage of 2.5 V and the masses of the electrode materials only) for the reaction above are 63.5 Ah/kg and 159 Wh/kg, respectively. The excellent electrochemical reversibility of such cells for the first five cycles is shown in Fig. 8. This figure illustrates the independent flat voltage response that is obtained at the anode and cathode, when monitored against a metallic lithium reference electrode during charge and discharge. Higher specific energies can be achieved if LiCoO$_2$ or LiNiO$_2$ electrodes are used. Because of their comparative specific energy, Li$_{4+y}$Ti$_5$O$_{12}$/Li$_{1-x}$CoO$_2$ and Li$_{4+y}$Ti$_5$O$_{12}$/Li$_{1-x}$NiO$_2$ cells may provide alternatives to nickel-cadmium cells. For $x = 0.6$ and $y = 3$, the theoretical energy densities of the former two systems are close to 200 Wh/kg; the nickel-cadmium system provides 194 Wh/kg [31].

![Charge/discharge characteristics](image)

**Fig. 8.** Charge/discharge characteristics of Li$_4$Ti$_5$O$_{12}$/LiZn$_{0.025}$Mn$_{1.95}$O$_4$ cell, showing the voltage response at both anode and cathode against a metallic lithium reference electrode [31]. The x-axis corresponds to the capacity delivered by the cathode.

**CONCLUSIONS**

The structural properties of lithiated transition metal oxide insertion electrodes play a key role in determining their rechargeability. Lithium insertion/extraction reactions should be accompanied by a minimum distortion of the oxygen-ion array and minimum
displacement of the transition metal cations within the host. Ideal layered and ideal spinel structures operate significantly better than structures that have "intermediate-type" structures. In principle, optimum electrochemical rechargeability can be expected from cubic structures that expand and contract isotropically with minimum change to the unit cell volume.

REFERENCES


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