

The mechanism of electrochemical activity of Li_2MnO_3

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Lithium intercalation compounds based on lithium manganese oxides are safer, cheaper and less toxic than the intercalation compound LiCoO_2 and, therefore, offer a particularly attractive replacement for the latter compound as a positive electrode in rechargeable lithium batteries.^[1,2] As a result, the lithium intercalation compound LiMn_2O_4 with the spinel structure, as well as orthorhombic and layered LiMnO_2 and their derivatives, have received intense interest in recent years.^[3-8] Extraction of lithium from these compounds involves oxidation of Mn^{3+} to Mn^{4+} .

It is generally believed that Mn cannot be oxidised beyond +4 in an octahedral oxygen environment.^[9] This limits the voltage of manganese-based cells since higher oxidation states correspond to d-levels lying at lower energy and hence higher electrode potentials. The inability to oxidise manganese beyond +4 also limits the amount of lithium that may be extracted from lithium manganese oxides, since removal of Li^+ is accompanied by oxidation of the Mn. This in turn limits the capacity of the cell to store charge. As a result Mn^{4+} compounds such as Li_2MnO_3 (which adopts a layered structure $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$), despite being rich in mobile Li^+ ions, were considered electrochemically inert. Recently, it has been suggested that Li^+ may be removed from Li-Mn⁴⁺-oxides. For example, one report suggested the surprising result that lithium can be removed from Li_2MnO_3 by oxidation of Mn^{4+} .^[10] Li_2MnO_3 is not the only compound which combines the presence of lithium ions with manganese in the +4 oxidation state. The non-stoichiometric spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ($\text{Li}[\text{Li}_{1/3}\text{Mn}_{5/3}]\text{O}_4$) is such a compound, as are the layered materials containing Mn^{4+} , Ni and Li within the transition metal layers e.g. $\text{Li}(\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3})\text{O}_2$ ($0 \leq x \leq 1/3$).^[11-13] It has been reported that lithium extraction is possible from these materials, not by oxidation of Mn^{4+} but by the simultaneous removal of oxygen to balance the charge i.e. the effective removal of Li_2O .^[14,15]

Clearly, the electrochemical activity of Li-Mn⁴⁺-oxides is an interesting phenomenon and one for which contradictory explanations have been proposed. It has important implications for the use of lithium manganese oxides in rechargeable lithium batteries. As a result, it is important to investigate fundamentally whether Mn^{4+} may indeed be oxidised in an octahedral oxygen environment or whether the removal of lithium is accompanied by the extraction of oxygen, or does some other mechanism occur?

We show that a substantial quantity of Li (at least 1.39Li) may be removed from Li_2MnO_3 . At 55°C this occurs exclusively by oxidation of the non-aqueous electrolyte thus generating H^+ which exchange for Li^+ to form $\text{Li}_{2-x}\text{H}_x\text{MnO}_3$.^[16] The reaction is partially reversible. On extended cycling the material converts to spinel. A range of results relating to the phenomenon of Mn^{4+} -oxide electrochemistry will be presented.

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Figure 1. Voltage versus composition for the first cycle of a Li_2MnO_3 composite electrode at 30 and 55°C.

