

Unusual Electrochemical Behavior in $\text{Li}_x\text{Mn}_{1-y}\text{Li}_y\text{O}_2$

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The layered compound LiMnO_2 was first synthesised several years ago. [1,2] Since then there has been considerable interest in this material, and solid solutions based on it, as a cathode for rechargeable lithium-ion batteries. Solid solutions based on LiMnO_2 in which Mn is replaced by other ions are of particular interest. For example we have shown that by doping with only 2.5% Co it is possible to obtain materials that can deliver discharge capacities in excess of 200 mAhg^{-1} at 30°C at C/8, fading by less than 0.08% per cycle over hundreds of cycles [3].

The solid solution $\text{Li}(\text{Mn}_{1-y}\text{Li}_y)\text{O}_2$ is particularly important for two reasons. Firstly doping is achieved without introducing any new elements, and secondly the average Mn oxidation state is raised with increasing lithium content according to the substitution mechanism $3\text{Mn}^{3+} \rightarrow 1\text{Li}^+ + 2\text{Mn}^{4+}$. On extracting lithium from $\text{Li}(\text{Mn}_{1-y}\text{Li}_y)\text{O}_2$ some Li will remain in the structure when all the Mn has been oxidised to Mn^{4+} . It is widely acknowledged that Mn^{4+} may not be further oxidised in an octahedral oxygen environment, implying that the maximum amount of lithium that may be removed is limited. However, this is not necessarily the case. Li_2MnO_3 is a layered compound and the formula may be written as $\text{Li}(\text{Mn}_{2/3}\text{Li}_{1/3})\text{O}_2$. Indeed it corresponds to $y = 1/3$ in the solid solution series under consideration here. We have shown recently that despite the fact that this material is already in the Mn^{4+} oxidation state, 309 mAhg^{-1} charge may be removed from the material corresponding to the removal of 1.39 Li ions per formula unit [4]. This is accompanied by replacement of the Li^+ by H^+ generated by oxidation of the electrolyte solution. This process is partially reversible on discharge. It has also been suggested that other Mn^{4+} materials can exhibit Li removal in which the charge is balanced by the removal of O^{2-} (the effective removal of Li_2O). The possibility of removing more charge from lithium manganese oxide compounds than anticipated based on a maximum oxidation state of Mn^{4+} and especially the mechanism by which this may occur, has important implications for the use of these materials in rechargeable lithium batteries.

Electrochemical cells containing the layered compounds $\text{Li}_x(\text{Mn}_{1-y}\text{Li}_y)\text{O}_2$ with lithium doping levels $y = 0.025, 0.05, 0.1$ and 0.2 and $x \sim 0.67$ were charged and then discharged at 25 mA g^{-1} and 30°C . The resulting charge-discharge curves are shown in Fig 1. There are two distinct regions of the charge curve; an initial rise in potential and a plateau at approximately 4.6 V. With increased lithium doping, the rising portion of the charge curve is reduced at the expense of an increasing capacity associated with the plateau. Chemical analysis at the end of the the first reaction confirms this involves a conventional de-intercalation mechanism in which Li^+ ions are removed with the simultaneous extraction of e^- .

Fig 1 shows that substantial charge may be removed beyond the point at which all Mn is Mn^{4+} . To explain this we have analysed the composition of electrodes the end of charge for the 10 and 20% Li doped materials. We have confirmed that lithium continues to be removed from the materials as they are charged through the plateau regions at 4.6 V. XPS measurements confirm that Mn remains in the +4 oxidation state. Thus the additional charge capacity associated with the plateau is not a conventional de-intercalation process.

In Li_2MnO_3 the dominant mechanism of lithium loss was associated with proton exchange. Electrolyte oxidation at 4.6 V generating H^+ ions which exchanged for Li^+ in the manganese oxide. To examine if the same mechanism operated here, 10 and 20% lithium doped materials were charged to the end of the plateau region then subjected to thermogravimetric analysis combined with mass spectrometry, permitting identification of the species evolved during heating. In the fully charged materials there is evidence for excess proton contents compared with the electrodes maintained at open circuit. However these proton contents are too low to suggest that all the removal of lithium is associated with proton exchange.

Results will be presented describing the processes associated with Li removal including conventional and unconventional mechanisms in these remarkable materials.

REFERENCES

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