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The origin of electrochemical activity in Li_2MnO_3

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The electrochemical activity of Li_2MnO_3 in non-aqueous media has been investigated and found to involve neither Mn^{4+}-Mn^{5+} oxidation nor simultaneous O^{2-} removal but exchange of Li^+ by H^+, the latter being generated in the electrolyte.

Intensive effort has been devoted to the investigation of lithium manganese oxides as positive electrodes for rechargeable lithium batteries because of their low cost, low toxicity and superior safety, compared with the currently used lithium intercalation compound $LiCoO_2$.[1] Attention has focussed on $LiMn_2O_4$ spinel, orthorhombic and layered $LiMnO_2$.[1–7] On charging cells containing these materials as positive electrodes, Li^+ deintercalation occurs and is accompanied by oxidation of Mn^{3+} to Mn^{4+}. Most authors have suggested that it is impossible to oxidise Mn^{4+} to Mn^{5+} in an octahedral oxygen environment.[7] However, it has been claimed such oxidation can occur, for example in the Li-Mn^{4+}-oxide, Li_2MnO_3.[8] An alternative mechanism proposed for the electrochemical extraction of Li^+ from oxides containing Mn^{4+}, without invoking Mn^{4+} oxidation, involves the simultaneous removal of O^{2-}.[9,10] As well as being of fundamental interest to manganese oxide chemistry, the possibility of oxidation in Li-Mn^{4+}-oxides is important in the context of rechargeable lithium batteries as it would lead to higher voltages or provide additional lithium, than is otherwise possible, on the first charge. Understanding the processes which occur on electrochemically charging (oxidising) then discharging (reducing) lithium-Mn^{4+}-oxides is therefore of considerable importance.

We have elected to study Li_2MnO_3.[11] It has the advantage of containing only Li, Mn^{4+} and O and is therefore free from complications that might arise in mixed transition metal oxides. Furthermore, being a layered compound, $Li[Li_{1/3}Mn_{2/3}]O_2$, the Li^+ ions are mobile in the alkali metal layers so that their removal is limited only by other factors *e.g.* the ease of oxidising tetravalent Mn.

Li_2MnO_3 was prepared by solid state reaction between Li_2CO_3 and $MnCO_3$ at 500 °C for 40 h in air. X-Ray powder diffraction was carried out using a Stoe STADI/P diffractometer operating in transmission mode. Chemical analysis for Li and Mn were conducted by flame emission and AAS, respectively. Average Mn oxidation states were determined by XPS measurements carried out on pristine, charged and discharged Li_2MnO_3 electrodes. Binding energies were charge corrected using the C_{1s} peak (284.4 eV). Thermal analysis was carried out at a heating rate of 5 °C min^{-1} under Argon using a Netzch STA 449 Jupiter combined TGA/MS instrument. Electrochemical measurements were conducted on pressed pellets made by dry mixing active material (50 mg) and graphite (79 : 21 w/w), then pressing. The electrochemistry of Li_2MnO_3 electrodes was investigated using two electrode cells comprising: Li_2MnO_3 working electrode and Li metal counter electrode and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1 : 1 V/V, Merck) non-aqueous electrolyte.

Variation of the cell voltage (Li_2MnO_3 *versus* Li^+ (1M)/Li) as charge was removed from the cell then reinserted is shown in Fig. 1. It is evident that significant charge may be removed from (320 $mAhg^{-1}$ at 55 °C) and reinserted (180 $mAhg^{-1}$ at 55 °C) into the cell. The lithium manganese oxide electrodes at the end of charge and discharge were removed from the cell and subjected to XPS analysis which revealed that Mn remained 4+ throughout ($Mn2p^{3/2}$ binding energies for as-cast, charged and discharged samples were 642.7, 642.4 and 642.4 eV, respectively). These data indicate that the electrochemical process is not simply one of removal and reinsertion of Li^+ and e^-, *i.e.* Li_2MnO_3 is not acting as a conventional intercalation compound. The flat potential profile on charging could be consistent with oxidation of the electrolyte. However, the electrode is not inert during the electrochemical process since it is only possible to insert approximately 3 $mAhg^{-1}$ of charge into a fresh electrode, whereas significant charge may be inserted after charging the cell, as demonstrated by Fig. 1. The above observations indicate that the electrode is not merely acting as a source and sink of electrons, instead, electrochemical reaction may involve active participation by both the electrode and electrolyte.

To understand the electrochemical reaction in more detail we chose to characterise the composition and structure of the electrode on charge and discharge at 55 °C, as significantly greater charge can be removed and reinserted under these conditions. Chemical analysis carried out on electrodes at the end of charge and discharge revealed Li/Mn ratios of 0.62 and 1.28 respectively. These compositions are in good agreement with theoretical values derived from the amount of charge extracted from (309 mA hg^{-1}) and reinserted into (125 mA hg^{-1}) the cells, corresponding to respective Li/Mn ratios of 0.65 and 1.20, Table 1. The results indicate clearly that Li is indeed removed and reinserted on charge and discharge but from the XPS results we know this is not associated with oxidation/reduction of Mn^{4+}. The invariance of the Mn oxidation state on charge was further confirmed by carrying out the process chemically using NO_2BF_4 as oxidant in the battery electrolyte. This was done in order to provide enough material for a reliable estimate of the oxidation state by redox titration using ferrous ammonium sulfate/$KMnO_4$ whilst maintaining the same condi-

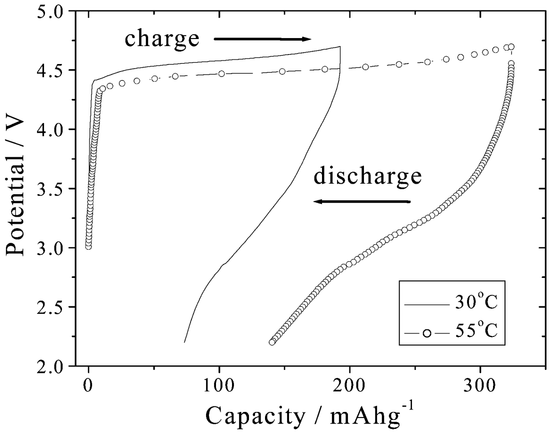

Fig. 1 Variation of the cell potential (Li_2MnO_3 *vs.* Li^+(1M)/Li) on first charging then discharging the cell at 10 mA g^{-1} and at two different temperatures.

Table 1 Analysis of delithiated then relithiated materials (flame emission, atomic absorption, XPS, TGA/MS)

Sample	Calculated Li : Mn ratio	Theoretical Li : Mn ratio	Calculated H	Bulk composition
1st charge 55 °C	$Li_{0.62}Mn$	$Li_{0.65}Mn$	$H_{1.29}$	$Li_{0.62}H_{1.29}MnO_{2.95}$
1st discharge 55 °C	$Li_{1.28}Mn$	$Li_{1.20}Mn$	$H_{0.66}$	$Li_{1.28}H_{0.66}MnO_{2.97}$

tions, as far as possible, as in the electrochemical oxidation. The result yielded a Mn oxidation state of +4.03. Combined TGA/MS measurements were carried out on the materials generated electrochemically and indicated substantial evolution of H_2O from charged and discharged material. An uncharged electrode yielded a negligible H_2O loss of 1.01 wt% of the active material, whereas after charging this rose to 10.70 wt% then fell to 5.31 wt% after subsequent discharge. The samples were transferred to the TGA without exposure to air. Furthermore, solid state ^1H NMR measurements, using a Varian Infinity Plus Spectrometer confirmed the presence of protons in the materials at the end of charge. Combining the results of the chemical analysis and TGA/MS allowed formulae for the compounds at the end of oxidation and subsequent reduction to be derived, Table 1. The oxygen content was calculated from the oxidation states of the cations plus the quantity of O associated with the H_2O *i.e.* $Li_xMn_yO_{x/2+2y}.zH_2O$.

Early studies of Li_2MnO_3 in aqueous acid (H_2SO_4) suggested that the predominant process was extraction of Li accompanied by removal of oxygen *i.e.* the effective loss of Li_2O.[12] However, subsequent studies by Tang *et al.* showed that the dominant process was exchange of Li^+ by H^+ at low proton concentrations, whereas oxygen loss accompanied exchange at high H^+ concentrations.[13] Their work was under hydrothermal conditions, however. Ion exchange, rather than oxygen loss, has also been shown to occur in other Li-Mn^{4+}-O compounds *e.g.* $Li_4Mn_5O_{12}$ when reacted with aqueous acids.[14] The studies reported here were carried out in an anhydrous environment using non-aqueous electrolytes. It is well known that fluorinated anions such as PF_6^- are notorious for the generation of some HF in the presence of even a small amount of the H_2O. Also pertinent to this paper are the results of Tarascon's group who showed, as part of a study concerning the stability of manganese spinels at elevated temperatures, that alkyl carbonates can also be oxidised to generate H^+.[15]

The basic elements of the electrochemical reaction involving Li_2MnO_3 in the PF_6-based non-aqueous electrolyte may now be considered. When charging, oxidation of the electrolyte generates H^+ at the electrode surface with the H^+ ions exchanging for Li^+ within the electrode. Now, both lithium ions and protons exist within the manganese oxide framework of the electrode. It has been shown that ethylene carbonate and dimethyl carbonate may be oxidised at the potentials used here. Oxidation initiates at the carbonyl group and can lead to expulsion of H^+.[16] Cyclic carbonates such as ethylene carbonate are more reactive than their linear analogues. Oxidation of electrolyte also supplies electrons to the external circuit. On discharge, electrochemical reduction within the electrolyte consumes H^+ thus driving its extraction from the electrode and its replacement by Li^+. The small deficiency (<1.7 mole%) in oxygen content, Table 1, could indicate some O loss, however, the value is too small to be taken as proof of such loss, at least at 55 °C.

A powder X-ray diffraction pattern for the charged electrode is shown in Fig. 2. Although a significant proportion of the material continues to exhibit the structure of the as-prepared compound, several additional peaks are observed. These agree well with additional peaks reported previously for Li_2MnO_3 delithiated using aqueous acid.[17] Given the presence of protons in the charged material we examined the possibility that these peaks could be related to the structure of a hydroxide or oxyhydroxide. The additional peaks, although limited in number, could be indexed on a unit cell based on the CrOOH structure.[18] This compound has a *P*3 structure where the oxide layers are stacked in an ABBCCA sequence and the transition metal ions are located between the A and B layers in the octahedral sites and the protons located between adjacent B layers. The driving force for adopting this stacking sequence is the presence of hydrogen bonding in the inter-layer space.

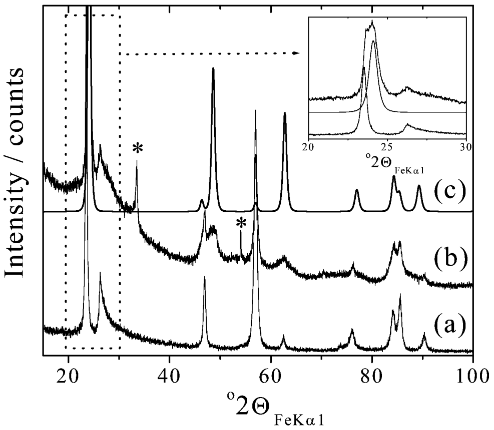

Fig. 2 Powder X-ray diffraction data for (a) as-synthesised Li_2MnO_3; (b) Li_2MnO_3-based electrode after electrochemical extraction of 1.35 Li at 55 °C and (c) simulated *P*3 pattern for a delithiated sample, space group *R*3*m*, $a = 2.885$ Å, $c = 13.91$ Å. Note * = graphite in (b).

In summary, Li-Mn^{4+}-oxides are electrochemically active but oxidation of Mn^{4+} to Mn^{5+}, as suggested previously, does not occur. Also, the dominant mechanism charge compensating Li^+ removal is not loss of O^{2-}. Instead, and despite the anhydrous nature of the electrode and electrolyte, the primary process involves exchange of Li^+ by H^+, the latter being generated in the electrolyte. PGB is indebted to the Royal Society and EPSRC for financial support.

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