Spectral, magnetic and electrochemical studies of layered manganese oxides with P2 and O2 structure

K. M. Shaju, a K. V. Ramanujachary, b S. E. Lofland, b G. V. Subba Rao a and B. V. R. Chowdari a

a Department of Physics, National University of Singapore, Singapore 119260
b Department of Physics and Chemistry, Rowan University, New Jersey 08028-1701, USA

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X-Ray photoelectron spectroscopy (XPS), infrared spectroscopy and magnetic susceptibility studies were performed on layered O2-phase compounds, Li2/3(Ni1/3Mn2/3)O2, Li(2/3)1−x(Ni1/3Mn2/3)O2, Li2/3(Co0.15Mn0.85)O2 and Li(2/3)1−x(Co0.15Mn0.85)O2 and their respective P2 phases, Na2/3(Ni1/3Mn2/3)O2 and Na2/3(Co0.15Mn0.85)O2. The observed electrochemical performance was correlated with the oxidation states of the M ions (M ~ Mn, Ni, Co). Li2/3(Ni1/3Mn2/3)O2 and Li(2/3)1−x(Co0.15Mn0.85)O2 show significant improvement in their first-charge capacity over Li2/3(Ni1/3Mn2/3)O2 and Na2/3(Co0.15Mn0.85)O2 when used as cathodes vs Li. Chemical analysis and XPS data indicate that the incorporation of x ~ 1/3 in the above two compounds is accompanied by the reduction of a corresponding amount of Mn4+ to Mn3+ ions in the lattice. The magnetic moments obtained in the paramagnetic region are in fair agreement with the oxidation state of the ions derived from the XPS data for the Ni-system but show deviations for the Co-system. Below 100 K, weak ferrimagnetic ordering is observed in Li2/3(Ni1/3Mn2/3)O2 and Li(2/3)1−x(Co0.15Mn0.85)O2.

1 Introduction

Mixed manganese oxides A,.(M,Mn1−,y)O2 (M = Co, Ni, Li; A = Na, Ni; x ≤ 1; y = 0–1.0) are of interest as positive electrodes in Li-ion batteries (LIB). They can adopt different types of layered structure, the so called P2, P3, T2, O2 and O3 structures. The terminology is based on the metal–oxygen stacking sequence and the oxygen coordination of the A ion (P: trigonal prismatic, T: tetrahedral and O: octahedral) and by the number of (M,Mn)O2 sheets (2 or 3) per unit cell.1–4 The [110] projections of some of the above structures are shown in Fig. 1. As can be seen, each MO2 layer in the O2-phase is mirrored and its oxygen stacking sequence necessitates breaking and rearrangement of M–O (M ~ Ni, Co, Mn) bonds to convert it to the O3 or spinel structure. Thus O2–O3 conversion does not occur under ‘soft’ chemistry or electrochemical charge–discharge cycling. The oxide cathode, LiCo3O2 used in the LIB and LiNi3O2 and its derivatives, Li(Ni1−xMx)O2 (M = Co, Cr, Mn) are O3-type.5–9 The O3 structure is rhombohedral–hexagonal (α–NaFeO2 type) with ordered Li and M layers.
in a fcc close-packed oxygen lattice. It is related to the spinel structure (LiMnO₄) in which Li and Mn ions respectively occupy the tetrahedral and octahedral holes in an fcc oxygen lattice. The O₃ LiMn²⁺O₄ transforms to LiMnO₂ (Li₂O₃:LiO₂) during the charging operation as the cathode, where the Li ions move from octahedral oxygen to tetrahedral coordination.³⁻¹²

The O₂ Liₓ₂(MₓMn₁₋ₓ)O₂ (M = Co, Ni, Li; y = ½–½) compounds have been recently studied by Dahn and his coworkers³⁻¹³⁻¹⁶ as prospective cathodes for LIB. The O₂ compounds are obtained by Na to Li ion exchange of the corresponding P₂ phases, Na₂ₓ(MₓMn₁₋ₓ)O₂, which can be prepared by a high-temperature solid-state reaction. The P₂-to-O₂ (and P₃-to-O₃) structure conversion involves only minor sliding of the MO₂ sheets with respect to one another in the layer structure (Fig. 1) and occurs during the ion-exchange process. The O₂-phase compounds, Liₓ₂(Ni₁/₃Mn₂/₃)O₂ and Liₓ₂(Co₀.₁₅Mn₀.₈₅)O₂, have received more attention due to their easy synthesis and interesting electrochemical behaviour.

We have incorporated extra lithium (x ≥ ½) to obtain O₂ Liₓ₂(MₓMn₁₋ₓ)O₂ (x = ½–½) and Liₓ₂(Co₀.₁₅Mn₀.₈₅)O₂ (x ≥ ½), using LiI during the ion-exchange process. Electrochemical studies have shown that they have a high first-charge capacity together with reversible and stable cycling performance as cathodes vs. the Li anode at ambient temperature (25 °C) and at 50 °C.⁷⁻¹⁷ Here, we report the physical properties of these oxide cathodes and make correlations with the observed electrochemical behaviour.

### 2 Experimental

The precursor compounds, Naₓ₂(MₓNi₁₋ₓ)O₂ and Naₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂, were synthesized by high-temperature (900–1000 °C) solid-state reactions as described elsewhere.⁴⁻¹⁷⁻¹⁹ Stoichiometric amounts of high purity (Alfa, USA) alkali carbonates, NiO/CₐO₂ and MnO₂ powders were used. Ion exchange of sodium (Na) for lithium (Li) was done using a melt of a eutectic mixture of LiNO₃ and LiCl (88 : 12 mol%) and a fresh batch of the precursors as reported elsewhere.¹⁷⁻¹⁹ The compounds were characterized by powder X-ray diffraction (Siemens D5005; Cu-Kα radiation).

Chemical analysis for Na, Li, Ni, Co and Mn in the compounds was done by inductively coupled plasma spectroscopic analysis. The infrared (IR) spectra in the range 400–4000 cm⁻¹ were recorded with a Bruker Equinox 55 Fourier-transform infrared (FTIR) spectrometer. Samples were mixed with KBr and pressed to form transparent pellets for measurement. X-ray photoelectron spectra (XPS) were obtained with a VG Scientific ESCA MK II spectrometer with monochromatic Mg-Kα radiation (hv = 1253.6 eV). The survey spectra in the range 0–1099 eV (constant-pass energy = 50 eV) and high-resolution spectra (constant-pass energy = 20 eV) were recorded. Charge referencing was made against the binding energy (BE) of adventitious carbon (C 1s = 284.6 eV). The spectra were analyzed with the XPS peak fit software. A Shirley-type background was subtracted from the recorded spectra and curve fitting of the peaks was done by non-linear least-squares fitting with a Gaussian–Lorentzian (ratio 60 : 40) curve. The BEs are accurate to ±0.1 eV. The magnetic susceptibility studies were performed on powders in the range 5 K < T < 300 K with a Physical Property Measurement System (Quantum Design, USA) at a field of 0.1 Tesla. Field-dependent magnetization measurements on selected samples were done at 5 K in fields of up to 9 Tesla. For the electrochemical measurements, coin cells (size, 1632) were assembled in an argon-filled glove box at <1 ppm of H₂O and O₂ (MBraun, Germany), with 1 M LiPF₆ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1 : 1 volume, Merck, Selectipur LP40) as the electrolyte and a Celgard 2502 membrane as separator. Li-metal foil (Kyoruto Metal Co., Japan) was used as the anode. Details of fabrication have been described elsewhere.¹⁷⁻¹⁹ Charge-discharge cycling and cyclic voltammetry tests at ambient temperature were carried out with a potentiotstat/galvanostat system (Mac-pile II, Bio-logic, France) and Bitrode multiple battery tester (Model SCN, Bitrode, USA).

### 3 Results and discussion

#### 3.1 Composition and structure

The precursor compounds, Naₓ₂(MₓNi₁₋ₓ)O₂, Naₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂ and their Li-ion-exchanged counterparts, Liₓ₂(MₓNi₁₋ₓ)O₂, Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂ are black whereas the respective excess Li-incorporated compounds, Liₓ₂(MₓNi₁₋ₓ)O₂ and Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂ are light brown in color and are stable in air. The X-ray diffraction results for the compounds Naₓ₂(MₓNi₁₋ₓ)O₂, Liₓ₂(MₓNi₁₋ₓ)O₂ and Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂ and Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂ revealed that the Na-to-Li ion exchange was incomplete and a small fraction (3–5%) of the parent phase remained in both Liₓ₂(MₓNi₁₋ₓ)O₂ and Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂. Paulsen et al.¹¹ also reported similar behavior for Liₓ₂(MₓNi₁₋ₓ)O₂. The Liₓ₂(MₓNi₁₋ₓ)O₂ phases adopt the O₂-structure with hexagonal symmetry.¹⁴⁻¹⁷⁻¹⁸ Complete Na-to-Li ion exchange was observed in Liₓ₂(MₓNi₁₋ₓ)O₂ and Liₓ₂(MₓNi₁₋ₓ)O₂ with the latter compounds crystallizing in the orthorhombic T₂-structure.⁴⁻¹⁷⁻¹⁸ Chemical analysis results for the compounds were in agreement with expected stoichiometry taking into account a ±5–8% uncertainty in determining the Na and Li content, and a ±2–4% uncertainty in the analysis of Ni, Mn and Co. Oxygen content was not analyzed and was assumed to be 2.0. Chemical analysis analysis also confirmed that the Li content is close to 1.0 (x ~ ½) in Liₓ₂(MₓNi₁₋ₓ)O₂ and Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂.

#### XPS binding energies/eV

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<th>Compound formula</th>
<th>Mn 2p½</th>
<th>Ni 2p½</th>
<th>Co 2p½</th>
<th>Mn 3p</th>
<th>Li 1s</th>
<th>O 1s</th>
<th>Weiss temperature, θ/K</th>
<th>Measured moment, µemu/cm²</th>
<th>Calculated moment a, µemu/cm²</th>
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<td>Naₓ₂(MₓNi₁₋ₓ)O₂</td>
<td></td>
<td></td>
<td></td>
<td>641.3</td>
<td>643.2</td>
<td>854.2</td>
<td>856.1</td>
<td>529.0</td>
<td>530.8</td>
</tr>
<tr>
<td>Liₓ₂(MₓNi₁₋ₓ)O₂</td>
<td>641.5</td>
<td>642.4</td>
<td>854.5</td>
<td>856.4</td>
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<td>49.7</td>
<td>54.1</td>
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<td>531.2</td>
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<td>Liₓ₂(MₓNi₁₋ₓ)O₂</td>
<td>641.8</td>
<td>643.1</td>
<td>854.4</td>
<td>856.1</td>
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<td>50.0</td>
<td>54.3</td>
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<tr>
<td>Naₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂</td>
<td>641.7</td>
<td>643.5</td>
<td>779.3</td>
<td>779.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>529.3</td>
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<td>Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂</td>
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<tr>
<td>Liₓ₂(MₓCo₀.₁₅Mn₀.₈₅)O₂</td>
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<td>643.2</td>
<td>780.0</td>
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<td>54.1</td>
<td>529.4</td>
<td>531.3</td>
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</tr>
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</table>

a: Assuming low-spin configuration for Ni²⁺ and Co³⁺ ions. Values in brackets are calculated as per ion equilibrium (see text).

Li_{2/3+y}(Co_{1/3}Mn_{2/3})O_2 (Co(Li)), Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2 (Ni(Li)) and Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2 (Ni(Li)) have been discussed in detail elsewhere. As mentioned therein, Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Co_{1/3}Mn_{2/3})O_2 have been found to have enhanced first-extraction capacity thereby making them suitable as cathodes in LIB. Studies on Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Co_{1/3}Mn_{2/3})O_2 revealed that extra Li incorporation also occurs by electrochemical means during the first-discharge process, 3,4,13,17-20 The process is accompanied by the reduction of a corresponding amount of Mn^{3+} to Mn^{4+} ions in the compounds. The first-extraction capacity of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 (190 mA h g⁻¹) is nearly a two-fold improvement over that of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 (108 mA h g⁻¹) as shown in Fig. 2a. This is due to the fact that only 1/3 of Ni^{3+} can be oxidized to Ni^{4+} in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 and Mn^{3+} ions are inactive above 4.0 V vs Li, whereas in the case of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 an additional 1/e mole extraction of Li is possible due to the oxidation of Mn^{3+} in the lattice. The reversible capacity and capacity retention of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 on cycling at 25 °C and 50 °C (at 15 mA g⁻¹; 2.5-4.6 V) was shown to be much better than that of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2, 17,18 Further, qualitative change in the charge–discharge profile was noticed in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 which delivers its total cationic capacity mostly above 3 V whereas Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 delivers its capacity between 2.5-4.6 V in two discrete stages: ~50% capacity between 4-3.5 V (Ni^{3+}/4 + redox) and ~50% between 3.0-2.5 V (Mn^{3+}/4 + redox). Cyclic voltammetry also showed qualitative and quantitative differences in the redox behavior of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2.

Similarly, Li_{2/3+y}(Co_{1/3}Mn_{2/3})O_2 shows an improved first-extraction capacity (250 mA h g⁻¹; 5 mA h g⁻¹; 2.5-4.6 V vs Li) as compared to 150 mA h g⁻¹ for Li_{2/3}(Co_{1/3}Mn_{2/3})O_2 and a reversible capacity of ~180 mA h g⁻¹ is observed (Fig. 2b).

The value of the first-extraction-capacity obtained at low current charging is in accord with the stoichiometry of the compound (150 mA h g⁻¹ corresponding to ~0.5 Li and 250 mA h g⁻¹ corresponding to 0.85 Li), and the Co ion is assumed to be electrochemically inactive in the voltage region.

3.3 XPS of A_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 and A_{2/3+y}(Co_{1/3}Mn_{2/3})O_2: A = Li, Na; x = 0, 1

XPS is a useful non-destructive technique for studying the chemical state of elements, particularly the non-equivalence of atoms resulting from differences in formal oxidation state, ionic environment and lattice site in a compound. 21 A change in the chemical environment and oxidation state of an element can cause small changes in its BE and this has been used for assignment of the oxidation states of elements in oxide cathodes. 22-30

Fig. 3 shows the Mn 2p3/2 and Ni 2p3/2 XPS core level spectra for Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2, Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2. The Mn ions in Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2 are supposed to be in the 4+ oxidation state as per the electrochemical results and stoichiometry. 4,17,18 However, curve fitting of the spectra of the above two compounds gives two peaks. Comparing the BEs with the values reported for different Mn-containing compounds, 7,19,22-26 the intense peak centered at 642–643 eV corresponds to Mn^{4+} and the other peak at 641–642 eV corresponds to Mn^{3+} (Table 1 and Figs. 3a and b). The Mn 2p 3/2 spectra of Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 can also be fitted to two peaks with nearly equal intensities (Fig. 3c). The peak at 643.1 eV can be assigned to Mn^{3+} and the one at 641.8 eV to Mn^{4+}. The slightly higher BEs observed for Mn^{3+} and Mn^{4+} ions in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 could be due to stronger Mn-O bonds as evidenced from the smaller c-lattice parameter (9.91 Å in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 vs. 10.06 Å in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2) and/or due to a change in the chemical environment of the Mn ions due to the extra Li (x = 1) in the lattice.

The Ni 2p3/2 XPS spectra show characteristic satellite peaks with a BE of ~861 eV (Fig. 3d-f). Such satellite peaks are the result of multiple splitting in the energy levels of Ni ions in oxides. 7,27,28,31 The curve fitting for the Ni 2p3/2 spectra of Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2, Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 gives two BE values in each case. The high intensity peaks correspond to a BE of ~854 eV which are attributed to Ni^{3+} ions and the less prominent peak at ~856 eV corresponds to Ni^{4+} ions (Table 1). The BE value for Ni^{4+} is slightly higher (by 0.5 eV) than that reported for other Ni oxides. 7,27,28,30 This could be due to the P2 and O2 structures adopted by the compounds described herein.

Thus, the XPS results show that the predominant oxidation states of Ni and Mn ions in Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2 and Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 are 2+ and 4+ respectively, and to a first approximation, the chemical formula can be written as shown in Table 1. The minor contribution of Ni^{3+} and Mn^{4+} is due to dynamic electron exchange between the Mn^{4+} and Ni^{3+} ions, and from the relative peak intensities, rough estimates give the Mn^{3+}/Ni^{3+} content as 10–12% in both the above compounds. It may be mentioned that a similar dynamic ion equilibrium, Ni^{4+} + Co^{3+} ↔ Ni^{3+} + Co^{4+} was reported in layered O3 Li(Ni_{0.15}Co_{0.85})O_2 at x ~ 0.732 and Fe^{3+} + Ni^{4+} ↔ Fe^{4+} + Ni^{3+} in O3 Li(Ni_{0.48}Fe_{0.52})O_2, (x ~ 0.9). 33

A rough estimate based on the relative intensities of the oxidation states of Mn in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 from the XPS data (Fig. 3c) yields 56% Mn^{4+} and 44% Mn^{3+}. This compares well with the 50 : 50 ratio expected from the chemical formula, considering the fact that contribution from Mn^{3+} is enhanced in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 due to the ion equilibrium (Figs. 3c and f). The amount of Ni^{4+} changed only slightly, from ~12% in Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2 to ~15% for Li_{2/3+y}(Ni_{1/3}Mn_{2/3})O_2. This shows that incorporation of extra lithium is facilitated by
the reduction of Mn4+ to Mn3+ in Li2/3(Ni1/3Mn2/3)O2. It is worth mentioning that the higher cathodic first-extraction capacity observed in Li2/3(Ni1/3Mn2/3)O2 as compared to Li2/3(Ni1/3Mn2/3)O2 can be easily accounted for by the presence of more Mn3+ ions in the Li2/3(Ni1/3Mn2/3)O2.

The Li 1s spectra are associated with the intense Mn 3p spectra in the 45–57 eV region (Fig. 4). Fitting of the Li 1s spectra gives a BE of 54.1 eV for Li2/3(Ni1/3Mn2/3)O2 and 54.3 eV for Li2/3(Ni1/3Mn2/3)O2; these values are in good agreement with the values reported in similar Li–oxide cathode materials.7,19,22,29,30 Similar to the Mn 2p3/2 spectra, the Mn 3p spectra are also asymmetric and can be fitted to two peaks, assigned to Mn3+ and Mn4+, as shown in Fig. 4 and Table 1.

The overlapping O 1s spectra commonly observed in oxide cathodes are a resultant contribution arising from Li-oxide and other (Li2CO3, LiOH) impurities on the surface in addition to the parent oxide.7,19,22,29,30 The O 1s spectra of Na2/3(Ni1/3Mn2/3)O2, Li2/3(Ni1/3Mn2/3)O2 and Li(2/3)x(Ni1/3Mn2/3)O2 are shown in Fig. 5 and the BEs are given in Table 1. Similar to the assignments made for Li(Ni1/2Mn1/2)O2 and Li(Ni1/3Co1/3–Mn1/3)O2, the peaks at ~529 eV are assigned to oxygen linked as Mn–O and those at ~310 eV together with contributions from the Li-compound impurities.

The XPS spectra of Na2/3(Co0.15Mn0.85)O2, Li2/3(Co0.15Mn0.85)O2 and Li(2/3)x(Co0.15Mn0.85)O2 have been reported recently,19 and the BEs of the Mn3+, Mn4+ and Co3+ ions are given in Table 1. The Co 2p3/2 spectra for all the above compounds fit to a single peak with a BE of 780.0 ± 0.2 eV (Table 1). This value matches well the BE reported for Co3+ in LiCoO2 and in Li(Ni1/3Co1/3–Mn1/3)O2, the peaks at ~529 eV are assigned to oxygen linked as Mn–O and those at ~531 eV to oxygen linked as Ni–O together with contributions from the Li-compound impurities.

The XPS spectra of Na2/3(Co0.15Mn0.85)O2, Li2/3(Co0.15Mn0.85)O2 and Li(2/3)x(Co0.15Mn0.85)O2 have been reported recently,19 and the BEs of the Mn3+, Mn4+ and Co3+ ions are given in Table 1. We re-analyzed the XPS data for 526–534 eV (O 1s) and 46–56 eV (Li 1s, Mn 3p). The Co 2p3/2 spectra for all the above compounds fit to a single peak with a BE of 780.0 ± 0.2 eV (Table 1). This value matches well the BE reported for Co3+ in LiCoO2 and in Li(Ni1/3Co1/3–Mn1/3)O2, and is in agreement with the observation that Co in oxide cathodes adopts the 3+ oxidation state irrespective of the structure.12,35 As can be seen from Table 1, the BE values for Mn3+ and Mn4+ in the Co-system and the respective values for the Ni-system compare well. The Li 1s spectra are associated with the Mn 3p signal in the 46–56 eV region in Li2/3(Co0.15Mn0.85)O2 and Li(2/3)x(Co0.15Mn0.85)O2 (Fig. 6). The Li 1s BEs (Table 1) are in accord with those reported for similar Li–M–oxides.7,19,22,29,30 The Mn 3p spectrum of Li2/3(Co0.15Mn0.85)O2 fits to a single peak indicating the presence of Mn3+.
only Mn$^{3+}$ ions whereas for Li$_{2/3}$(Co$_{0.15}$Mn$_{0.85}$)O$_2$, the asymmetric peak can be fitted to two peaks (Fig. 6), assigned to Mn$^{3+}$ and Mn$^{4+}$ ions as shown in Table 1. Fitting to the O 1s spectra (Fig. 7) show that two species contribute to these spectra. Following the arguments made earlier, peaks at ~529 eV can be assigned to oxygen linked as Mn−O in the compounds and those at ~531 eV have contributions from both Co−O linking and Li compound impurities.

3.4 FTIR spectra

The FTIR spectra of Na$_{2/3}$(Ni$_{1/3}$Mn$_{2/3}$)O$_2$, Li$_{2/3}$(Ni$_{1/3}$Mn$_{2/3}$)O$_2$ and Li$_{2/3}$+(Ni$_{1/3}$Mn$_{2/3}$)O$_2$ compounds along with those of the manganese spinel, LiMn$_2$O$_4$ and O$_3$ Li(Co$_{0.1}$Mn$_{0.9}$)O$_2$ (synthesized as described elsewhere$^{19,36}$) are shown in Fig. 8. The IR
spectra of the corresponding Co system of compounds have been reported earlier.\textsuperscript{19} The band positions are accurate to $\pm$ 3 cm\textsuperscript{-1}. It is clear that the IR spectra of the layered compounds are distinctly different from that of the spinel, which shows two symmetric bands centered at 521 and 617 cm\textsuperscript{-1}, reflecting the high local symmetry of the cubic structure.\textsuperscript{37,38} In the layered oxides, $\text{Li}_3\text{MO}_2$ ($\text{M} = \text{Co, Ni}$) there are three IR active modes in the range 400–800 cm\textsuperscript{-1}, assigned to the stretching and bending vibrations of $\text{MO}_6$ octahedra.\textsuperscript{8,19,39,40} In $\text{LiCoO}_2$ these bands are seen at 420, 540 and 600 cm\textsuperscript{-1}. A broad shoulder at 650 cm\textsuperscript{-1} is also observed. The spectrum of the P2 \textsuperscript{1} [$\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$] is similar to that reported for other layered oxides, with bands at around 440, 513 and 640 cm\textsuperscript{-1} and one shoulder peak at around 491 cm\textsuperscript{-1}. The positions of the bands in $\text{Li}_2\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ shift to higher frequency compared to those of $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$: the intense peak shifts to 531 cm\textsuperscript{-1}, the shoulder becomes a clear peak at 504 cm\textsuperscript{-1} and the peak at 640 cm\textsuperscript{-1} becomes a broad peak centred at $\sim$665 cm\textsuperscript{-1}. The shifting of the IR bands to higher wave number in $\text{Li}_2\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ is expected from the difference in ionic mass and change in the lattice size. The XRD data show smaller crystallographic lattice parameters for both the compounds are identical. However, minor shifts in the cationic environment in $\text{O}_3\text{LiMO}_2$ phases are expected since the cationic environment in $\text{MO}_2$ phases is $\text{Li}_2\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, $\text{Co}, \text{Ni}$:17,18 and hence an increased bond strength can be expected in the former, in agreement with the IR results.

In the case of $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, the main absorption band is broadened with its center at 529 cm\textsuperscript{-1} and with shoulders at 446 and 665 cm\textsuperscript{-1}. This spectrum is similar to that of $\text{O}_3\text{LiCo}_3\text{O}_2$:19 shown in Fig. 8 for comparison. These similarities in the IR spectral features of O3 and O2 phases are expected since the cationic environment in both the compounds are identical. However, minor shifts in the main band and shoulder peaks are expected since the stacking sequence and orientation of the $\text{MO}_2$ and $\text{LiO}_2$ sheets are different (Fig. 1). Similar behaviour was noted in the IR spectra of $\text{Na}_{2/3}\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$, $\text{Li}_{2/3}\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$ and $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$.\textsuperscript{19}

3.5 Magnetic susceptibility

Magnetic susceptibility studies on oxide cathodes have been reported.\textsuperscript{22,35,41–48} The susceptibility ($\chi$) and $1/\chi$ vs. $T$ plots for the compounds presently being investigated are shown in Fig. 9. The Curie constant ($C$) and Weiss temperature ($\theta$) were obtained by fitting the straight line portion of the $1/\chi(T)$ plots in the paramagnetic region, 180–300 K to the Curie–Weiss law, $\chi = C/(T - \theta)$. The $\theta$ and $\mu_{\text{eff(exp)}}$ values are given in Table 1. Since the measurements were made only up to 300 K, these values are not very accurate though the general trends in the variation are reliable. The calculated $\mu_{\text{eff(cal)}}$ values, where $n_i$ is the molar fraction of the magnetic ion and $\mu_i$ its moment given by $\mu_i = g[S(S_i + 1)]^{1/2}$ where $g = 2$ and $S_i$ is the spin of the magnetic ion, are also given in Table 1. The susceptibility plots are typical of canted antiferromagnetic (AFM) materials: the susceptibility at high temperature has a negative $\theta$ value (AFM correlations) and is accompanied by ferromagnetic-like behavior at low temperature ($<150$ K). Taking into account the information obtained from the XPS data, the chemical formulae of $\text{Li}_2\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ and $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ can respectively be written as $\text{Li}_2\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ (12% each of Ni$^{3+}$ and Mn$^{4+}$) and $\text{Li}_{1/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ (15% Ni$^{3+}$ and 56% Mn$^{4+}$) due to ion equilibria. The respective $\mu_{\text{eff(cal)}}$ values are 3.63$\mu_B$ and 3.97$\mu_B$ assigning Ni$^{3+}$ to the low-spin (LS) state. These are slightly higher than the calculated values using the stoichiometry given in Table 1. As can be seen, there is a reasonable agreement between the $\mu_{\text{eff(cal)}}$ and the $\mu_{\text{eff(exp)}}$ values for the Ni-system of compounds (Table 1). Similar is the case with O2 $\text{Li}_{2/3}\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$ if we assume Co$^{3+}$ to be in the low-spin (LS) state. Other oxide cathodes like LiCoO$_2$, LiNiO$_2$, Li[$\text{Co}_{1-x}\text{Ni}_x$]$^{3+}$O$_2$, Li[Co,Mn]O$_4$, the Ni$^{3+}$ and Co$^{3+}$ ions have been found to be in the LS state.\textsuperscript{5,6,35,44,46,49,50} On the other hand, the P2 Na$_{2/3}$ ($\text{Co}_{1/3}\text{Mn}_{2/3}$)O$_2$ and O2 $\text{Li}_{2/3}\text{Co}_{1/3}\text{Mn}_{2/3}$O$_2$ have markedly lower $\mu_{\text{eff(exp)}}$ values. The reasons for this are not known at present and $\chi$ vs. $T$ data at $T > 300$ K will be helpful in resolving

![Fig. 9 Temperature variation of (a) and (b) the inverse molar susceptibility ($1/\chi$) and (c) and (d) the molar susceptibility ($\chi$) for the P2- and O2-phase compounds.](Image 92x91 to 507x378)
the discrepancy. At $T < 100$ K, all the compounds display magnetic ordering. We can rule out ferromagnetism because at all values of $T$, the magnetization is much smaller than that expected from the alignment of all the spins. Similar ferrimagnetic or canted AFM behaviour has been reported for O3 Li(Ni1-xCo)xO2, $y < 0.2$,46 and for Li(Ni1/3Mn2/3)O2.45

The magnetic ordering in the O3- and O2-type layered compounds containing Mn and Ni ions in the metal layer can arise from uncompensated spins as a result of strong AFM interactions. In these oxides, two types of magnetic interaction exist within the metal layers:46–48 (i) AFM Mn–Mn interactions between overlapping half-filled t2g orbitals across a shared octahedral-site edge where both Mn3+ ($t_2g^6$; high spin (HS)) and Mn4+ ($t_2g^0$; HS) ions participate; (ii) 90° Mn–O–Mn interactions. In the latter case, if both ions are Mn4+, which have empty e_g orbitals, the interaction will be ferromagnetic whereas if one or both the ions are Mn3+, the interaction will be AFM.45,48 In addition, for Ni3+ (or Ni2+) AFM interactions predominate for both direct M–M and M–O–M (M = metal) interactions since these contain electrons in the e_g orbitals. Interlayer exchange also occurs through the 90° M–O–M pathway. This interaction is expected to be weak and AFM but it is pertinent in yielding three-dimensional character to the overall magnetic structure. In the compounds P2Na2/3(Ni1/3Mn2/3)O2 and O2 Li2/3(Ni1/3Mn2/3)O2, magnetic ordering may arise from uncompensated spins via Ni3+-Mn4+ or Ni2+-Mn4+ interactions whereas in Li2/3(Ni1/3Mn2/3)O2, the Mn3+ ions will also participate to a significant extent (Table 1) to give additionally Ni2+-Mn3+-Mn4+ and Mn3+-Mn4+-type interactions. Further, minor amounts of Ni3+(d^6 system; $t_2g^6$; low spin (LS)) and Mn3+(HS) present in Na2/3(Ni1/3Mn2/3)O2 and Li2/3(Ni1/3Mn2/3)O2 can also contribute to magnetic ordering. Ferrimagnetic behavior is evident from the hysteresis observed in the magnetization curve (Fig. 10) taken at 5 K for Li2/3(Ni1/3Mn2/3)O2. This is definitely due to the presence of more Mn3+ in Li2/3(Ni1/3Mn2/3)O2 as compared to that in Li2/3(Ni1/3Mn2/3)O2.

P2Na2/3(Co0.15Mn0.85)O2 and O2 Li2/3(Co0.15Mn0.85)O2 show predominantly AFM interactions with high negative values of $\theta$ (Fig. 9b and Table 1) and no clear magnetic ordering down to 5 K. This may be due to the fact that the Co3+ (d^6 system; $t_2g^6$; LS) is expected to be diamagnetic. Though the Mn3+-Mn4+ interactions are AFM, dilution due to the diamagnetic Co3+ ion must also be considered. Weak ferrimagnetism in Li1.5(Ni0.15Co0.85)O2 is also evident from the hysteresis loop shown in Fig. 10, which shows no magnetic saturation at 5 K. We also note that the $\theta$ value for Na2/3(Co0.15Mn0.85)O2 is lower than that of Li2/3(Co0.15Mn0.85)O2, which is opposite to the trend noted in Na2/3(Ni1/3Mn2/3)O2 and Li2/3(Ni1/3Mn2/3)O2. Compound Li2/3(Ni1/3Mn2/3)O2 shows pronounced ferrimagnetic behavior similar to that of Li2/3(Ni1/3Mn2/3)O2 (Fig. 9b and Table 1). As Li2/3+x(Co15Mn85)O2 has all its Mn ions in the 3+ oxidation state, the large negative $\theta$ in the paramagnetic region is understandable due to the strong Mn3+-Mn4+ and Mn3+-O–Mn4+ AFM interactions. However, the well-defined magnetic ordering below 25 K (Fig. 9b) was not expected. A plausible explanation for the magnetic ordering is the ‘canting’ of the Mn3+ spins below 100 K leading to weak ferrimagnetism. Indeed, a canted-spin ferrimagnetism below 100 K has been observed in the orthohombically distorted layer compound, LiMn3+O2, by Greedan et al.48

4 Conclusions

Layered O2-phase compounds have been prepared from the respective P2-phases with or without LiI treatment during ion exchange. The Li2/3+x(Ni1/3Mn2/3)O2 shows an improved first-charge capacity compared to that of Li2/3(Ni1/3Mn2/3)O2 when used as a cathode vs Li metal in the voltage range, 2.5–4.6 V. Similarly, an increase in the first-charge capacity from 150 mA h g$^{-1}$ in Li2/3(Co15Mn85)O2 to 250 mA h g$^{-1}$ in Li2/3+x(Co15Mn85)O2 occurs. XPS studies have shown that the extra Li ($x \sim 5$) is incorporated by the reduction of a corresponding amount of Mn3+ to Mn4+ ions in Li2/3+x(Ni1/3Mn2/3)O2 and Li2/3+x(Co15Mn85)O2 in agreement with the chemical analysis and electrochemical performance. The XPS BEs of the transition elements, Li and oxygen in the compounds obtained by the fitting of the raw spectra have been discussed. Minor changes in the IR band positions in the P2 and O2 phases as compared to those in the O3-phase are due to differences in the stacking sequences and orientation of the metal–oxygen octahedra. Magnetic susceptibility data show Curie–Weiss behavior at $T > 180$ K and weak ferrimagnetic ordering at $T < 100$ K, especially in Li2/3+x(Ni1/3Mn2/3)O2 and Li2/3+x(Co15Mn85)O2.

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References


Fig. 10 Magnetization vs. magnetic field curves at 5 K for Li2/3+x(Ni1/3–
Mn2/3)O2 (Ni(Li+x)) and L2/3(Co0.15Mn0.85)O2 (Co(Li)).