LiM_{0.5}Mn_{1.5}O_{4-δ} (M = Co or Fe) spinels with a high oxidation state obtained by ultrasound-assisted thermal decomposition of nitrates. Characterization and physicochemical properties


1. Introduction

In recent years, studies on transition metal oxides nanostructures have increased significantly due to their interesting properties as electrocatalysts, supercapacitors, semiconductors, thermistors, etc. [1–3]. Manganese-based spinel compounds have been the most studied because their structural and chemical properties allow them to be used for lithium-ion batteries [4]. In particular, the LiMn_{2}O_{4} spinel-related phase has been extensively investigated as cathode for lithium-ion batteries due to its high energy density, high potential (4 V vs. Li), environmental friendliness and low cost [4]. However, it is well-known that LiMn_{2}O_{4} presents two problems: dissolution of Mn^{2+} ions due to Jahn Teller (J-T) effect (consequence of the presence of Mn^{3+} ions in the structure) and the formation of parasite phases, resulting in energy losses during the charge-discharge cycles [5, 6]. One of the strategies to improve the structural stability of LiMn_{2}O_{4} contemplates the partial substitution of Mn-ions by other divalent or trivalent metal cations at the 16d octahedral sites of the spinel structure aimed at blocking the J-T distortion. Examples of these other phases include LiM_{x}Mn_{2-x}O_{4} (M = Ni, Co, Cr) [6], Li[Ni_{0.5}Co_{0.5}Mn_{1.5}O_{4} [7], LiNi_{0.5}Mn_{1.5}Al_{0.5}O_{4} (M = Cr, Al, Zr) [8], LiMn_{2}M_{0}O_{4} (M = Ni, Fe; x = 0.1 to 0.5) [9]. B. Scrosati et al. [10] studying the oxides of composition LiNi_{0.5}Co_{0.5}Mn_{1.5}O_{4} attributed the increase in their electrochemical performance to the presence of the Mn^{3+}/Mn^{4+} couple brought about by the incorporation of cobalt. Recently, E. Talik and et al. [9] have shown the effect of the metallic substitution in LiMn_{2}M_{0}O_{4} (M = Fe, Ni):
while the substitution by iron increases the Mn$^{3+}$ concentration, the substitution by nickel increases the Mn$^{4+}$ concentration. Apart from that, the electrical transport mechanisms are sensitive to both the nature and occupation factors of the cations at the different sites in the spinel structure [11]. And, finally, it is worth noting that the preparation method conditions the purity, the electronic structure and the physico-chemical properties of the oxides as well as the lithium mobility in the structure.

LiCo$_{0.5}$Mn$_{1.5}$O$_4$ and LiFe$_{0.5}$Mn$_{1.5}$O$_4$ spinels have been synthesized using different methods such as sol-gel [9], ceramic [12], solid state [13] or produced as thin films [14]. Most of these methods are very expensive requiring high calcination temperatures, long synthesis times and complicated procedures. Recently other synthetic routes such as the ultrasound-assisted method (20 kHz - 10 MHz) have been explored in order to obtain nanostructures having low preparation costs and being environmentally acceptable [15,16]. The effect of the ultrasound technique on chemical reactions is based on cavitation, that is, on the creation, growth and implosive collapse of bubbles in the solution. In this method, the ultrasonic irradiation provides very high local temperatures and pressures (about 5000 K and 20 MPa) [17], which favor chemical changes. The ultrasound technique allows obtaining new materials with high purity without applying high pressures or temperatures or using long calcination times, as in conventional methods. This technique has been used to synthesize Li-Al-Mn spinels [18] and Li-Ni-Mn oxides [19]. In our previous work [20,21] we have synthesized a series of mixed Mn oxides by ultrasound-assisted sol-gel (UASG) methods and examined their properties as cathodes for Li-ion batteries. In particular, we have focused on their cation distributions and the surface Li-ion diffusion.

This work focuses on the preparation of lithium manganese mixed oxides involving metals with high oxidation states, so that they could be used as electrode materials in lithium batteries. Our interest is centered on Li-Mn-O spinels with partial Co and Fe substitutions due to their low cost and toxicity. In addition, these compositions LiMn$_{1.5}$O$_4$ (M = Co or Fe) have been prepared by very few methods and therefore their physical-chemical properties have not been too much explored [12,22,23].

We report on the preparation and characterization of the spinel-related LiCo$_{0.5}$Mn$_{1.5}$O$_4$ and LiFe$_{0.5}$Mn$_{1.5}$O$_4$ oxides synthesized by the ultrasound-assisted thermal decomposition nitrates (UA-TDN) method. The materials resulting from this specific synthesis method have not been studied in depth so far, particularly from the point of view of their structural, morphological and surface properties. We report herein on our main results on the characterization of these materials by X-ray powder diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), oxygen stoichiometry determinations and X-ray photoelectron spectroscopy (XPS) measurements. These results have allowed us proposing the respective cation distributions for these related-spinel Li-Fe-Mn and Li-Co-Mn oxides.

2. Experimental

2.1. Synthesis of LiMn$_{0.5}$Mn$_{1.5}$O$_4$ (with M = Co and Fe) oxides

The powdered oxides of LiMn$_{0.5}$Mn$_{1.5}$O$_4$ (M = Co and Fe) were synthesized by an ultrasound-assisted thermal decomposition of nitrates (UA-TDN) route using the sonochemical method as it was previously reported [17]. Briefly, lithium nitrate (LiNO$_3$), cobalt nitrate hexahydrate (II) (Co(NO$_3$)$_2$·6H$_2$O), iron nitrate nonahydrate (III) (Fe(NO$_3$)$_3$·9H$_2$O) and manganese nitrate monohydrate (Mn(NO$_3$)$_2$·H$_2$O) (supplied by Sigma-Aldrich ≥ 98%), were used as precursors in stoichiometric quantities. These precursors were dissolved in 50 mL water under agitation during 20 min. Then the solution was placed in an ultrasound equipment (Sonics VCX) powered at 500 W, 20 kHz, for 1 h. The obtained product was dried at 95 °C in a 6 h and heated at a rate of 5 °C/min up to 800 °C and then maintained at this temperature for 6 h [20] in air. The black powder obtained was quenched in air at room temperature.

2.2. Characterization techniques

The phase identification and phase purity of the final products was checked by XRD using CuKα radiation (λ = 1.5418 Å) in a Bruker D2 Phaser diffractometer (30 kV, 10 mA). The crystal structure was refined using the Rietveld method [24,25].

The sample morphology was examined by means of SEM using a Zeiss EVO MA10 apparatus at an acceleration voltage of 20 keV. The microscope was equipped with an Oxford X-Act Energy Dispersive Spectrometer (EDS) for quantitative elemental characterization. The samples were examined by EDS analysis and characterized by TEM using a Hitachi HT7700 microscope equipped with a thermionic LaB$_6$ filament and an EXALENS system. The particles were imaged at an accelerating voltage of 120 kV using a carbon-coated copper grid.

The oxygen stoichiometry was obtained from the determination of the sample oxidation power which was evaluated by chemical reduction using a 0.04 N VOSO$_4$ acid solution. In this method, approximately 60 mg of oxide were mixed with 50 mL of VOSO$_4$ solution and the mix was kept at 90 °C for 24 h. After the oxide dissolution, the unreacted reducing agent was titrated with a standard K$_2$Cr$_2$O$_7$ N 0.0626 solution. The oxides prepared were analyzed by Raman spectroscopy. The spectra were recorded using a WTI Tech Alpha 300 confocal Raman micro-scope system equipped with an electrically cooled CCD camera. The signal was calibrated using a Si wafer and a 20x objective by following the 520 cm$^{-1}$ characteristic band. The spectra were recorded in the 200-800 cm$^{-1}$ region after 10 scans with an integration time of 1s using the 785 nm laser line and a beam power of 2 mW.

XPS data were recorded using an electron PHOIBOS-150 hemispherical electron analyzer under a vacuum better than 7·10$^{-10}$ mbar using Al Kα radiation and constant pass energies of 100 eV and 20 eV for the wide and narrow scan spectra, respectively. All binding energies (BE) were referred to the main C 1s signal of the adventitious contamination layer (284.6 eV). Relative atomic concentrations were calculated after background subtraction using the Shirley method and peak area integration using tabulated atomic sensitivity factors [27].

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the experimental and calculated intensities of the XRD patterns corresponding to LiMn$_{0.5}$Mn$_{1.5}$O$_4$$_{δ}$ (M = Co, Fe). Both oxides crystallize in a cubic FCC structure (Fd$ar{3}$m SG) as single-phase spinels. No additional peaks were observed. The results of the Rietveld refinement of the XRD data are summarized in Table 1.

The main diffraction peaks were assigned to the (111), (220), (311), (222), (400), (331), (422), (511) (440), (531) crystal planes of the spinel structure. The lattice parameters calculated for the Co- and Fe-containing oxides (a = 0.81166(4) nm and 0.82536(1) nm respectively) were in good agreement with those reported in the literature (a = 0.815(8) nm and a = 0.8248 nm, respectively [6,23]). The calculated crystal data for LiCo$_{0.5}$Mn$_{1.5}$O$_4$ and LiFe$_{0.5}$Mn$_{1.5}$O$_4$ are summarized in Table 2. We have located Li$^+$ ions in the 8a positions while Co$^{3+}$, Fe$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$ ions have been placed in the 16d positions (see the XPS data below for a discussion on the oxidation states of the cations). The O$^{2-}$ anions occupy the 32e atomic positions. The crystallite sizes (where coherent diffraction patterns occur) of LiCo$_{0.5}$Mn$_{1.5}$O$_4$ and LiFe$_{0.5}$Mn$_{1.5}$O$_4$ were calculated using the W-H method [28] $\beta_{\text{W-H}} = \beta_{\text{lat}} + \beta_{\text{strain}} = \left( \frac{K \lambda}{W \cos \theta} \right) + 4\eta \tan \theta$. This method gives a more precise evaluation of this value since it considers that micro-strain, arising from crystal imperfections and distortion of the crystal lattice, also affecting the broadening of the diffraction peaks. In the previous expression $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum of the considered diffraction.
peak (FWHM), \( \theta \) is the Bragg angle and \( \eta \) is the micro-strain parameter. Fig. 2 shows the \((\beta \text{totalcos} \theta) = K \lambda \) vs. \((4 \sin \theta) = K \lambda \) plots for both oxides. The intercept of the linear fit with the y-axis gives the inverse of the crystallite size. The values obtained were found to be 52 nm and 45 nm for LiCo_{0.5}Mn_{1.5}O_{4-\delta} and LiFe_{0.5}Mn_{1.5}O_{4-\delta}, respectively. The crystallite sizes obtained from the W–H plot were in relative good agreement with those measured using the Debye-Scherrer method [29], which were 68 nm and 56 nm, respectively.

### 3.2. Raman spectroscopy

The obtained Raman spectral profile of both obtained products is displayed in Fig. 3. The assignment of the signals was performed on the basis of reported data [30–32].

Structurally, the presence of the metal-oxygen (M – O) stretching mode for both LiCo_{0.5}Mn_{1.5}O_{4} and LiFe_{0.5}Mn_{1.5}O_{4}, was corroborated by their characteristic Raman signals. Regarding the LiCo_{0.5}Mn_{1.5}O_{4} oxide, the O–O stretching was observed at 245, 400, 598 and 639 cm\(^{-1}\). In the case of LiFe_{0.5}Mn_{1.5}O_{4} the Fe–O stretching modes appeared at 267, 448, 574 and 625 cm\(^{-1}\). Finally, Mn–O stretching modes [33] were observed at 739 and 737 cm\(^{-1}\) in LiCo_{0.5}Mn_{1.5}O_{4} and LiFe_{0.5}Mn_{1.5}O_{4}, respectively.

### 3.3. Morphology characterisation

The morphology and particle size of the oxides was characterized by SEM (see Fig. 4a–b). SEM images showed that all the samples presented irregular polyhedral morphology [21], with particle sizes below the submicron range and forming agglomerates 1–2 \( \mu \text{m} \) in size showing, besides, a high degree of agglomeration, especially for LiCo_{0.5}Mn_{1.5}O_{4-\delta}. In this case, the estimated average size of the LiCo_{0.5}Mn_{1.5}O_{4-\delta} particles was 600 nm, while for LiFe_{0.5}Mn_{1.5}O_{4-\delta} oxide it was 750 nm. Yoon et al. [6] have observed similar morphologies to those shown here for LiCo_{0.5}Mn_{1.5}O_{4-\delta}. It is known that the application of ultrasounds in the synthesis of materials, promotes the formation of nano-sized particles [34]. Being a synthesis route, which is carried out in solution it opens the possibility of mixing the starting materials at the molecular level.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Atomic positional parameters and site occupation factors for LiM_{0.5}Mn_{1.5}O_{4-\delta} (M = Co, Fe).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide</td>
<td>LiCo_{0.5}Mn_{1.5}O_{4-\delta}</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>( a (\text{nm}) )</td>
<td>0.81166(4)</td>
</tr>
<tr>
<td>( \text{Vol (nm)}^3 )</td>
<td>0.82536(1)</td>
</tr>
<tr>
<td>( R_p (%) )</td>
<td>1.62</td>
</tr>
<tr>
<td>( R wp (%) )</td>
<td>2.05</td>
</tr>
<tr>
<td>( \beta \text{Bragg} )</td>
<td>1.8(1)</td>
</tr>
<tr>
<td>( \chi^2 (%) )</td>
<td>1.0</td>
</tr>
<tr>
<td>( \beta \text{exp} )</td>
<td>1.92</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>2.29</td>
</tr>
<tr>
<td>Oxide</td>
<td>LiFe_{0.5}Mn_{1.5}O_{4-\delta}</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>( a (\text{nm}) )</td>
<td>0.82536(1)</td>
</tr>
<tr>
<td>( \text{Vol (nm)}^3 )</td>
<td>0.56225(13)</td>
</tr>
<tr>
<td>( R_p (%) )</td>
<td>1.96</td>
</tr>
<tr>
<td>( R wp (%) )</td>
<td>2.74</td>
</tr>
<tr>
<td>( \beta \text{Bragg} )</td>
<td>0.5(6)</td>
</tr>
<tr>
<td>( \chi^2 (%) )</td>
<td>2.29</td>
</tr>
<tr>
<td>( \beta \text{exp} )</td>
<td>1.81</td>
</tr>
</tbody>
</table>

(*) \( \text{focc} \) were calculated in the “3.5 Oxygen stoichiometry and cation distribution” paragraph.
Consequently, materials with a high degree of homogeneity having small particle sizes and high surface area can be obtained.

The EDS analysis (see Fig. 4c–d) confirmed the presence of Fe, Co and O. In addition, specific analyzes taken on the oxides verified the proportion of Mn/M cations according to formula 1.5/0.5 = 3. Concerning the oxygen content, it is well-known that its determination by EDS is affected by a large error [35]. Therefore, we have used an indirect determination method based on the total reduction of the oxide cation valences to the value +2 (see below).

TEM was also employed to investigate the size and shape of the oxide particles as well as to confirm the crystalline nature of the prepared materials. Fig. 5a and b shows TEM images recorded from LiCo0.5Mn1.5O4-δ and LiFe0.5Mn1.5O4-δ, respectively. As it can be observed, both oxides presented a large agglomeration of polycrystalline particles with polyhedral shape. The crystalline character of the prepared compounds was corroborated by electron diffraction which showed clearly defined diffraction patterns (see inset in Fig. 5a and b). The average size of the particles as determined by TEM was estimated to be around 500 nm, approximately. Results of correlating the Scherrer equation and the SEM-TEM indicated that the synthesized material presents a polycrystalline character. This means that per particle there is more than one crystallographic domain and was confirmed by the electron diffraction pattern observed.

3.4. XPS analysis

The wide scan XPS spectra recorded from both oxides showed (Fig. 6a) intense signals characteristic of the elements which compose the materials. In the case of the Co-containing oxide the Co 2p spectrum showed a very narrow spin-orbit doublet (Fig. 6b) with binding energies (BE’s) of the Co 2p3/2 and Co 2p1/2 core levels of 780.2 and 795.3 eV, respectively. The spectrum also contained minor peaks at 789.9 eV and 805.0 eV. The binding energies of the main doublet lines, their energy separation (15.1 eV) and the occurrence of these two small energy loss peaks are all characteristic of the presence of low spin (S = 0) CoIII [36]. This contrasts strongly with that reported by J. Kim et al. [6] who only mentioned the presence of CoII. The Fe 2p spectrum recorded from the iron-containing oxide is shown in Fig. 6c. The spectrum is composed by an asymmetric spin-orbit doublet and shake-up satellite structure 8.5–9.0 eV above the main photoemission lines. It is well-known that the observed asymmetry is due to unresolved multiplet splitting. Therefore, we fitted

![Fig. 3. Raman spectra of a) LiCo0.5Mn1.5O4 and b) LiFe0.5Mn1.5O4 between 200 and 800 cm⁻¹.](image-url)

![Fig. 4. SEM-EDS micrographs of (a,c) LiCo0.5Mn1.5O4-δ and (b,d) LiFe0.5Mn1.5O4-δ oxides.](image-url)
Although we tried to fit a Mn$^{2+}$ contribution, we could not succeed. The fit gave always a negligible concentration of Mn$^{2+}$. The O 1s spectra (not shown) contained a main contribution (ca. 76% of the spectral area) at 529.3–529.5 eV which is characteristic of metal-oxygen bonds and some other minor contributions at higher binding energies due to OH groups, organic oxygen and adsorbed water. If we do not take into account the extra oxygen species, i.e. if we only consider that corresponding to reticular oxygen, we obtain the following relative atomic ratios (calculated from the Mn 2p, Co 2p, O 1s and Li 1s spectra) for LiCo$_{0.5}$Mn$_{1.5}$O$_{4.6}$-δ Co/O = 0.092, Mn/O = 0.34, Li/O = 0.37 while the nominal ones would be: 0.125, 0.375 and 0.25, respectively. While the Mn/O and Co/O atomic ratios are close to the nominal values, the Li/O atomic ratio is much higher. This would imply a surface enrichment in Li and would explain why we have only found very high oxidation states of Mn and the lack of Mn$^{2+}$; it would be compensated by an excess in lithium. In the case of LiFe$_{0.5}$Mn$_{1.5}$O$_{4}$-δ, the Li/O atomic ratio cannot be calculated as the Li 1s core level peak overlaps (almost matches) that of Fe 3p core level. For this oxide we obtain: Mn/O = 0.355 and Fe/O = 0.135, values which are very close to the nominal ones. We would like to point out that the excess in lithium at the surface is not related with the formation of lithium carbonate, something which has been sometimes to occur in Li-containing spinels [38], since no strong carbonate contributions were observed in the C 1s and O 1s spectra.

3.5. Oxygen stoichiometry and cation distribution

The cation oxidation power results determined using the redox titration technique are shown in Table 3. As it has been reported, this allows the quantification of the oxygen content in the oxides [39]. As we have described in a recent paper, the cation distribution of oxides like these can be established taking into account the oxidation state and relative concentrations of the different cations as determined by XPS (in this case Li$^{+}$, Fe$^{3+}$; Co$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$), the energy preferences of these cations to occupy the A and B sites in the spinel-related structure, the oxygen content obtained by chemical methods, and the length of the different Me–O bonds according to the oxidation state of the cations and their possible coordination. So, the cell parameter “a” can be expressed as:

\[
a = 2.0995a + (5.8182\beta^2 - 1.4107\alpha^2)^{1/2}
\]

where \(a = \sum x_i(|M_i - O)| Td\) and \(2\beta = \sum y_i(|M_i - O|) Oh\). \(x_i\) and \(y_i\) are the stoichiometric coefficients and \(|M_i - O| Td\) and \(|M_i - O| Oh\) are the cation-oxygen distances in the tetrahedral and octahedral sites, respectively. In our case we have considered the cation-oxygen distance values given by Shannon and Prewitt [40] which take into account the spin state and the energy preference of the cations in the different spinel sites (namely, Li$^{+}$ - O$_{Li}$ = 0.2041, Fe$^{3+}$ - O$_{Fe}$ = 0.202, Co$^{3+}$ - O$_{Co}$ = 0.189, Mn$^{3+}$ - O$_{Mn}$ = 0.205, Mn$^{4+}$ - O$_{Mn}$ = 0.1843 nm).

On the other hand, the proposed ionic distribution must be corrected with the stoichiometry in oxygen, since are compounds of neutral global charge. The global charge is determined indirectly by chemical methods from the proposed ionic distributions. The relative variation in oxygen stoichiometry with respect to metal ions was determined indirectly using vanadyl sulphate (VOSO$_4$) which is a weak reducer. For this method it is required that the oxides have cations in oxidation state greater than +2, allowing to calculate the oxygen present in the oxide [39]. The moles of reduced electrons (e$^-$) were determined with a potentiometric titration, then through a balance of the reduced charge (q) the stoichiometry was determined in oxygen. The reactions involved are the following:

\[
VO^{2+} + 3 H_2O \rightarrow V(OH)_3^+ + 2H^+ + \pi
\]

\[
Me^{n+} + (n - 2)\pi \rightarrow Me^{(n-2)+}
\]

The correlation of the electrons transferred with the stoichiometry in oxygen, of the overall reduction of the oxide by vanadyl sulphate, is represented by

Fig. 5. TEM images recorded from a) LiCo$_{0.5}$Mn$_{1.5}$O$_{4.6}$ and b) LiFe$_{0.5}$Mn$_{1.5}$O$_{4.6}$ (the corresponding electron diffraction patterns are shown in the insert).
The amount of $e^-$ exchanged per gram of sample is determined by the expression:

$$q = \frac{Z}{mM} = \left( \frac{V_0 \cdot N_0}{N} - V \right) \frac{N}{m}$$

where $Z$ the average charge of the ions per mole of product, $m$ the oxide mass in milligrams, $V_0$ and $N_0$ the volume and normality of $\text{VOSO}_4$ and $V$ and $N$ the volume spent and normality of $\text{KMnO}_4$ and $mM$ the theoretical molar mass of the oxide. Finally, the global charge is determined from the proposed ionic distributions by relating the number of equivalent electrons per mole of each ionic species reduced to the state of valence $\pm 2$.

With all that information and parameters, we arrive to a system of equations that, when solved, allows determining the cation distributions, lattice parameters and global charge values collected in Table 3. The values of the lattice parameter $a$ and the global charge $z$ calculated on the basis of the ion distributions obtained by Rietveld analysis are also shown in Table 3. Inspection of Table 3 shows good agreement between the $a$ and $z$ experimental parameters and the calculated ones for the proposed cation distributions.

In previous works we have studied the synthesis of manganese-containing mixed oxides with spinel-related structure by different methods such as sol-gel (SG) and sol-gel ultrasound assisted (UASG) synthesis. In the ultrasound-assisted synthesis method, we obtained materials having greater crystallinity, better defined morphology and a reduced average particle size than those obtained by other conventional methods. In the case of the nickel manganite, $\text{NiMn}_2\text{O}_4$, made by UASG [37] the results also showed a higher concentration of cations in high

### Table 3

<table>
<thead>
<tr>
<th>Oxide</th>
<th>a Obs. (nm)</th>
<th>a Calc. (nm)</th>
<th>$Z$ Obs. (eq e$^-$ mol$^{-1}$)</th>
<th>$Z$ Calc. (eq e$^-$ mol$^{-1}$)</th>
<th>Cationic distribution</th>
<th>Mn$^{4+}$/Mn$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LiCo}<em>{0.5}\text{Mn}</em>{1.5}\text{O}_{4+\delta}$</td>
<td>0.8117</td>
<td>0.8291</td>
<td>2.52</td>
<td>2.30</td>
<td>$\text{Li}^+\text{Co}^{3+}<em>{0.5}\text{Mn}^{4+}</em>{1.5}\text{O}_{4+\delta}$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{LiFe}<em>{0.5}\text{Mn}</em>{1.5}\text{O}_{4+\delta}$</td>
<td>0.8254</td>
<td>0.8285</td>
<td>2.61</td>
<td>2.50</td>
<td>$\text{Li}^+\text{Fe}^{3+}<em>{0.5}\text{Mn}^{4+}</em>{1.5}\text{O}_{4+\delta}$</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jssc.2020.121175.

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