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Investigation of the possible incorporation of protons into oxide cathodes during chemical delithiation

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Abstract

Chemical delithiation of layered $LiCoO_2$, $LiNi_{0.5}Mn_{0.5}O_2$, and Li_2MnO_3 and spinel $LiMn_2O_4$ cathodes have been investigated with both an acetonitrile (non-aqueous) solution of the oxidizer NO_2BF_4 and an aqueous acid. The products have been characterized by X-ray diffraction, wet chemical analyses for lithium and oxygen contents, infrared spectroscopy, and thermogravimetric analysis to determine whether or not protons are incorporated into the lattice during the delithiation process. While the delithiation in aqueous acid medium leads to an incorporation of protons into the layered oxide lattice, the non-aqueous delithiation with NO_2BF_4 does not involve any proton insertion into the lattice. In contrast to the layered oxides, the chemical delithiation of spinel $LiMn_2O_4$ even in the aqueous acid medium does not involve any proton insertion into the lattice.

Keywords: Lithium-ion battery; Layered oxide; Chemical delithiation; Proton insertion

1. Introduction

The layered LiMO$_2$ (M=Mn, Co, and Ni) oxides crystallizing in the O3-type structure (Fig. 1a) exhibit facile lithium intercalation properties at ambient temperatures, and they have become attractive cathodes for lithium-ion batteries. Commercial lithium-ion batteries presently use the layered $LiCoO_2$ as the cathode [1], but only 50% of its theoretical capacity (140 mAh/g) could be utilized in practical cells. On the other hand, compositions such as $LiNi_{0.5}Mn_{0.5}O_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and $LiNi_{0.85}Co_{0.15}O_2$ having the same O3 type structure as $LiCoO_2$ (Fig. 1a) exhibit higher reversible capacities of, respectively, 160, 170, and 180 mAh/g [2–7]. The reason for the differences in the capacity values and the factors that control the reversible capacity limits of the layered LiMO$_2$ cathodes are not fully understood in the literature.

The lack of such an understanding is due to the fact that most of the studies have invariably focused mainly on the structural characterization of the electrochemically charged cathodes [8,9]. Not much attention has been focused experimentally towards the chemical instabilities that could occur due to a near-equivalence of the highly oxidized $M^{3+/4+}$:3d and O^{2-}:2p energies, and a consequent oxidation of the O^{2-} ions to release oxygen from the lattice at deep charge. Although Ceder's group [10] has predicted based on theoretical calculations that the average valence charge on oxygen decreases with decreasing lithium content in $Li_{1-x}CoO_2$, not much experimental data are available with respect to the chemical instabilities. With an aim to experimentally assess the chemical instabilities, our group has been focusing on monitoring the variation of oxygen content with lithium content in bulk $Li_{1-x}MO_2$ samples that were obtained by chemically extracting lithium from LiMO$_2$ with the oxidizer NO_2BF_4 in an acetonitrile medium and are free from binder and carbon [11–16]. Our study has shown that the $Li_{1-x}MO_{2-\delta}$ systems tend to lose oxygen for $(1-x)<0.5$, 0.3, 0.4, 0.3, and 0.35,

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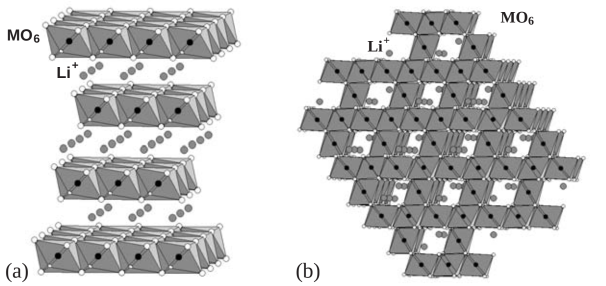

Fig. 1. Crystal structures of (a) layered LiMO$_2$ and (b) spinel LiM_2O$_4$.

respectively, for M = Co, $Ni_{0.85}Co_{0.15}$, $Ni_{0.75}Mn_{0.25}$, $Ni_{0.5}Mn_{0.5}$ and $Ni_{1/3}Mn_{1/3}Co_{1/3}$ due to an overlap of the $M^{3+/4+}$:3d band with the top of the O^{2-}:2p band [11–16].

However, the oxygen content values of the $Li_{1-x}MO_{2-\delta}$ samples were obtained based on iodometric titration data for the oxidation state of the transition metal ions and charge neutrality principle [17] by assuming that no proton is inserted into the oxide lattice during the chemical delithiation process. Any proton inserted, on the other hand, could adversely affect the oxygen content data and the conclusions on the relative chemical stabilities of the various $Li_{1-x}MO_2$ compositions. Although one would expect little or no proton insertion from the acetonitrile solvent used in our experiments, recent work by Bruce's group [18,19] on Li_2MnO_3 and $Li_xMn_{1-y}Li_yO_2$ cathodes indicates that an ion-exchange of Li^+ by H^+ ions may occur on charging beyond Mn^{4+} the electrochemical cells fabricated with non-aqueous electrolytes, especially at higher temperatures of 55 °C. The protons in this case were perceived by the authors to be electrochemically generated from the electrolyte solvent at higher potentials of around 4.5 V and then to ion exchange with Li^+ in Li_2MnO_3. The authors reported that both the ion-exchange of Li^+ by H^+ as well as loss of oxygen from the lattice takes place on deep charging. Also, chemical delithiation studies on Li_2MnO_3 with aqueous acids have indicated that the delithiation proceeds both by an ion-exchange of Li^+ by H^+ as well as by an oxidation of oxide ions, involving an effective removal of Li_2O from the lattice [20–24].

With an aim to address the issue of whether or not proton could be inserted into the lattice during the chemical delithiation process, we focus in this paper on a comparison of the characterization of the products obtained by a chemical delithiation of layered $LiCoO_2$, $LiNi_{0.5}Mn_{0.5}O_2$, and Li_2MnO_3, and spinel $LiMn_2O_4$ (Fig. 1b) oxides in both non-aqueous and aqueous media. While the non-aqueous delithiation is performed with the oxidizer NO_2BF_4 in acetonitrile medium, the aqueous delithiation is carried out with 2.5 N sulfuric acid. The samples are characterized by X-ray diffraction, wet-chemical analysis, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA).

2. Experimental

Layered $LiCoO_2$ was synthesized by a solid-state reaction between Li_2CO_3 and Co_3O_4 at 900 °C for 24 h in air. Layered Li_2MnO_3 was synthesized by a solid-state reaction between $LiOH \cdot H_2O$ and Mn_2O_3 at 750 °C for 24 h in air. Layered $LiNi_{0.5}Mn_{0.5}O_2$ was synthesized by a co-precipitation procedure involving a drop by drop addition of an aqueous solution containing required amounts of nickel (II) and manganese (II) acetates into a 0.1 M KOH solution, followed by filtering the co-precipitated hydroxide, washing with deionized water, drying overnight at 100 °C in an air oven, and then firing with a required amount of $LiOH \cdot H_2O$ first at 480 °C for 3 h and then at 900 °C for 3 h in air. $LiMn_2O_4$ was synthesized by a solid-state reaction between Li_2CO_3 and Mn_2O_3 at 800 °C for 48 h in air.

The chemical extraction of lithium in non-aqueous medium was carried out at room temperature by stirring the oxide powders in an acetonitrile solution of NO_2BF_4 for 2 days under argon atmosphere using a Schlenk line:

$$LiMO_2 + xNO_2BF_4 \rightarrow Li_{1-x}MO_2 + xNO_2 + xLiBF_4 \quad (1)$$

The products formed after the reaction were washed three times with acetonitrile under argon atmosphere to remove $LiBF_4$ and dried under vacuum at ambient temperature. After drying, the reaction flasks were opened in an argon-filled glove box. The chemical extraction of lithium in aqueous medium was carried out at room temperature by stirring the oxide powders in 2.5 N H_2SO_4 for 2 days, followed by filtering, washing with de-ionized water, and drying at 100 °C overnight in an air-oven. Extraction of lithium with aqueous acid is known to occur by a disproportionation of, for example, Mn^{3+} into Mn^{4+} (in solid) and Mn^{2+} (into solution) in the spinel $LiMn_2O_4$ [25] and Co^{3+} into Co^{4+} (in solid) and Co^{2+} (into solution) in the layered $LiCoO_2$ [26].

The lithium contents in the chemically delithiated samples were determined by atomic absorption spectroscopy. The oxidation state of the transition metal ions and the oxygen contents were determined by iodometric titration [17]. Structural characterizations were carried out with X-ray powder diffraction using Cu$K\alpha$ radiation with a Philips 3550 diffractometer. TGA data were collected with a Perkin–Elmer Series 7 Thermogravimetric Analyzer with a heating rate of 2 °C/min in flowing air. FTIR spectra were recorded with pellets made with KBr and the sample using a Nicolet AVATAR 360 FT-IR spectrometer.

3. Results and discussion

3.1. Chemical delithiation of layered $LiCoO_2$

Lithium was extracted chemically from $LiCoO_2$ in both aqueous and non-aqueous media. Wet-chemical analyses for lithium content and oxidation state of cobalt and the application of charge neutrality principle gave a composition of $Li_{0.3}H_{0.1}CoO_2$ for the product obtained by aqueous delithiation assuming an extreme case of no oxygen is lost from the lattice, and $CoO_{2-\delta}$ ($\delta = 0.28$) for the product obtained by non-aqueous delithiation [13] assuming an extreme case of no proton insertion occurs during the delithiation process. These assumptions are consistent with the fact that while plenty of protons are available in an aqueous acidic medium that can promote an ion exchange of Li^+ by H^+ without involving any redox reaction, little or no proton will be available in an acetonitrile solution of NO_2BF_4. However, it is possible that both an ion exchange of Li^+ by H^+ and a loss of oxygen could occur in both the media, and they could be verified by analyzing the products for protons by techniques such as FTIR, which is the purpose of this investigation.

Fig. 2 compares the FTIR spectra of $Co(OH)_2$, $HCoO_2$ obtained by oxidizing $Co(OH)_2$ with 2.5 N H_2SO_4 [27], as-prepared $LiCoO_2$, aqueous delithiated $Li_{0.3}H_{0.1}CoO_2$, and non-aqueous delithiated $CoO_{2-\delta}$. The spectra of $Co(OH)_2$ and $HCoO_2$ are given in Fig. 2 as a reference to indicate the positions of the characteristic O–H bands in these type of compounds. In metal oxides, while the M–O vibrations from the MO_6 octahedra occur in the low wavenumber region of 600–900 cm^{-1}, the characteristic absorption bands from the lattice hydroxyl (O–H) groups occur around 3400 cm^{-1} [28,29]. $Co(OH)_2$ shows a sharp absorption band at 3600 cm^{-1} while $HCoO_2$ shows broad absorption band at 3000–3400 cm^{-1}, confirming the presence of lattice hydroxyl groups in them. On the other hand, $LiCoO_2$ shows absorption bands only around 650 cm^{-1} corresponding to the vibrations of CoO_6 octahedra, but no bands corresponding to O–H vibrations as one would expect. However, the delithiated $Li_{0.3}H_{0.1}CoO_2$ and $CoO_{2-\delta}$ samples do not show any absorption bands. The vanishing of the absorption bands on extracting lithium from $LiCoO_2$ indicates the introduction of metallic conduction behavior since free electrons in metallic systems can oscillate to any incident wavelength, resulting in no characteristic absorption [12]. While $LiCoO_2$ with a completely filled Co^{3+}:t_{2g}^{6} (low-spin) band exhibits semiconducting behavior, both the $H_{0.1}Li_{0.3}CoO_2$ and $CoO_{2-\delta}$ samples exhibit metallic behavior due to the direct Co–Co interaction across the edge-shared CoO_6 octahera via the partially filled $Co^{3+/4+}$:t_{2g}^{6-x} orbitals. These results indicate that IR spectroscopy cannot be used to detect the presence of hydroxyl groups in metallic $Li_{1-x}MO_2$ oxides.

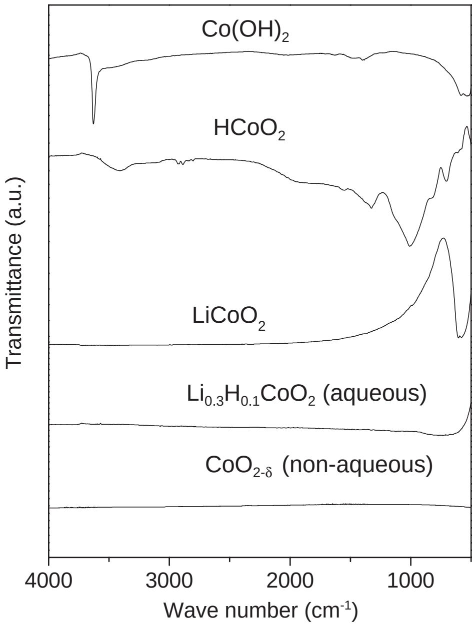

Fig. 2. Comparison of the FTIR spectra of $Co(OH)_2$, $HCoO_2$, $LiCoO_2$, aqueous delithiated $Li_{0.3}H_{0.1}CoO_2$, and non-aqueous delithiated $CoO_{2-\delta}$.

3.2. Chemical delithiation of layered $LiNi_{0.5}Mn_{0.5}O_2$

Since the metallic nature of the chemically delithiated $Li_{1-x}CoO_2$ samples pose a difficulty to detect protons by FTIR, we turned to the chemical delithiation of the $LiNi_{0.5}Mn_{0.5}O_2$ system as both $Ni^{3+/4+}$ and $Mn^{3+/4+}$ are characterized by a completely filled t_{2g} band and the $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$ system is expected to be a semiconductor for the entire $0 \leqslant (1-x) \leqslant 1$. Moreover, assuming no proton incorporation occurs during the non-aqueous chemical delithiation process with NO_2BF_4, the wet-chemical analysis data based on charge neutrality principle gave a composition of $Ni_{0.5}Mn_{0.5}O_{2-\delta}$ with a high $\delta = 0.25$ [15] similar to that in $CoO_{2-\delta}$ ($\delta = 0.28$). On the other hand, if the charge balance is maintained by an incorporation of protons (ion exchange of some Li^+ by H^+), then based on the oxidation state analysis by the iodometric titration, the end member would be expected to have a composition of $H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ with a significant amount of protons. Therefore, a FTIR investigation of the product obtained by the chemical delithiation of $LiNi_{0.5}Mn_{0.5}O_2$ can help to clarify whether or not protons are incorporated during the chemical delithiation process. Accordingly, we pursued a FTIR analysis of the samples obtained by both the aqueous and non-aqueous chemical delithiation

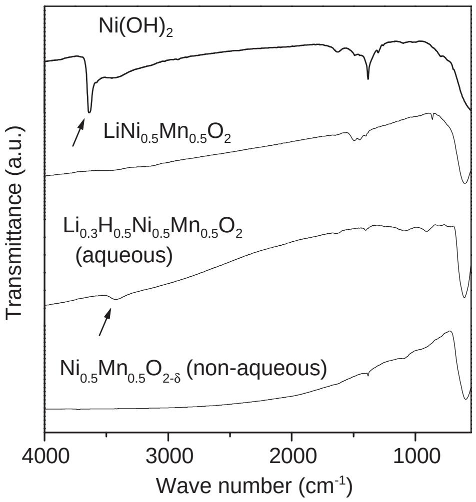

Fig. 3. Comparison of the FTIR spectra of $Ni(OH)_2$, $LiNi_{0.5}Mn_{0.5}O_2$, aqueous delithiated $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$, and non-aqueous delithiated $Ni_{0.5}Mn_{0.5}O_{2-\delta}$. The arrow indicates the position of the characteristic absorption band (~3500 cm^{-1}) corresponding to O–H groups.

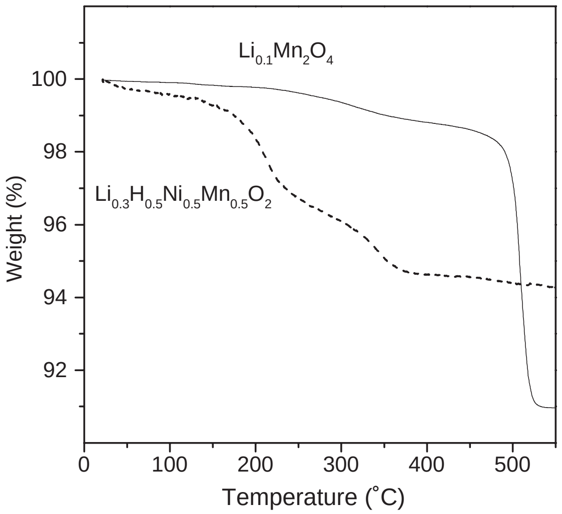

Fig. 4. Comparison of the TGA plots of aqueous delithiated layered $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ and spinel $Li_{1-x}Mn_2O_4$.

processes. With the aqueous delithiation, chemical analysis indicated a composition of $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$, assuming no oxygen loss from the lattice occurs during the aqueous chemical delithiation process.

Fig. 3 compares the FTIR spectra of the reference $Ni(OH)_2$, $LiNi_{0.5}Mn_{0.5}O_2$, aqueous delithiated $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$, and non-aqueous delithiated $Ni_{0.5}Mn_{0.5}O_{2-\delta}$. It is clear from the IR data that while both $Ni(OH)_2$ and the aqueous delithiated $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ samples show characteristic absorption bands at around 3500 cm^{-1} corresponding to O–H groups, both the parent $LiNi_{0.5}Mn_{0.5}O_2$ and non-aqueous delithiated $Ni_{0.5}Mn_{0.5}O_{2-\delta}$ do not. The results suggest that while proton incorporation does occur during aqueous delithiation, it may not occur during chemical delithiation with NO_2BF_4 in acetonitrile medium. Additionally, the occurrence of bands around 650 cm^{-1} corresponding to the $(Ni_{0.5}Mn_{0.5})$-O vibrations in both the chemically delithiated samples confirms that the $Li_{1-x}Ni_{0.5}Mn_{0.5}O_2$ system remains semiconducting for the entire $0 \leqslant (1-x) \leqslant 1$.

In addition to IR spectroscopy, TGA data could also be used to indicate presence of protons indirectly. Typically, weight loss from the samples up to about 400 °C may be indicative of loss of lattice proton as water. Fig. 4 shows the TGA plot of aqueous delithiated $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ recorded in air. The data indicate that $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ experiences a weight loss of around 5.5% up to 450 °C, which corresponds to the loss of 0.54 $g\,mol^{-1}$ of protons as H_2O. This is in agreement with the observation of O–H bands in the FTIR spectrum and the chemical formula derived from the lithium and oxidation state analyses. The close agreement of the proton content obtained from the TGA data with that in the formula $Li_{0.3}H_{0.5}Ni_{0.5}Mn_{0.5}O_2$ also indicate that no oxygen may be lost during the chemical delithiation of $LiNi_{0.5}Mn_{0.5}O_2$ in aqueous medium.

3.3. Chemical delithiation of layered Li_2MnO_3

Li_2MnO_3 has the O3 type layered structure similar to that of $LiCoO_2$ (Fig. 1a), but the transition metal plane consists of 67% Mn^{4+} and 33% Li^+ instead of 100% transition metal ions, and it can be represented as $[Li]_{3a}(Li_{0.33}Mn_{0.67})_{3b}\{O_2\}_{6c}$. In Li_2MnO_3, all manganese is present in the 4+ oxidation state. Since the oxidation of Mn^{4+} to Mn^{5+} in an octahedral oxygen environment is not common or accessible, one would expect Li_2MnO_3 to be electrochemically inactive. However, this compound has been reported to show some electrochemical activity [18,19] due to the ion-exchange of Li^+ by H^+ as well as by the loss of oxygen from the lattice, similar to that observed on the acid leached Li_2MnO_3 samples [20–24].

We have investigated the chemical delithiation of Li_2MnO_3 in both the aqueous and non-aqueous media, and Table 1 gives the chemical analysis data of the products formed. In the non-aqueous medium, only a maximum of 0.29 lithium could be extracted from Li_2MnO_3 with the oxidation state of Mn remaining at 4+, resulting in a product composition of $Li_{1.71}MnO_{3-\delta}$ with $\delta = 0.13$, assuming no proton incorporation occurs. On the other hand, a maximum of 0.68 lithium could be extracted in the aqueous acid medium with the oxidation state of Mn dropping to 3.86+, resulting in a product composition of $Li_{1.32}H_{0.68}MnO_{2.93}$, assuming both oxygen loss and proton incorporation (ion exchange of some Li^+ by H^+) occur.

Table 1
Chemical analysis data of Li_2MnO_3 before and after chemical delithiation

	As-prepared Li_2MnO_3	Delithiated product	
		Non-aqueous medium	Aqueous medium
Lithium content	1.98	1.71	1.32
Oxidation state of Mn	4.03	4.02	3.86
Proton content	—	—	0.68
Oxygen content	3.00	2.87	2.93

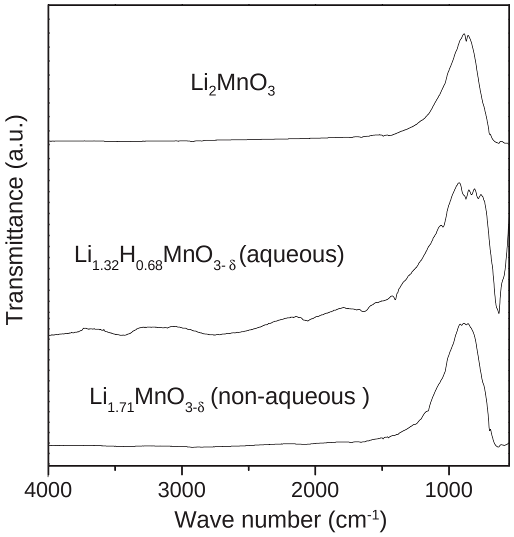

Fig. 5. Comparison of the FTIR spectra of the layered Li_2MnO_3, aqueous delithiated $Li_{1.32}H_{0.68}MnO_{2.93}$, and non-aqueous delithiated $Li_{1.71}MnO_{3-\delta}$.

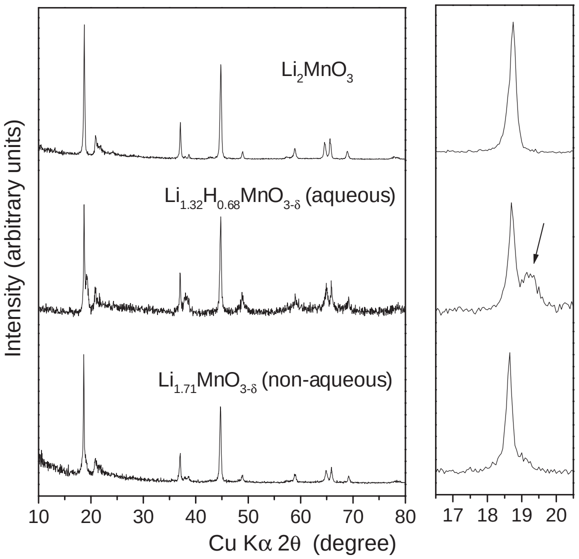

Fig. 6. Comparison of the X-ray diffraction patterns of the layered Li_2MnO_3, aqueous delithiated $Li_{1.32}H_{0.68}MnO_{2.93}$, and non-aqueous delithiated $Li_{1.71}MnO_{3-\delta}$. The arrow indicates the formation of a new phase for the aqueous delithiated sample.

Fig. 5 compares the FTIR spectra of Li_2MnO_3 and the aqueous and non-aqueous delithiated products. All the samples show absorption bands around $650\,cm^{-1}$, corresponding to the vibrations of MnO_6 octahedra. While the spectra of the non-aqueous delithiated $Li_{1.71}MnO_{3-\delta}$ is similar to that of the parent Li_2MnO_3 showing only the bands corresponding to MnO_6 octahedra without any O–H bands, the aqueous delithiated product shows additional absorption bands, including the characteristic absorption band at $\sim 3500\,cm^{-1}$ corresponding to O–H groups. The results suggest that while the non-aqueous chemical delithiation occurs by the oxidation of oxide ions in Li_2MnO_3, the aqueous delithiation may occur both by an ion-exchange of Li^+ by H^+ and an oxidation of O^{2-} ions, with the former occurring predominantly. It is interesting to note that while the aqueous delithiation of layered $LiNi_{0.5}Mn_{0.5}O_2$ does not seem to involve any oxygen loss, that with the layered Li_2MnO_3 does, which could be due to the availability of redox active Ni^{2+} in the former and oxidation beyond the redox inactive Mn^{4+} in the latter.

Fig. 6 compares the X-ray diffraction patterns of the parent Li_2MnO_3, and the aqueous and non-aqueous delithiated products. While the non-aqueous delithiated $Li_{1.71}MnO_{3-\delta}$ remains as a single phase product with its X-ray pattern similar to that of the parent Li_2MnO_3, the aqueous delithiated $Li_{1.32}H_{0.68}MnO_{2.93}$ shows the formation of an additional phase as indicated by the arrow in Fig. 6, corresponding to a proton incorporated P3-type phase reported in the literature [20,24]. The proton incorporated $Li_{2-x}H_xMnO_{3-\delta}$ has been reported to adopt a P3-type (oxygen stacking sequence of …AABBCC… along the *c* axis) structure similar to CrOOH and the hydrogen bonding in $Li_{2-x}H_xMnO_{3-\delta}$ has been considered to be the driving force for the transformation of the O3-type (oxygen stacking sequence of …ABCABC…along the *c* axis) Li_2MnO_3 to P3-type $Li_{2-x}H_xMnO_{3-\delta}$ phase [20,24]. These X-ray diffraction results further illustrate the difference between the aqueous and non-aqueous chemical delithiation processes.

3.4. Chemical delithiation of spinel $LiMn_2O_4$

With an aim to compare the chemical delithiation processes occurring in the layered $LiMO_2$ and spinel LiM_2O_4 oxides (Fig. 1b), we have also carried out the chemical delithiation from $LiMn_2O_4$ spinel in both the aqueous acid and non-aqueous acetonitrile media. Wet-chemical analysis indicated both the delithiation processes to give a product composition of $Li_{0.1}Mn_2O_4$ with an oxidation state of 3.95+ for Mn. The wet-chemical

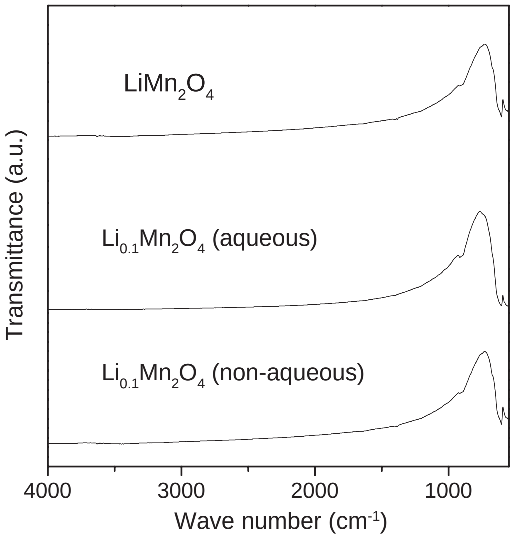

Fig. 7. Comparison of the FTIR spectra of the spinel $LiMn_2O_4$ and the aqueous and non-aqueous delithiated $Li_{0.1}Mn_2O_4$.

analysis data indicate that the $LiMn_2O_4$ spinel does not lose any oxygen from the lattice unlike the layered $LiMO_2$ oxides containing Co or Ni, which is consistent with the fact that the $Mn^{3+/4+}$:e_g lie well above the top of the O^{2-}:2p band unlike the $Co^{3+/4+}$:t_{2g} and $Ni^{3+/4+}$:e_g bands [12,30].

Fig. 7 compares the FTIR spectra of the parent $LiMn_2O_4$ and the aqueous and non-aqueous delithiated $Li_{0.1}Mn_2O_4$. All the samples show absorption bands around 650 cm^{-1}, corresponding to the vibrations of the MnO_6 octahedra. However, both the aqueous and non-aqueous delithiated samples do not show any characteristic IR absorption band (~3500 cm^{-1}) corresponding to O–H groups, indicating that no proton incorporation occurs into the spinel lattice even in aqueous acid medium. In addition, the TGA plot of the aqueous delithiated $Li_{0.1}Mn_2O_4$ (Fig. 4) shows little or no weight loss below 250 °C, indicating the absence of lattice protons and complementing the FTIR data. Also, the X-ray diffraction data compared in Fig. 8 reveal that both the aqueous and non-aqueous delithiated $Li_{0.1}Mn_2O_4$ maintains the cubic symmetry like the parent $LiMn_2O_4$, indicating that no structural changes occur.

It is interesting to note that while proton incorporation occurs readily into the layered oxide lattice during the aqueous delithiation process, it does not occur with the spinel lattice even in the proton-rich aqueous acid medium. These results are in agreement with the earlier literature reports [31–33] that an incorporation of protons by an ion-exchange mechanism occurs only into lithium rich $Li_{1+y}Mn_{2-y}O_4$ spinels with all the manganese present in the 4+ oxidation state. If Mn^{3+} ions are present in the structure as in the case of $LiMn_2O_4$, then the chemical lithium extraction takes place only by a redox mechanism involving the oxidation of Mn^{3+} to Mn^{4+}. Thus the incorporation of protons during the aqueous acid delithiation of layered Li_2MnO_3 could also be considered to be due to the absence of redox active Mn^{3+}. However, proton incorporation occurs during the aqueous delithiation of $LiNi_{0.5}Mn_{0.5}O_2$ even though it contains the redox active $Ni^{2+/3+}$ (Section 3.2). This could be due to the inability to fully convert all the Ni^{2+} to Ni^{4+} in acid medium and a consequent ion exchange by H^+ of the Li^+ ions present.

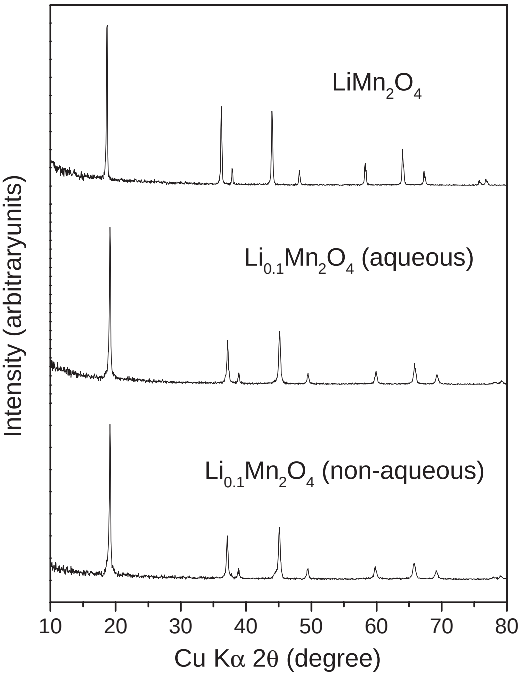

Fig. 8. Comparison of the X-ray diffraction patterns of the spinel $LiMn_2O_4$ and the aqueous and non-aqueous delithiated $Li_{0.1}Mn_2O_4$.

4. Conclusions

The possible incorporation of protons into the lattice during the chemical delithiation processes in both aqueous and non-aqueous media has been investigated with layered $LiCoO_2$, $LiNi_{0.5}Mn_{0.5}O_2$, and Li_2MnO_3 and spinel $LiMn_2O_4$. While FTIR could not be used to determine the incorporation of protons in the case of $LiCoO_2$ system as the products become metallic on extracting lithium, the technique could be used successfully with other layered $LiNi_{0.5}Mn_{0.5}O_2$ and Li_2MnO_3 systems as well as the spinel $LiMn_2O_4$ system as the delithiated products are semiconducting. The characterization data reveal that the delithiation of layered oxides involves an incorporation of protons into the lattice with aqueous acid, but not with an acetonitrile solution of the oxidizer NO_2BF_4. In contrast, the chemical delithiation of the spinel $LiMn_2O_4$ does not involve any proton insertion in both the aqueous and non-aqueous media. The results confirm that the loss of oxygen observed previously by us [11–16] at deep chemical lithium extraction of the layered LiMO$_2$ oxides with an acetonitrile solution of NO$_2$BF$_4$ is not adversely influenced by any proton insertion into the lattice. We are in the process of characterizing further the delithiated phases by prompt-gamma ray activation analysis (PGAA), which can quantitatively determine the proton contents [34,35] and complement the FTIR data.

Acknowledgments

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