Ion Exchange in Manganese Dioxide Spinel: Proton, Deuteron, and Lithium Sites Determined from Neutron Powder Diffraction Data

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The structures of deuterated, protonated, and relithiated forms of MnO_2 spinel, obtained by ion exchange of Li ions with D or H in a well-crystallized spinel $Li_{1.27}Mn_{1.73}O_4$ compound, have been determined by powder neutron diffraction. Refinements were carried out using the Rietveld method of powder profile analysis in the space group $Fd3m$. Li ions are removed from both tetrahedral 8*a* and octahedral 16*d* sites when $Li_{1.27}Mn_{1.73}O_4$ is contacted with DCl or HCl solution. The neutron diffraction data show that deuterium and hydrogen ions are predominantly incorporated into the crystal as $-OD$ and $-OH$ by bonding to lattice oxygen atoms without any other major change to the MnO_2 spinel structure. The $-OD$ and $-OH$ groups are directed into the interstitial space of the 8*a* tetrahedra, but with an orientation which suggests that the deuteron or proton site is favored for occupation only when the nearest neighbor octahedral 16*d* site contains no Mn ion. When the protonated compound is contacted with LiOH solution, reinserted Li ions relocate on tetrahedral 8*a* sites in preference to vacant octahedral 16*d* sites in the MnO_2 framework.

Introduction

Spinel-phase lithium manganates are three-dimensional insertion compounds with a high specificity for lithium.[1-15] The structure of spinel $LiMn_2O_4$, shown schematically in Figure 1, can be described in the $Fd3m$ space group in terms of a cubic close-packed array of oxygen ions in 32*e* sites. Manganese ions occupy half of the octahedral interstices (the 16*d* sites), forming a
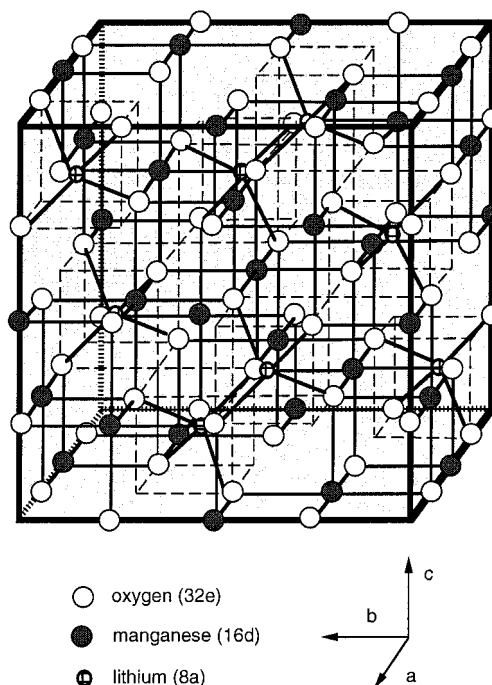

**Figure 1.** Representation of the spinel unit cell of $LiMn_2O_4$.

three-dimensional framework of edge-sharing MnO_6 octahedra. Lithium ions occupy one-eighth of the tetrahedral interstices (the 8*a* sites). Extraction of lithium from $LiMn_2O_4$ by chemical or electrochemical

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means leaves a spinel [Mn_2O_4] framework commonly denoted λ-MnO_2.[1] Lithium ions may then be reinserted into the vacant sites of the three-dimensional interstitial space.[3-15] In lithium batteries, the reinsertion of lithium occurs at 4 V vs Li/Li$^+$, hence the strong interest in the spinel manganates as electrode materials.[16-26] In aqueous solutions, λ-MnO_2 selectively scavenges lithium ions and is thus used for lithium recovery, separation, and sensing.[3-9]

Delithiated λ-MnO_2 may be prepared by extraction of lithium from $LiMn_2O_4$ in acid solution, because Mn^{3+} in the $LiMn_2O_4$ undergoes disproportionation to Mn^{2+} and Mn^{4+}, according to the reaction[1,5-7]

$$4LiMn^{3+}Mn^{4+}O_4 + 8H^+_{(aq)} \rightarrow$$
$$3[Mn^{4+}_2O_4] + 4Li^+_{(aq)} + 2Mn^{2+}_{(aq)} + 4H_2O \quad (1)$$
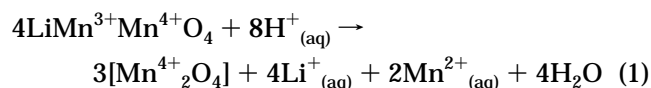
However, lithium is also extracted in acid solution from spinel lithium manganates containing little or no Mn^{3+}.[7,10] Such Mn^{4+}-rich spinels are usually formed by increasing the Li/Mn ratio and using low preparation temperatures (<600 °C) to give compounds of composition $Li_{1+x}Mn_{2-x}O_{4+\delta}$, with $0 \le x \le 0.33$ and $0 \le \delta \le 0.5(1 - 3x)$.[11,22,23] It has been shown that the mechanism of lithium extraction in these compounds is by ion exchange with protons.[7,11-13] The protonated MnO_2 phases give powder X-ray diffraction patterns which closely resemble those of λ-MnO_2 prepared by oxidation, suggesting that protons may be inserted topotactically, i.e., with little crystallographic rearrangement.

The $Li_{1+x}Mn_{2-x}O_{4+\delta}$ spinels are currently of special interest because of their high theoretical capacity for lithium insertion.[27-32] The high hydrogen content of the delithiated phases, up to 0.8 H per Mn, has also attracted attention to their properties as protonic oxides.[12] Determination of the proton insertion mechanism and the protonic species present in the lattice is

therefore of fundamental importance for developing applications. Spectroscopic studies have indicated that both hydroxyl groups and water form in manganese oxide spinel lattices when hydrogen is inserted.[11,12] However, the positions of the hydrogen atoms have not yet been determined directly.

We present here chemical and neutron powder diffraction data for protonated and deuterated MnO_2 compounds obtained by acid delithiation of a well-crystallized spinel $Li_{1+x}Mn_{2-x}O_{4+\delta}$ phase prepared using a novel high-temperature synthesis, as well as data for the parent and relithiated phases. The objectives of this study were to characterize the structures and chemical properties of the compounds, to determine proton/deuteron positions in the lattice, and to locate the sites for lithium sorption in the proton-form spinel. While neutron powder diffraction studies have been previously reported for $Li_{1+x}Mn_{2-x}O_{4+\delta}$ spinels prepared from lithium and manganese carbonates at 400 °C[23] and from eutectic mixtures of lithium acetate and manganese nitrate heated at 500 and 700 °C,[32] to our knowledge the data presented here are the first for protonated, deuterated, and chemically relithiated phases. The results complement and extend the conclusions of our recent studies using infrared and neutron spectroscopies,[11,12] X-ray absorption spectroscopy,[13,14] and atomistic simulations.[33]

Experimental Section

Samples. $Li_{1+x}Mn_{2-x}O_{4+\delta}$ was prepared from a commercial γ-MnO_2 product (Aldrich) by chemical insertion of lithium followed by oxidation and structural transformation through heating with oxygen. Five grams of γ-MnO_2 was immersed in a 3-fold excess of 2.3 M LiI solution in acetonitrile and reacted at 70 °C for 7 h. According to reported data,[34] these reaction conditions were expected to give a lithium-inserted Li_xMnO_2 product with $x > 0.5$. The oxide product was separated from the solution and washed thoroughly with acetonitrile and acetone. Analysis for Li, Mn, and O gave a composition of $Li_{0.74}MnO_2$, and powder X-ray diffraction showed that the γ-MnO_2 had retained its original structure but with some anisotropic expansion of the unit cell, in agreement with previously reported results.[34] The oxide was then placed in flowing oxygen and heated at 2°/min to 700 °C, maintained at 700 °C for 36 h, and cooled slowly while maintaining the oxygen flow, to obtain the oxidized spinel phase. Heating followed by slow cooling under a flow of oxygen has been shown to favor a high oxygen and Mn^{4+} content in lithium manganate spinels, allowing higher temperatures to be used for the obtainment of better crystallinity.[30-32] Well-crystallized Mn^{4+} lithium manganates are difficult to obtain in air due to the reduction of tetravalent Mn above 400 °C.[22,35]

Delithiation and proton insertion in the spinel lithium manganate to give protonated MnO_2 were achieved by stirring a portion of the oxide powder in 0.5 M HCl for 3 days, followed by washing with distilled water. Deuterated MnO_2 was obtained by delithiating a portion of the lithium manganate in 0.5 M DCl (37% DCl in D_2O, Merck > 99% purity, diluted in D_2O, Aldrich 99.9% purity) under dry nitrogen, followed by washing with D_2O and drying under dynamic vacuum. The deuterated sample was maintained sealed under dry nitrogen throughout the neutron experiment. Lithium was reinserted

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Table 1. Unit Cell Parameters (XRD, Standard Deviations in Parentheses) and Chemical Compositions of the Spinels Determined by Chemical and Thermogravimetric Analyses

sample	a_0 (Å)	wt % Li (± 0.1)	wt % Mn (± 0.7)	Li/Mn molar ratio (± 0.02)	wt % lattice H_2O (± 0.2)	H/Mn molar ratio (± 0.02)	n^+_{Mn} (± 0.02)	spinel composition[a]
$Li_{1+x}Mn_{2-x}O_{4+\delta}$	8.159(2)	5.0	55.4	0.73			3.95	$Li_{1.27}Mn^{III}_{0.09}Mn^{IV}_{1.64}O_{4.05}$
Deuterated MnO_2	8.063(2)	0.3	57.1	0.05	7.0^b	0.74^b	4.00	$H_{1.10}Li_{0.08}Mn^{IV}_{1.73}O_{4.05}$
Protonated MnO_2	8.069(3)	0.3	57.0	0.05	7.0	0.74	4.00	$H_{1.10}Li_{0.08}Mn^{IV}_{1.73}O_{4.05}$
Relithiated (H)MnO_2	8.184(3)	2.9	56.8	0.41	2.7	0.29	3.79	$H_{0.49}Li_{0.71}Mn^{III}_{0.36}Mn^{IV}_{1.37}O_{3.88}$

[a] Compositions for the deuterated, protonated and relithiated spinels are normalized to the Mn stoichiometry of the parent compound. H stoichiometry in the deuterated and protonated compositions has been written consistent with charge balance; up to 15% additional H may be present as lattice water according to thermogravimetry. [b] Assuming complete H/D exchange after exposure of the sample to atmospheric moisture.

into the protonated (H)MnO_2 by immersion in 0.025 M LiOH solution for 9 h.

Characterization of crystalline phases and calculation of unit cell parameters were initially performed from X-ray powder diffraction data recorded on a Philips diffractometer using Cu Kα radiation. Lithium and manganese contents were determined by flame spectrometry, and the oxygen content, which provides the average manganese oxidation state n^+_{Mn}, by backtitrating samples dissolved in oxalic acid with permanganate solution.[36] Lattice proton contents were estimated from the water loss between 100 and 300 °C,[7,11] measured by thermogravimetry using an automated Stanton Redcroft STA-781 series thermal analyzer at a heating rate of 2 °C/min.

Neutron Data Collection. Neutron diffraction data were collected on the neutron powder diffractometer (NPD) at the steady-state research reactor R2 at the Neutron Research Laboratory, Studsvik, Sweden. A monochromator system with two copper crystals (220 reflection) in parallel alignment was used. Samples were contained in vanadium cans. Data for the parent lithium manganate compound and for the deuterated sample were collected at ambient temperature (295 K) in the 2θ range 4.00–129.92° using a neutron wavelength of 1.47 Å. Data for the protonated and relithiated samples were collected at 10 K in the 2θ range 4.00–139.92° using a neutron wavelength of 1.21 Å.

The incoherent inelastic neutron scattering (INS) spectrum of the protonated MnO_2 was recorded on the TFXA spectrometer at the spallation neutron source ISIS (Rutherford Appleton Laboratory, U.K.). The sample was contained in aluminum foil, and data were collected at ca. 10 K for 2400 μAh.

Structure Refinement. Structure refinements of the neutron diffraction data sets were based on the Rietveld method[37] using the program Fullprof.[38] The powder diffraction profiles used in the refinements covered the 2θ range 15.00–129.92/139.92°. Neutron scattering lengths used were b(Li) = −1.9 fm, b(H) = −3.74 fm, b(D) = 6.67 fm, b(Mn) = −3.73 fm, and b(O) = 5.80 fm. The diffraction peaks were described by a pseudo-Voigt function, in which the Lorentzian contribution to a Gaussian peak-shape was refined. Peak asymmetry corrections were made for angles below 45° in 2θ. The angular dependence of the line widths was expressed by $H^2 = U \tan^2 \theta + V \tan \theta + W$, where H is the full width at half-maximum, θ is the Bragg angle, and U, V, and W are refinable parameters. Absorption effects were corrected by using the value $\mu R = 0.24$ experimentally determined from transmission measurements at $2\theta = 0°$. Background intensities were described by the polynomial expression $y_i = \sum B_m (2\theta_i/90 − 1)^m$, where $0 \leq m \leq 5$. The B_m coefficients for m = 0, 1, 2, 3, and 4 were refined together with one zero-point refinement parameter.

For each sample, the scale factor, lattice parameter, and atomic position parameter for oxygen were refined for the cubic phase in the space group $Fd3m$. Manganese ions were constrained to $16d$ octahedral sites, in accordance with diffraction and X-ray absorption data for spinel lithium manga-

nates.[13,23,32,39] Oxygen, manganese, and lithium contents were fixed to the mean values determined from the chemical analyses. The thermal displacement parameters B for the different sites in the parent $Li_{1+x}Mn_{2-x}O_{4+\delta}$ compound were refined. To determine the amount of deuterium in the deuterated sample, the B parameters of all other atoms were fixed at the values refined for the parent compound. This is valid since the data were collected at the same temperature for both samples. In view of the correlation between occupancy factors and displacement parameters, the B parameter for deuterium was fixed at the same value as that for $8a$ lithium atoms. Allowing the deuterium B value to vary in a final stage had no significant effect, either on the refined deuterium occupancy or on the other structural parameters; therefore, the fixed value was retained. Refinement of the data for the protonated sample was carried out in the same way as for the deuterated sample, but the displacement parameters for the manganese and oxygen atoms were refined because of the lower data collection temperature. The values of the displacement parameters for the lithium and hydrogen atoms were fixed at $B = 1.0$ Å^2, scaled to 1.6 times the refined oxygen value to maintain the same relationship between the B values as that used for the deuterated compound. Again, allowing the hydrogen B parameter to vary did not affect the other structural parameters or the refinement agreement factors. For the relithiated (H)MnO_2 compound, the displacement parameters for oxygen and manganese were refined together with the coordinates and occupancy factors for the remaining protons.

Results and Discussion

X-ray Diffraction and Chemical Characterization. The unit cell parameters calculated from the X-ray diffraction patterns and the chemical compositions determined by the chemical and thermal analyses are given in Table 1 for the parent, deuterated, protonated, and relithiated samples. The parent compound, after heating under oxygen flow, had a Li/Mn ratio of 0.73 and a high O/Mn content (n^+_{Mn} = 3.95). This gives values of x = 0.27 and δ = 0.05 if the composition is expressed in the notation $Li_{1+x}Mn_{2-x}O_{4+\delta}$. The XRD pattern showed sharp diffraction peaks for a single spinel phase with a unit cell parameter a_0 = 8.159(2) Å. The unit cell parameters of spinel lithium manganates are highly correlated with the manganese oxidation state,[22,35] and a value of 8.159 Å is consistent with the high Mn^{4+} content determined by chemical analysis. We note that there was no evidence in the XRD pattern for the parasitic rock-salt phase Li_2MnO_3 which often forms at the surface of spinel particles when high Li/Mn ratios are used in the preparation.[35] The high phase purity of the spinel can be attributed to the atomic-level mixing of lithium and manganese in the γ-MnO_2 pre-

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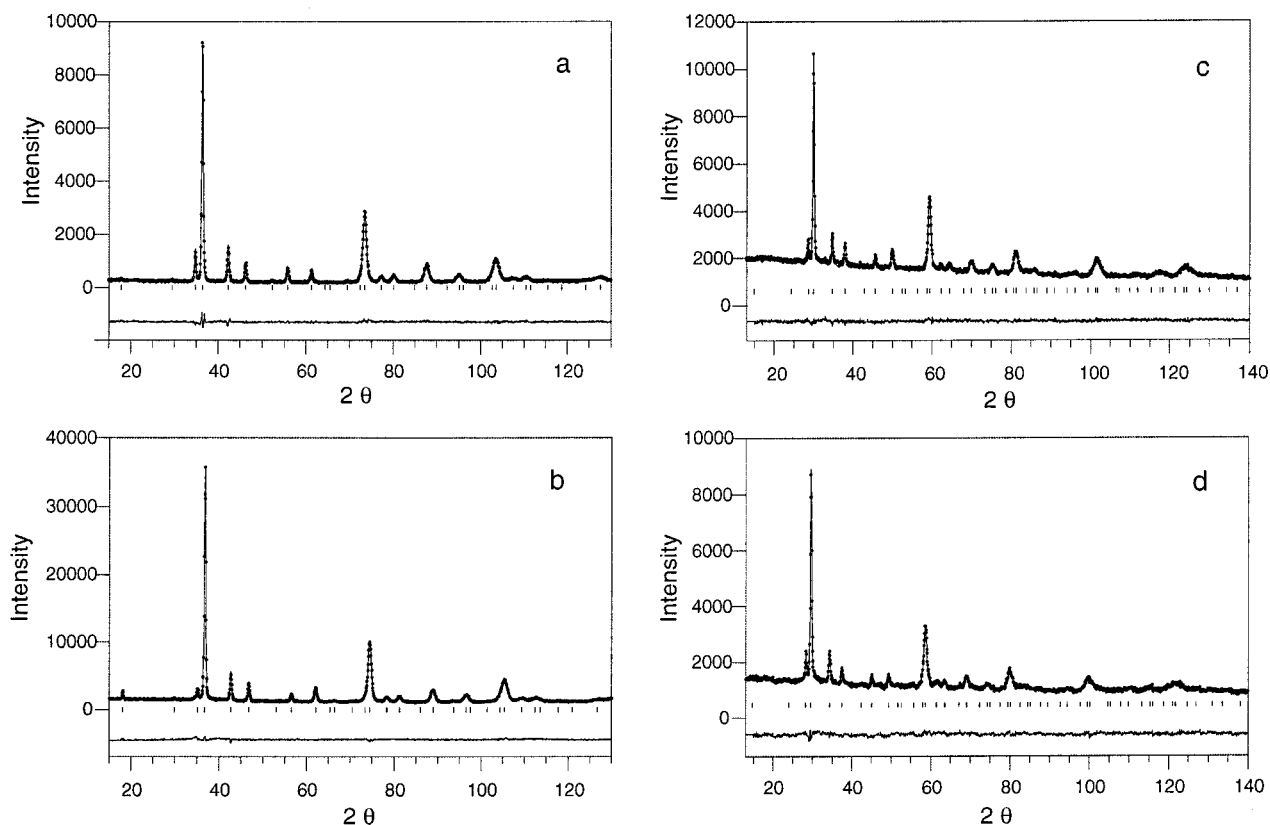(39) Fong, C.; Kennedy, B. J.; Elcombe, M. M. *Z. Kristallogr.* **1994**, *209*, 941.

Figure 2. Observed and calculated neutron diffraction profiles for (a) $Li_{1.27}Mn_{1.73}O_{4.05}$, (b) the deuterium-exchanged phase, (c) the proton-exchanged phase, and (d) the relithiated phase. Positions of theoretically allowed reflections and the difference between the observed and calculated profiles are shown below.

cursor, in which the lithium is dispersed by chemical insertion into specific crystallographic sites.

The products obtained by acid leaching in HCl and DCl solutions were single-phase cubic spinels with unit cell parameters of 8.069(3) and 8.063(2) Å. The compositional analyses showed that ca. 95% of the lithium had been extracted in both cases. The high Mn^{4+} content and phase purity of the parent lithium manganate compound was expected to favor a high level of proton or deuteron exchange for lithium. This expectation was confirmed by thermogravimetric analysis which showed a 7% weight loss attributable to lattice water[7,11] in the compounds after treatment in HCl and DCl, corresponding to a H(D)/Mn ratio of ca. 0.74, i.e., very close to the Li/Mn ratio of the parent lithium manganate. An increase of the manganese oxidation state to ca. 4.0 in both cases indicates disproportionation of the small amount of Mn^{3+} which was present in the parent lithium manganate according to the redox mechanism (reaction 1), which would also have contributed to a small fraction of the total lithium extraction.

In LiOH solution, the $(H)MnO_2$ compound sorbed Li ions to give a single relithiated phase containing ca. 56% of the lithium content of the original parent compound. The difference between the proton contents of the (H)-MnO_2 and the relithiated phase, as determined by thermogravimetry, corresponded closely to the amount of lithium reinserted, indicating that the reinsertion took place by a lithium−proton exchange mechanism. Consequently, ca. 40% of the protons inserted during delithiation remained in the relithiated material. It is noteworthy that the unit cell parameter of the relithi-

ated phase, 8.184(3) Å, was significantly higher than that of the parent lithium manganate. This correlates with a Mn^{3+} content in the relithiated compound which is markedly higher than that of the original parent phase. This reduction of lattice manganese to Mn^{3+} does not appear to be associated with lithium reinsertion, since practically all the reinserted lithium can be accounted for by lithium−proton exchange. It appears to be the result of some surface disproportionation of Mn^{4+} in the hydroxide solution, which also produced dissolved permanganate ions. As a result, the relithiated spinel compound is slightly oxygen-deficient relative to its precursor phases.

Analysis of the Neutron Diffraction Data. The observed and calculated neutron diffraction profiles of the four samples are shown in Figure 2. The refined crystallographic parameters are given in Table 2, and the refined cation distributions are summarized in Table 3. Bond angles and interatomic distances in the structures are given in Table 4.

The excess oxygen content of the parent compound, $\delta = 0.05$, implies that the spinel structure contained a fraction of cation vacancies. The Mn/O stoichiometry leaves ca. 15% of the $16d$ octahedral sites unoccupied by manganese. The best agreement between the calculated and observed data during refinement was obtained when all these remaining $16d$ octahedral sites were filled with lithium but only 96% of the $8a$ tetrahedral sites were occupied. Difference Fourier maps confirmed that the $8a$ and $16d$ sites were preferred for lithium compared to the $16c$ site. The cation distribution is therefore similar to that determined from neutron

Table 2. Refined Crystallographic Parameters Determined from the Neutron Diffraction Data (Space Group $Fd\bar{3}m$)[a]

atom	position	x	y	z	B (Å²)	occupancy
(a) $Li_{1.27}Mn_{1.73}O_{4.05}$, $a_0 = 8.1484(4)$ Å (295 K)[b]						
Li(1)	8a	0.125	0.125	0.125	1.6(2)	0.24
Li(2)	16d	0.5	0.5	0.5	0.41(5)	0.07
Mn	16d	0.5	0.5	0.5	0.41(5)	0.43
O	32e	0.2631(1)	0.2631(1)	0.2631(1)	0.96(3)	1.00
(b) Deuterated MnO_2, $a_0 = 8.0537(3)$ Å (295 K)[c]						
D	96g	0.221(2)	0.167(1)	0.167(1)	1.6	0.13(1)
Li	8a	0.125	0.125	0.125	1.6	0.02
Mn	16d	0.5	0.5	0.5	0.41	0.43
O	32e	0.2617(1)	0.2617(1)	0.2617(1)	0.96	1.00
(c) Protonated MnO_2, $a_0 = 8.0956(7)$ Å (10 K)[d]						
H	96g	0.216(4)	0.170(2)	0.170(2)	1.00	0.15(1)
Li	8a	0.125	0.125	0.125	1.00	0.02
Mn	16d	0.5	0.5	0.5	0.16(6)	0.43
O	32e	0.2619(1)	0.2619(1)	0.2619(1)	0.65(4)	1.00
(d) Relithiated (H)MnO_2, $a_0 = 8.1962(11)$ Å (10 K)[e]						
H	96g	0.21(1)	0.17(1)	0.17(1)	1.00	0.07(2)
Li	8a	0.125	0.125	0.125	1.00	0.18
Mn	16d	0.5	0.5	0.5	0.27(9)	0.45
O	32e	0.2620(2)	0.2620(2)	0.2620(2)	0.99(6)	1.00

[a] Standard deviations are in parentheses. B and occupancy values given without standard deviations have been fixed (see text). [b] $R_p = 5.17\%$. $R_{wp} = 6.87\%$. $R_{exp} = 5.18\%$. $R_{Bragg} = 3.97\%$. $\chi^2 = 1.76$ for 45 reflections and 15 variables. [c] $R_p = 2.79\%$. $R_{wp} = 3.77\%$. $R_{exp} = 2.40\%$. $R_{Bragg} = 3.99\%$. $\chi^2 = 2.46$ for 41 reflections and 16 variables. [d] $R_p = 2.23\%$. $R_{wp} = 2.83\%$. $R_{exp} = 2.52\%$. $R_{Bragg} = 6.12\%$. $\chi^2 = 1.27$ for 69 reflections and 18 variables. [e] $R_p = 3.23\%$. $R_{wp} = 4.05\%$. $R_{exp} = 2.89\%$. $R_{Bragg} = 8.94\%$. $\chi^2 = 1.96$ for 70 reflections and 18 variables.

Table 3. Cation Distributions in Spinel Notation

sample	cation distribution
$Li_{1.27}Mn_{1.73}O_{4.05}$	$(Li_{0.96}\square_{0.04})_{8a}[Li_{0.29}Mn_{1.71}]_{16d}O_4$
deuterated MnO_2	$(Li_{0.08}\square_{0.92})_{8a}[Mn_{1.71}\square_{0.29}]_{16d}O_4\{D_{0.53}\square_{11.47}\}_{96g}$
protonated MnO_2	$(Li_{0.08}\square_{0.92})_{8a}[Mn_{1.71}\square_{0.29}]_{16d}O_4\{H_{0.61}\square_{11.39}\}_{96g}$
relithiated (H)MnO_2	$(Li_{0.73}\square_{0.27})_{8a}[Mn_{1.78}\square_{0.22}]_{16d}O_4\{H_{0.27}\square_{11.73}\}_{96g}$

data for $Li_{1+x}Mn_{2-x}O_{4+\delta}$ compounds ($x = 0.17$ and 0.22) prepared in air at 400 °C, which also contained vacancies on 8a tetrahedral sites while the 16d octahedral sites were fully occupied by manganese and lithium.[23]

The structures of the deuterated and protonated compounds were refined with the manganese occupancy in the 16d octahedral sites fixed at the same value as that of the parent spinel, consistent with the chemically determined stoichiometries. For both compounds the difference Fourier maps indicated the presence of some lithium in 8a tetrahedral sites. The small amounts of lithium remaining in the compounds were therefore refined fully in that position. Attempts to refine any lithium on the vacant 16d octahedral sites led to significantly worse fits to the experimental data.
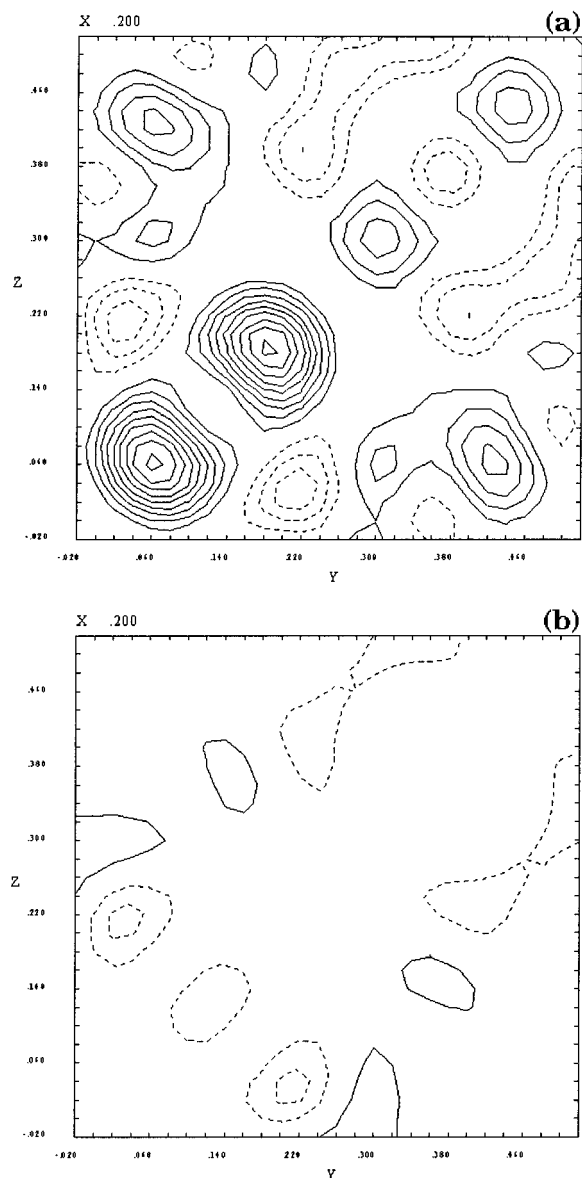

Figure 3. Contour plots of the Fourier difference calculations for the deuterium-exchanged MnO_2 (a) before and (b) after inclusion of deuterium in the refinement, indicating the presence of deuterium atoms in the interstitial space of the 8a tetrahedron (section at height $x = 0.20$ perpendicular to the *ab*-plane; arbitrary contour interval).

Refinement of the neutron diffraction profile for the deuterated MnO_2 sample confirmed the presence of deuterium atoms in ordered positions. After an initial refinement including only oxygen, manganese, and lithium atoms, the difference Fourier map (Figure 3a)
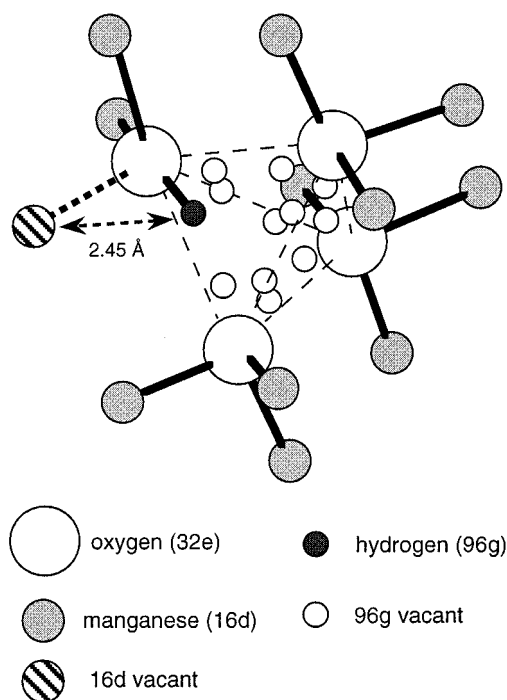
Table 4. Interatomic Distances (Å) and Bond Angles (deg)[a]

sample	Mn/Li_{16d}–O	Li/o_{8a}–O	O–H(D)	H(D)···O	O–H(D)···O	∠O–H(D)···O	H(D)–$Mn/\square_{16d}$
$Li_{1.27}Mn_{1.73}O_{4.05}$	1.94(1)	1.95(1)					
deuterated MnO_2	1.92(1)	1.91(1)	1.12(1)	2.07(1)	3.12(1)	154.2(2)	2.43(1)
				2.49(1)	3.12(1)	113.8(2)	2.77(1)
				2.49(1)	3.12(1)	113.8(2)	2.77(1)
protonated MnO_2	1.93(1)	1.92(1)	1.11(2)	2.12(2)	3.13(1)	150.6(4)	2.47(3)
				2.48(3)	3.13(1)	116.4(5)	2.76(2)
				2.48(3)	3.13(1)	116.4(5)	2.76(2)
relithiated (H)MnO_2	1.96(1)	1.94(1)	1.10(6)	2.19(6)	3.18(1)	148.3(9)	2.51(8)
				2.50(7)	3.18(1)	118.5(8)	2.77(6)
				2.50(7)	3.18(1)	118.5(8)	2.77(6)

[a] Standard deviations are in parentheses.

Figure 4. Schematic representation of an 8*a* tetrahedral interstice in hydrogen- or deuterium-exchanged MnO_2 spinel, showing the 96*g* H (D) sites determined from the neutron diffraction data. The 96*g* site is considered to be occupied when the near 16*d* site at 2.45 Å distance is vacant.

showed positive residual peaks in 96*g* sites ca. 1 Å from the oxygen atoms. Deuterium was therefore refined at these sites to give good agreement between the calculated and observed data. The difference Fourier map at this stage showed no other pronounced features (Figure 3b). The [111] peak at ca. 19° in 2θ could be reproduced only when deuterium was included in the refinements at the 96*g* sites in the MnO_2 structure.

Refinement of the hydrogen positions in the protonated MnO_2 compound using the 96*g* deuterium coordinates as a starting point also produced a significantly better fit between the calculated and experimental profiles for this compound than initial refinements which included only oxygen, manganese, and lithium. The final hydrogen position was identical within the 3σ limit to that of the deuterium in the deuterated MnO_2.

Loss of oxygen from the protonated MnO_2 compound during relithiation resulted in a small loss of cation vacancies and a corresponding increase in the fraction of 16*d* octahedral sites occupied by manganese. The total negative scattering in 16*d* sites was consistent with the presence of manganese only, and attempts to refine lithium in these sites produced negative site occupancy factors. It was concluded that reinserted lithium was in 8*a* tetrahedral sites only. A small amount of hydrogen was also refined in the same site as that determined for the protonated MnO_2 before relithiation.

Structural Model for Hydrogen and Deuterium in Spinel MnO_2. The 96*g* position refined for the protons and deuterons is related to the 32*e* oxygen site in the spinel structure as illustrated in Figure 4. In a regular $(Li)_{8a}[Mn_2]_{16d}O_4$ spinel, oxygen is on a 3-fold axis of symmetry which lies along the O–Li bond. There are three equivalent proton (deuteron) sites for each oxygen distributed around this axis at O–H(D) dis-

tances of 1.1 Å. In these positions, the protons (deuterons) are directed toward the three oxygen atoms defining the opposite corners of the 8*a* tetrahedron, displaced off the O–O lines by ca. 19°. A maximum of only one proton (deuteron) can be bonded to any oxygen, as two protons (deuterons) attached to the same oxygen would give rise to unreasonably short H–H or D–D distances of 0.62 Å. The hydrogen and deuterium observed in this site can therefore be assigned to –OH and –OD groups directed in one of three equivalent orientations into the 8*a* tetrahedral space of the spinel interstitial channels.

There are twelve 96*g* proton (deuteron) sites neighboring each 8*a* tetrahedral site, but only ca. 5% of these appear to be occupied in the structure. Those 8*a* tetrahedra containing residual lithium ions will be excluded from occupation of any of the twelve sites, as this would correspond to a short Li–H(D) distance of ca. 0.9 Å. Nevertheless, the chemical analyses for lithium content and manganese oxidation state in the protonated and deuterated phases indicated that ca. 1.1 H (or D) had been inserted per spinel formula unit, supported by thermogravimetric analyses which showed up to 0.64 mol of lattice water in these compounds. If all this inserted H (D) was to form hydroxyl (deuterioxyl) with lattice oxygen, at least 20% of the vacant 8*a* tetrahedra would be required to accommodate two hydroxyl or deuterioxyl species. However, it may be noted that the simultaneous occupation of more than one of the twelve sites in a vacant 8*a* tetrahedron would give rise to close H–H or D–D interactions of between 1.00 and 1.75 Å. Therefore, if two hydroxyl or deuterioxyl groups were to form around the same 8*a* interstice, the H or D atoms might be expected to be displaced off these sites, producing disordering effects and resulting in the calculation of a reduced site occupancy from the diffraction data. The difference between the inserted H (D) content determined by chemical and thermogravimetric analyses and the occupancies calculated for the 96*g* sites from the diffraction data (ca. 0.6 H per formula unit) might be partly attributed to such a disordering effect.

Complementary data concerning the protonic species in the protonated MnO_2 compound were obtained from the inelastic neutron scattering (INS) spectrum shown in Figure 5. The essential characteristics of the spectrum of this sample, prepared by the novel higher-temperature route, are the same as those observed in the INS spectra of proton-exchanged $Li_{1.33}Mn_{1.67}O_4$ compounds prepared at 400 °C.[11] The spectrum is dominated by one intense peak at 908 cm^{-1} assigned to the γ(OH) deformation mode of a hydroxyl group[11,12] which indicates, in agreement with the diffraction data, that the majority of protons inserted into the compound form hydroxide ions located in one type of site. Scattering between 300 and 700 cm^{-1} corresponds to vibrations of $[MnO_6]$ octahedra which would be activated in INS if the hydrogen atoms were carried with the vibrating oxygen atoms, confirming that the hydroxide ions are located in the MnO_2 framework.

The O–H(D) distance of 1.1 Å determined from the neutron refinements may be compared to similar values determined for deuterioxyl and hydroxyl groups in
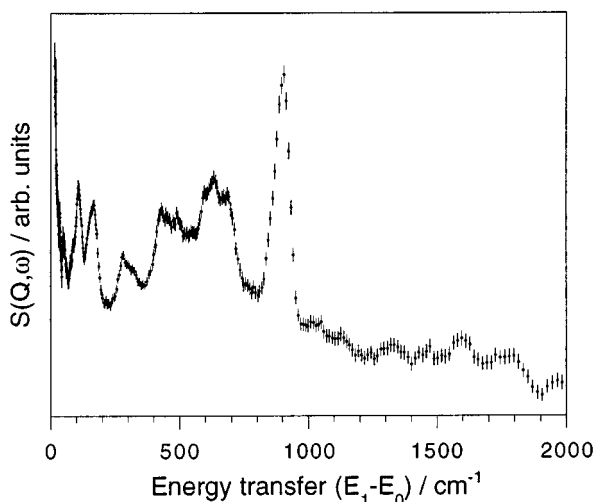
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Figure 5. Inelastic neutron scattering spectrum of the proton-exchanged MnO_2 spinel phase.

chromium, molybdenum, and tungsten oxides.[40–43] However, the O–H(D) and O–H(D)$\cdots$O distances should be regarded as upper limits to the actual values, since oxygen atoms are likely to be slightly relaxed from their average positions when a deuterium or hydrogen atom is attached. Nonetheless, only weak hydrogen bonding to the neighboring oxygen would be expected for O–H(D)$\cdots$O distances > 3 Å, which is consistent with the relatively low energy of the OH deformation mode at 908 cm^{-1}. Indeed, the low wavenumber of this mode in spectroscopic data for protonated lithium manganate spinels prepared at 400 °C led to an earlier prediction that hydroxyl groups in spinel MnO_2 would be orientated toward the neighboring oxygen across the $8a$ tetrahedral site, as other orientations would lead to stronger hydrogen bond interactions and give rise to deformation modes at higher frequencies.[11] The orientation determined here by neutron diffraction supports such an analysis.

The neutron diffraction data can afford no direct information as to whether the hydroxyl (deuterioxyl) groups are randomly distributed in the structure or ordered in some respect with regard to the host MnO_2 lattice. However, it is significant that these data show that ca. 15% of the $16d$ octahedral sites are vacant in the delithiated phases. Chemical analyses have shown that insertion of protons in spinel MnO_2 is systematically correlated with the presence of $16d$ octahedral vacancies in the MnO_2 host framework.[7,12,15] The $16d$ vacancies are expected to induce local electronic and structural perturbations in the lattice, particularly affecting the octahedron of six oxygen atoms surrounding the vacant site. These oxygen atoms, coordinated to only two rather than three Mn ions, will also be more basic sites for the formation of chemical bonds with hydrogen than oxygen atoms not localized at Mn vacancies.

(40) Christensen, A. N.; Hansen, P.; Lehmann, M. S. *J. Solid State Chem.* **1976**, *19*, 299.
(41) Christensen, A. N.; Hansen, P.; Lehmann, M. S. *J. Solid State Chem.* **1977**, *21*, 325.
(42) Wiseman, P. J.; Dickens, P. G. *J. Solid State Chem.* **1973**, *6*, 374.
(43) Dickens, P. G.; Birtell, J. J.; Wright, C. J. *J. Solid State Chem.* **1979**, *28*, 185.

Table 4 shows that one of the three $16d$ octahedral sites neighboring each proton (deuteron) position is at a relatively close distance of 2.45 Å to the H(D) atom. Orientation of the hydroxyl or deuterioxyl in this position should therefore be considered unfavorable with regard to a close Mn$\cdots$H(D) interaction, if the $16d$ site is occupied by manganese. On the other hand, this orientation would actually be favored if the near $16d$ site in the local structure were indeed one of the ca. 15% unoccupied sites. In support of these conclusions, recent modeling of the spinel MnO_2 lattice using atomistic simulation methods has predicted that the absence of a cation in one of the three neighboring $16d$ sites would favor the formation of hydroxyl groups in the local structure, and would result in a preferential orientation of the hydroxyl proton into nearly the same site as that determined here from the neutron data.[33]

To further test this structural model, the frequency of the $\gamma(OH)$ mode was calculated for the hydroxyl proton located in the position determined from the neutron data, both with all three neighboring $16d$ sites occupied by manganese and with a vacancy in the $16d$ site at 2.45 Å from the proton [B. Ammundsen and M. S. Islam, unpublished; calculations were performed using GULP (General Utility Lattice Programme), developed by J. D. Gale, Royal Institution of GB and Imperial College, London, 1991–1997]. With all three neighboring $16d$ sites occupied by manganese ions, the frequency of the $\gamma(OH)$ mode was calculated as 990 cm^{-1}. However, when the Mn ion in the $16d$ site at 2.45 Å from the proton was removed, the calculation gave a frequency of 906 cm^{-1}, in excellent agreement with the observed vibration at 908 cm^{-1}.

Finally, it has been observed that reinsertion of lithium into protonated spinel MnO_2 compounds results in the disappearance of the lattice hydroxyl mode at 908 cm^{-1} from the vibrational spectrum.[12] The neutron diffraction data presented here show that lithium ions are reinserted preferentially into $8a$ tetrahedral sites. The disappearance of the hydroxyl vibration with reinsertion of lithium is therefore explained; simultaneous occupation of the $8a$ tetrahedron by lithium and hydroxyl is excluded by a prohibitively close Li–H distance. The hydrogen atoms remaining in the relithiated MnO_2 phase after the incomplete reexchange with lithium ions as seen by neutron diffraction, other than those occupying positions neighboring the small fraction of $8a$ sites which remain vacant, could not be located from the diffraction data. Previous studies suggest that the nonexchanged hydrogen remaining in the relithiated structure of MnO_2 is predominantly in the form of disordered structural water.[12]

Conclusions

The method of synthesis described here produces well-crystallized $Li_{1+x}Mn_{2-x}O_{4+\delta}$ compounds with high phase purity, which take up high amounts of deuteron and proton during the extraction of lithium from both $8a$ tetrahedral and $16d$ octahedral sites in acid solution. The proton/deuteron sites identified by neutron diffraction in the spinel MnO_2 structure are located in the three-dimensional interstitial channel space, and correspond to hydroxyl or deuterioxyl groups oriented toward neighboring oxygen atoms along the edge of the

vacated 8*a* tetrahedra. These sites appear to be favored for occupation when the nearest neighboring 16*d* octahedral site has also been vacated by the extraction of a lithium ion. The chemical and structural data demonstrate the key relationship between the occupied cation sites in a spinel lithium manganate and its chemical properties with regard to lithium−proton exchange. Development of lithium manganates for proton insertion and ion-exchange applications therefore requires a knowledge of the cation distribution of the lattice framework and its optimization to induce the desired chemical properties.