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Thermochemistry of $Li_{1+x}Mn_{2-x}O_4$ ($0 \leqslant x \leqslant 1/3$) spinel

Miaojun Wang, Alexandra Navrotsky*

Thermochemistry Facility and NEAT ORU, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA

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Abstract

Lithium substituted $Li_{1+x}Mn_{2-x}O_4$ spinel samples in the entire solid solution range ($0 \leqslant x \leqslant 1/3$) were synthesized by solid-state reaction. The samples with $x < 0.25$ are stoichiometric and those with $x \geqslant 0.25$ are oxygen deficient. High-temperature oxide melt solution calorimetry in molten $3Na_2O \cdot 4MoO_3$ at 974 K was performed to determine their enthalpies of formation from constituent binary oxides at 298 K. The cubic lattice parameter was determined from least-squares fitting of powder XRD data. The variations of the enthalpy of formation from oxides and the lattice parameter with x follow similar trends. The enthalpy of formation from oxides becomes more exothermic with x for stoichiometric compounds ($x < 0.25$) and deviates endothermically from this trend for oxygen-deficient samples ($x \geqslant 0.25$). This energetic trend is related to two competing substitution mechanisms of lithium for manganese (oxidation of Mn^{3+} to Mn^{4+} versus formation of oxygen vacancies). For stoichiometric spinels, the oxidation of Mn^{3+} to Mn^{4+} is dominant, whereas for oxygen-deficient compounds both mechanisms are operative. The endothermic deviation is ascribed to the large endothermic enthalpy of reduction.
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1. Introduction

$LiMn_2O_4$ is considered as a promising replacement for $LiCoO_2$ as the active cathode material in lithium ion batteries due to the low cost, non-toxicity of manganese. It has the spinel structure ($A[B]_2X_4$, space group $Fd\bar{3}m$) with Li ions occupying one-eighth of the tetrahedral sites (8*a* sites) and Mn ions occupying half of the octahedral sites (16*d* sites) in a cubic close-packed array of oxygen ions (32*e* sites). The unoccupied 16*c* sites form a three-dimensional network which is the pathway for the transport of lithium ions. Lithium can be extracted from or inserted into $LiMn_2O_4$. Lithium extraction from and insertion into $LiMn_2O_4$ occur at approximately 4 and 3 V, respectively. Lithium intercalation at 3 V ($Li_xMn_2O_4$, $1 \leqslant x \leqslant 2$) is accompanied by a symmetry reduction from cubic to tetragonal resulted from cooperative Jahn–Teller distortion of Mn^{3+} ions [1]. The structural change results in rapid capacity loss of the cell. When operating at 4 V ($Li_xMn_2O_4$, $0 \leqslant x \leqslant 1$), the cubic symmetry of the electrode is retained through the cycle. Symmetry change caused by Jahn–Teller distortion is one of the factors for the slow capacity loss [1,2]. It is believed that there is a critical average oxidation state (AOS) of manganese (3.5) above which Jahn–Teller effect is suppressed [3]. Substitution of lower valent metals for manganese in $LiMn_2O_4$ increases the AOS of manganese.

$Li_{1+x}Mn_{2-x}O_4$, the lithium substituted spinel, demonstrated longer charge–discharge cycle life. However, excess lithium reduces the capacity of the electrode [2]. In $Li_{1+x}Mn_{2-x}O_4$ ($Li[Li_{x/2}Mn_{(1-x/2)}]_2O_4$, put in the form of the spinel formula), the excess lithium shares the 16*d* octahedral sites with manganese.

$Li_{1+x}Mn_{2-x}O_4$ is the solid solution between the end members $LiMn_2O_4$ and $Li_{4/3}Mn_{5/3}O_4$ ($Li_4Mn_5O_{12}$). In stoichiometric $Li_{1+x}Mn_{2-x}O_4$, upon the substitution of lithium for manganese, charge compensation is realized by the oxidation of Mn^{3+} to Mn^{4+}. Thus, all

*Corresponding author. Fax: +1 530 752 9307.
E-mail address: anavrotsky@ucdavis.edu (A. Navrotsky).

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manganese is tetravalent in $Li_{4/3}Mn_{5/3}O_4$. However, the oxygen content and AOS of manganese are strong functions of synthesis conditions. $Li_{1+x}Mn_{2-x}O_4$ with large x values ($x>0.25$) tends to be oxygen deficient and the AOS of manganese is smaller than the maximum theoretical value [4,5]. In these cases, oxygen vacancies are formed for charge balance. The electrochemical properties are influenced by the stoichiometry of oxygen. Gao and Dahn [6] showed that oxygen-deficient compounds have inferior electrochemical properties.

Despite extensive studies on these compounds, little has been reported on their thermodynamic properties. Idemoto et al. [7–9] determined the enthalpy of formation for $Li_{1+x}Mn_{2-x}O_4$ ($0\leqslant x\leqslant 0.1$), $LiMn_{2-x}Mg_xO_4$ ($0\leqslant x\leqslant 0.2$), and $Li_4Mn_5O_{12}$ and $Li_2Mn_4O_9$ using acid solution calorimetry. They found that the enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ became only slightly exothermic with increasing x for the range they studied [7]. The effect of oxygen deficiency on charge and magnetic ordering in $LiMn_2O_{4-\delta}$ was studied through heat capacity measurements by Tachibana et al. [10]. Yamaguchi et al. [11] studied the heat of formation at 876 K for $LiM_yMn_{2-y}O_4$ (M = Co, Cr, Ni, Mg, Li) by measuring the reaction heat of the starting materials to form the solid solutions in a Tian–Calvet-type high-temperature microcalorimeter. However, not knowing the degree of completion of the reaction and the actual composition of the final product in the calorimeter for the short time of each calorimetric experiment (1 h) makes it hard to evaluate their data. In this work, we report the enthalpies of formation from oxides and investigate the energetic trends for $Li_{1+x}Mn_{2-x}O_4$ in the entire solid solution range. The substitution mechanisms of lithium for manganese and the corresponding energetics are discussed.

2. Experimental

2.1. Sample preparation and characterization

All samples used in this study are synthetic. $Li_{1+x}Mn_{2-x}O_4$ ($0\leqslant x\leqslant 0.1$) were synthesized by solid-state reaction of Li_2CO_3 (Alfa Æsar, 99.0% min assay) and MnO_2 (Johnson Matthey Electronics, 99+% metals basis). The starting materials mixture in stoichiometric ratio was pelletized and calcined at 723 K for 12 h and then heated at 1023 K for 24 h in air to synthesize $LiMn_2O_4$. For $Li_{1.05}Mn_{1.95}O_4$ and $Li_{1.10}Mn_{1.90}O_4$, the heat treatment was 4 h at 873 K followed by 24 h at 1023 K in flowing oxygen. $Li_{1+x}Mn_{2-x}O_4$ ($0.15\leqslant x\leqslant 1/3$) was synthesized by reacting appropriate amounts of $LiMn_2O_4$ and Li_2CO_3 in flowing oxygen. For $x<0.25$, the reactants were heated at 823 K for 12 h. For $x\geqslant 0.25$, the reactants were heated at 673 K for 12 h one–three times with intermediate grinding and pelletizing followed by a final heating at 773 K for 12 h. The sample with $x=0.25$ and heat-treated at 673 K for 12 h was cooled at a cooling rate of 1 K/min. Other samples were cooled at a cooling rate of 5 K/min.

The manganese oxides used in the in situ weight change (TG) experiments are MnO_2, Mn_2O_3, Mn_3O_4 and MnO. MnO_2 is high-purity (99.999%) pyrolusite phase (Alfa Æsar). Mn_2O_3 was prepared by heating MnO_2 (99.999%) in air at 973 K for 6 h and furnace cooled. Mn_3O_4 was obtained by heating MnO_2 in air at 1273 K for 12 h and then quenched in air. MnO was synthesized from decomposition of manganese oxalate ($MnC_2O_4\cdot 2H_2O$, Alfa Æsar, Mn 30% min; washed by deionized water, filtered and dried) at 673 K under reducing atmosphere (10% H_2 + Ar) for 4 h followed by annealing at 973 K in argon for 6 h [12]. The same oxide samples MnO_2, Mn_2O_3 and Mn_3O_4 were used for calorimetry.

Phase identification and phase purity evaluation were carried out by powder X-ray diffraction (XRD). The XRD data were collected on a Scintag PAD V diffractometer using Cu$K\alpha$ radiation with a step size of 0.02° in the 2θ range of 15–70° with a dwell time of 3 s for phase identification, and in the 2θ range of 20–34° with a dwell time of 10 s to check phase purity (if there is any Li_2MnO_3 impurity). The 2θ range of 20–34° was used because of the overlap of the main XRD peaks of the spinel phase and Li_2MnO_3. At this 2θ range, there are some weak reflections from Li_2MnO_3 and only one weak reflection from the spinel phase and no overlap of peaks. For $Li_{1+x}Mn_{2-x}O_4$ samples with $x\leqslant 0.25$, no Li_2MnO_3 impurity was detected and the samples are considered single phase. For samples $Li_{1.3}Mn_{1.7}O_4$ and $Li_{4/3}Mn_{5/3}O_4$, there is a small amount of Li_2MnO_3 impurity. Other synthesis methods [4,13] were also tried but these two samples could not be synthesized without the accompanying Li_2MnO_3 impurity. Therefore the samples from solid-state reaction were used for subsequent experiments. The amount of Li_2MnO_3 was estimated by refinement of the XRD data collected from 10° to 100° 2θ with a step size of 0.02° and a dwell time of 10 s.

Lattice parameters were determined from the XRD data. The sample powders for each composition were mixed with a silicon standard (SRM 640*b*, NIST) in a~4:1 weight ratio. Powder XRD data were collected from 15° to 70° 2θ with a step size of 0.02° and a dwell time of 3 s. Peak positions were calibrated using the silicon as the standard, and lattice parameter a was refined with the program MDI JADE 6.0.

The AOS of manganese was determined by a potentiometric-redox titration method described in detail in Ref. [14]. The titration method includes two steps. The first step (potentiometric titration) determines the total amount of manganese in the sample and the second step (redox titration) determines the amount of

manganese with oxidation states larger than 2. In the first step, ~20 mg (W_1) sample was completely dissolved in 2 ml of concentrated hydrochloric acid with stirring and mild heating on a hot plate. The resulting solution was diluted with deionized water to 100 ml in a 100 ml volumetric flask. Twenty-five milliliters of diluted sample solution and 50 ml saturated sodium pyrophosphate solution were mixed and the pH value was adjusted to ~7 with hydrochloric acid. The system was titrated with a ~0.001 M potassium permanganate solution which was standardized against $Na_2C_2O_4$. The potential (in mV) of the system during titration was measured using an Orion 250Aplus pH meter with a Corning platinum combination redox electrode. The end point was determined from the inflection point of the titration curve (potential vs. volume of titrant added). The potentiometric titration was repeated three times and the average volume of the $KMnO_4$ solution was taken as V_1. In the second step, ~20 mg (W_2) sample was dissolved in 10 ml 0.05 M $FeSO_4$ solution with stirring and mild heating on a hot plate. The solution was titrated with the same potassium permanganate solution and the end point (V_3) was reached when the color of the solution changed to pale purple. A blank titration was carried out on 10 ml 0.05 M $FeSO_4$ solution. The volume of $KMnO_4$ solution used in the blank titration is denoted V_2. Thus, the AOS of manganese is

$$\mathrm{AOS} = \frac{5}{16} \times \frac{V_2 - V_3}{V_1} \times \frac{W_1}{W_2} + 2. \quad (1)$$

The redox titration was also repeated three or four times.

2.2. Calorimetry

High-temperature oxide melt solution calorimetry was performed using a Tian Calvet twin calorimeter described by Navrotsky [15,16] to determine the enthalpy of formation from binary oxides for the samples. Samples in the form of pellets (~6 mg) were dropped from room temperature (298 K) into molten sodium molybdate ($3Na_2O \cdot 4MoO_3$) solvent at 974 K in platinum crucibles located in the calorimeter chambers. The heat of drop solution (ΔH_{ds}) is the sum of heat content of the sample from 298 to 974 K and the heat of dissolution into the solvent (with evolution of O_2). An appropriate thermodynamic cycle is designed to determine the enthalpy of formation from binary oxides for the samples. Flushing argon gas was employed to maintain the desirable atmosphere and bubbling argon gas introduced into the solvent to help the sample dissolve and to prevent local saturation of the solvent.

Because of the mixed oxidation states of manganese in the samples, the reproducibility of the final state of manganese in sodium molybdate at 974 K has to be established. The oxidation state of manganese in sodium molybdate at 974 K was determined by the in situ weight change experiment conducted on a Netzsch STA 409 TGA/DTA analyzer. The experiment was run with a TG sample carrier using an alumina crucible that can accommodate a relatively large sample volume (~6 ml). The sodium molybdate solvent (~4.8 g) was heated in a small platinum crucible (which fits into the alumina TGA crucible) and brought to constant weight before the TG experiment. A baseline was obtained with the crucible and the solvent only. The manganese oxide powders were added and the TG runs were done in an argon atmosphere with a heating/cooling rate of 10 K/min and held at 974 K for 1.5 h to attain equilibrium. The weight change involved in the reaction of manganese oxides (MnO_2, Mn_2O_3, Mn_3O_4 and MnO) dissolving in sodium molybdate at 974 K was determined. The accuracy of the TG experiments was checked by dissolving Co_3O_4 in sodium molybdate at 974 K in an argon atmosphere (with known weight loss of 6.64% to form dissolved CoO). The observed weight loss was 6.50% and 6.72% (two runs). For manganese oxides, Table 1 shows that there is the same mixture of oxidation states in the melt ($4.8 \pm 0.7\%$ trivalent, $95.2 \pm 0.7\%$ divalent in argon atmosphere) regardless of the oxidation state of manganese in the starting oxide samples. Note that the data for weight changes on dissolution of MnO are less accurate because of the very small weight changes involved, and we interpret them as being consistent with the experiments on other manganese oxides. Thus the final state of manganese in the solvent, though a mixture of oxidation states, is reproducible and constant and is thus suitable for calorimetry.

3. Results and discussion

3.1. Chemical compositions and average oxidation state of manganese in spinels

The AOS of manganese determined experimentally (Table 2) shows that for excess lithium $x \geqslant 0.25$ in $Li_{1+x}Mn_{2-x}O_4$, AOS of Mn is smaller than the theoretical value, i.e., the amount of Mn^{4+} is smaller than $(1+2x)$. The synthesis conditions play an important role in the AOS of Mn of the product. An example is the sample with $x = 0.25$. The sample calcined at 673 K for a shorter period of time has a higher AOS of Mn. The AOS of Mn of $Li_{4/3}Mn_{5/3}O_4$ (nominal) was reported to be smaller than 4 [4,5,9] indicating that there are Mn^{3+} ions and oxygen vacancies.

The total amount of manganese determined from the titration is listed in Table 2. It is very close to the nominal manganese content. The lithium content was taken as nominal as well since the synthesis temperature

Table 1
In situ TG experiment results in sodium molybdate at 974 K in an argon atmosphere

Sample	Sample mass (mg)	Weight change			Mn^{2+} (mol%)	Mn^{3+} (mol%)
		(mg)	(%)	Average (%)		
MnO_2	41.17	–7.41	–17.99	–17.99	95.5	4.5
Mn_2O_3	50.89	–5.05	–9.93	–9.68	95.6	4.4
	47.19	–4.45	–9.44			
Mn_3O_4	79.85	–5.12	–6.41	–6.41	94.5	5.5
MnO[a]	40.69	+0.24	+0.590	+0.985	91.3	8.7
	40.83	+0.56	+1.38			

[a]Data for MnO are considered less accurate because of small weight change. However, the observed sign of change (weight gain) confirms that the oxidation state in the solvent is a mixture of Mn^{2+} and Mn^{3+}.

Table 2
Chemical compositions of $Li_{1+x}Mn_{2-x}O_4$

x	Experimental AOS of Mn	Theoretical AOS of Mn	Total Mn[a] (mol/formula)	Nominal Mn content (mol/formula)	Oxygen content[b]	Composition
0.00	3.517±0.001	3.500	1.982±0.004	2.00	4.017	$LiMn_2O_4$
0.05	3.571±0.001	3.564	1.943±0.003	1.95	4.007	$Li_{1.05}Mn_{1.95}O_4$
0.10	3.630±0.003	3.632	1.912±0.011	1.90	3.999	$Li_{1.10}Mn_{1.90}O_4$
0.15	3.701±0.001	3.703	1.843±0.004	1.85	3.998	$Li_{1.15}Mn_{1.85}O_4$
0.20	3.770±0.002	3.778	1.792±0.007	1.80	3.993	$Li_{1.20}Mn_{1.80}O_{3.993}$
0.25	3.779±0.001	3.857	1.750±0.002	1.75	3.932	$Li_{1.25}Mn_{1.75}O_{3.932}$[c]
0.25	3.795±0.003	3.857	1.758±0.004	1.75	3.946	$Li_{1.25}Mn_{1.75}O_{3.946}$[d]
0.25	3.805±0.001	3.857	1.759±0.002	1.75	3.954	$Li_{1.25}Mn_{1.75}O_{3.954}$[e]
0.30	3.787±0.001	3.941	1.703±0.002	1.70	3.869	$Li_{1.30}Mn_{1.70}O_{3.869}$
1/3	3.819±0.001	4.000	1.669±0.002	5/3	3.849	$Li_{4/3}Mn_{5/3}O_{3.849}$

[a]Determined by potentiometric titration.
[b]Calculated from the nominal lithium and manganese content, and AOS of manganese determined experimentally.
[c,d,e]Samples heated at 673 K for 36, 24, and 12 h, respectively, before heating at 773 K.

is low and evaporation of lithium should be negligible. The oxygen content was calculated based on charge neutrality from the nominal lithium and manganese content and AOS of manganese determined experimentally. For samples with $x = 0.05, 0.1, 0.15, 0.20$, the composition was considered stoichiometric. For $x \geqslant 0.25$, there is appreciable oxygen deficiency. For the sample with $x = 0$, the calculated oxygen content is 4.017 if the nominal manganese content is used. It is 3.985 if the experimentally determined manganese content is used. This shows that the error associated with the calculated oxygen content is relatively large. Considering the synthesis conditions (calcined in air and cooled within the furnace), this sample is expected to be stoichiometric. Thus the composition $LiMn_2O_4$ was taken for this sample in further calculations. The compositions of $Li_{1+x}Mn_{2-x}O_4$ listed in Table 2 were used in the calorimetric calculations. The coefficients for the binary oxides in the cycles are calculated according to the composition to satisfy mass balance and charge neutrality.

For the two samples with $x = 0.30$ and 0.333, a good fit of the XRD data was not achieved in the refinement for the estimation of the amount of Li_2MnO_3 impurity due to the overlap of the main peaks of the spinel phase and Li_2MnO_3. The amount of Li_2MnO_3 in these two samples was estimated to be less than 10 wt%. The correction to the enthalpy of drop solution data was carried out for 10 wt% of Li_2MnO_3. The corrected and uncorrected data overlap within experimental error. Therefore, the small amount of Li_2MnO_3 does not make an appreciable difference in the enthalpy of drop solution. The average compositions of these two samples were used in the calorimetric calculations. The enthalpies of formation from oxides determined in this work for these two samples should thus be taken as good estimations only for $Li_{1+x}Mn_{2-x}O_{4-\delta}$ samples with $x =$ 0.3 and 0.333, and comparable oxygen deficiency.

3.2. Enthalpy of formation at 298 K

The enthalpies of formation from constituent binary oxides (Li_2O, Mn_2O_3 and MnO_2) and from the elements for $Li_{1+x}Mn_{2-x}O_4$ at 298 K were calculated from the enthalpies of drop solution of $Li_{1+x}Mn_{2-x}O_4$, and the binary oxides, Li_2O, Mn_2O_3 and MnO_2, using the thermodynamic cycles (1) and (2) shown in Table 3. The thermochemical data determined in this work are listed in Table 4. Idemoto et al. [7] determined the enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ ($0 \leqslant x \leqslant 0.1$) with samples synthesized in three different conditions using solution ($HClO_4$ acid) calorimetry. The samples that are most similar to the ones in this study are those calcined at 973 K with oxygen partial pressure of 1.01×10^5 Pa (series B) though the AOS of Mn still shows a significant difference (3.517 vs. 3.562 for $LiMn_2O_4$ and 3.630 vs. 3.671 for $Li_{1.1}Mn_{1.9}O_4$). The enthalpies of formation from the elements at 298 K for $Li_{0.99}Mn_{2.01}O_{4.07}$ and $Li_{1.10}Mn_{1.90}O_{4.04}$ are -1360.1 ± 0.5 and -1371.0 ± 0.9 kJ/mol, respectively [7] in comparison to -1380.9 ± 2.2 and -1380.3 ± 2.9 kJ/mol in this work for $LiMn_2O_4$ and $Li_{1.1}Mn_{1.9}O_4$. The relatively large discrepancy can arise from the difference in the actual composition of the samples. This is also reflected in the data from Idemoto et al. on different $LiMn_2O_4$ samples. The enthalpy of formation for $LiMn_2O_4$ was reported to be -1368.1 ± 1.8 kJ/mol [9] and -1368.5 kJ/mol [8] for samples with the actual compositions of $Li_{0.989}Mn_{2.011}O_{4.054}$ and $LiMn_2O_{4.05}$, respectively, about 7 kJ/mol different from $Li_{0.99}Mn_{2.01}O_{4.07}$.

The enthalpy of formation from oxides for each composition is exothermic, indicating that the complex oxides are stable with respect to the constituent binary oxides (Li_2O, Mn_2O_3, and MnO_2). Fig. 1 shows that the enthalpy of formation from oxides becomes more exothermic with increasing x in $Li_{1+x}Mn_{2-x}O_4$ for stoichiometric compounds ($x < 0.25$), and deviates endothermically from this trend for oxygen-deficient samples ($x \geqslant 0.25$). This trend is consistent with that displayed by the variation of the lattice parameter with x in $Li_{1+x}Mn_{2-x}O_4$ (Fig. 2).

Fig. 2 shows the variation of the lattice parameter with x in $Li_{1+x}Mn_{2-x}O_4$. For $x \leqslant 0.2$, the lattice parameter decreases approximately linearly with x. This trend was reported by Gao and Dahn for $Li_{1+x}Mn_{2-x}O_4$ ($x \leqslant 0.2$) samples prepared with different synthesis conditions [19]. The decrease of the lattice parameter is a combined result of substitution of Li^+ ions for Mn^{3+} ions and oxidation of Mn^{3+} to Mn^{4+} (ionic radius: $Mn^{4+} < Mn^{3+} < Li^+$). For $x \geqslant 0.25$, the compounds tend to be deficient in oxygen. The formation of oxygen vacancies is accompanied with less Mn^{3+} being oxidized, which causes a deviation in the trend of decreasing lattice parameter and increasing AOS of Mn as well.

Table 3
Thermodynamic cycles used for the determination of enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ at 298 K from binary oxides (cycle 1) and from the elements (cycle 2)

Reaction	ΔH
Cycle 1: Enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ from oxides	
Li_2O (s, 298 K) → Li_2O (sln, 974 K)	$\Delta H_1 = \Delta H_{ds}(Li_2O)$
MnO_2 (s, 298 K) → MnO_2 (sln, 974 K)	$\Delta H_2 = \Delta H_{ds}(MnO_2)$
Mn_2O_3 (s, 298 K) → Mn_2O_3 (sln, 974 K)	$\Delta H_3 = \Delta H_{ds}(Mn_2O_3)$
$Li_{1+x}Mn_{2-x}O_{4-\delta}$ (s, 298 K) → 0.5 (1 + x) Li_2O (sln, 974 K) + (1 + 2x–2δ) MnO_2 (sln, 974 K) + 0.5(1–3x + 2δ) Mn_2O_3 (sln, 974 K)	$\Delta H_4 = \Delta H_{ds}(Li_{1+x}Mn_{2-x}O_{4-\delta})$
Formation of $Li_{1+x}Mn_{2-x}O_4$ from binary oxides	
0.5 (1 + x) Li_2O (s, 298 K) + (1 + 2x–2δ) MnO_2 (s, 298 K) + 0.5 (1–3x + 2δ) Mn_2O_3 (s, 298 K) → $Li_{1+x}Mn_{2-x}O_{4-\delta}$ (s, 298 K)	$\Delta H_5 = \Delta H^0_{f,ox}$
$\Delta H_5 = 0.5\ (1+x)\ \Delta H_1 + (1+2x-2\delta)\ \Delta H_2 + 0.5\ (1-3x+2\delta)\ \Delta H_3 - \Delta H_4$	
Cycle 2: Enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ from elements	
2 Li (s, 298 K) + 0.5 O_2 (g, 298 K) → Li_2O (s, 298 K)	$\Delta H_6 = \Delta H^0_f$ (Li_2O)
2 Mn (s, 298 K) + 1.5 O_2 (g, 298 K) → Mn_2O_3 (s, 298 K)	$\Delta H_7 = \Delta H^0_f$ (Mn_2O_3)
Mn (s, 298 K) + O_2 (g, 298 K) → MnO_2 (s, 298 K)	$\Delta H_8 = \Delta H^0_f$ (MnO_2)
0.5 (1 + x) Li_2O (s, 298 K) + (1 + 2x–2δ) MnO_2 (s, 298 K) + 0.5 (1–3x + 2δ) Mn_2O_3 (s, 298 K) → $Li_{1+x}Mn_{2-x}O_{4-\delta}$ (s, 298 K)	$\Delta H_5 = \Delta H^0_{f,ox}$
Formation of $Li_{1+x}Mn_{2-x}O_4$ from the elements	
(1 + x) Li (s, 298 K) + (2–x) Mn (s, 298 K) + (2–0.5δ) O_2 (g, 298 K) → $Li_{1+x}Mn_{2-x}O_{4-\delta}$ (s, 298 K)	$\Delta H_9 = \Delta H^0_{f,el}$
$\Delta H_9 = 0.5\ (1+x)\ \Delta H_1 + (1+2x-2\delta)\ \Delta H_8 + 0.5\ (1-3x+2\delta)\ \Delta H_7 + \Delta H_5$	

s = solid, g = gas, sln = in solution, ds = drop solution.Mn_2O_3, MnO_2 were written as the form in solution for simplicity as long as the final state of manganese is consistent, see text.ΔH^0_f (Li_2O), ΔH^0_f (Mn_2O_3), and ΔH^0_f (MnO_2) are enthalpy of formation of Li_2O, Mn_2O_3, and MnO_2, respectively, from Robie and Hemingway [17].

Table 4
Thermochemical data of manganese oxides and $Li_{1+x}Mn_{2-x}O_4$

Compound	ΔH_{ds} (kJ/mol)[a]	$\Delta H^0_{f,ox}$ (kJ/mol)[b]	$\Delta H^0_{f,el}$ (kJ/mol)
$LiMn_2O_4$	247.84±0.91 (15)	−82.47±1.79	−1380.9±2.2
$Li_{1.05}Mn_{1.95}O_4$	253.41±1.28 (13)	−89.92±2.06	−1383.4±2.5
$Li_{1.10}Mn_{1.90}O_4$	253.45±1.91 (13)	−91.83±2.55	−1380.3±2.9
$Li_{1.15}Mn_{1.85}O_4$	256.34±1.44 (14)	−96.60±2.28	−1380.1±2.8
$Li_{1.20}Mn_{1.80}O_{3.993}$	259.20±1.71 (18)	−101.98±2.53	−1380.0±2.6
$Li_{1.25}Mn_{1.75}O_{3.954}$	260.35±1.42 (16)	−108.56±2.38	−1378.4±2.6
$Li_{1.25}Mn_{1.75}O_{3.946}$	259.54±1.61 (15)	−108.56±2.49	−1377.7±3.0
$Li_{1.25}Mn_{1.75}O_{3.932}$	253.38±2.22 (18)	−103.68±2.91	−1371.7±2.8
$Li_{1.30}Mn_{1.70}O_{3.869}$	252.14±1.06 (11)	−110.09±2.18	−1368.1±2.7
$Li_{4/3}Mn_{5/3}O_{3.849}$	249.25±1.71 (13)	−110.26±2.60	−1363.3±3.1
MnO_2	128.92±0.91 (11)		
Mn_2O_3	165.92±1.08 (10)		
Li_2O	–93.02±2.24[c]		

[a]Uncertainties are two standard deviations of the mean, numbers in ( ) are the numbers of experiments. ΔH_{ds} is enthalpy of drop solution.
[b]Enthalpy of formation from oxides, Li_2O, Mn_2O_3 and MnO_2, at 298 K.
[c]Ref. [18].

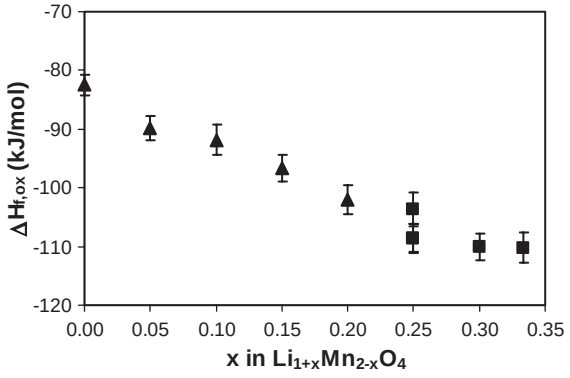

Fig. 1. Variation of enthalpy of formation from oxides with x in $Li_{1+x}Mn_{2-x}O_{4-\delta}$. ▲ Samples without oxygen vacancies. ■ Samples with oxygen vacancies.

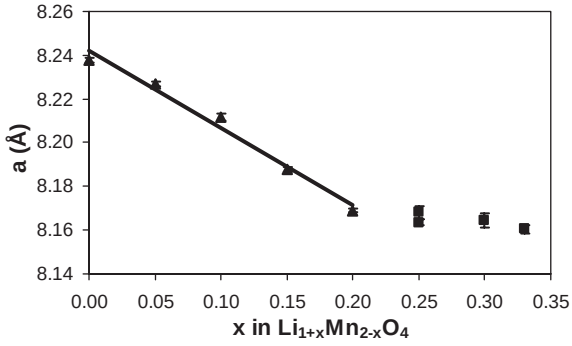

Fig. 2. Variation of lattice parameter with x in $Li_{1+x}Mn_{2-x}O_{4-\delta}$. ▲ Samples without oxygen vacancies. ■ Samples with oxygen vacancies.

3.3. Substitution mechanisms of lithium for manganese and related energetic issues

The variation of the enthalpy of formation from oxides with x in $Li_{1+x}Mn_{2-x}O_4$ can be separated into two regions: $x<0.25$ and $x\geqslant 0.25$. In the first region, the compounds have no oxygen vacancies. The enthalpy of formation from oxides becomes more exothermic with increasing lithium substitution level x in $Li_{1+x}Mn_{2-x}O_4$. In the second region, the compounds are oxygen deficient and the enthalpy of formation deviates from the above trend endothermically (Fig. 1). This energetic trend is the overall effect of several competing factors related to charge-coupled substitution of lithium for manganese including oxidation of Mn^{3+} to Mn^{4+} and formation of oxygen vacancy.

When lithium substitutes for manganese, to maintain charge neutrality, there are two possible competitive mechanisms: (1) oxidation of Mn^{3+} to Mn^{4+} (Eq. (2)), or (2) formation of oxygen vacancy (Eq. (3)) (Kroger–Vink notation [20]):

$$Li^{\times}_{Li} + 2Mn(III)^{\times}_{Mn(III)} \rightarrow Li''_{Mn(III)} + 2Mn(IV)^{\cdot}_{Mn(III)}, \quad (2)$$

$$Li^{\times}_{Li} + O^{\times}_{O} \rightarrow Li''_{Mn(III)} + V^{\cdot\cdot}_{O} + 0.5O_2 \uparrow . \quad (3)$$

For oxygen stoichiometric spinels, the oxidation of Mn^{3+} to Mn^{4+} is the only reaction that maintains change balance. For compounds with oxygen deficiency, charge compensation is achieved both through oxidation of Mn^{3+} to Mn^{4+} and formation of oxygen vacancies. The formation of $Li_{1+x}Mn_{2-x}O_{4-\delta}$ can be separated into two steps:

$$0.5(1+x)Li_2O + 0.5(1-3x)Mn_2O_3 + (1+2x)MnO_2 \rightarrow Li_{1+x}Mn_{2-x}O_4, \quad (4)$$

$$Li_{1+x}Mn_{2-x}O_4 \rightarrow Li_{1+x}Mn_{2-x}O_{4-\delta} + 0.5\delta O_2. \quad (5)$$

The corresponding defect chemistry can be written as

$$Li_{Li}^{\times} + 2Mn(III)_{Mn(III)}^{\times} \rightarrow Li_{Mn(III)}'' + 2Mn(IV)_{Mn(III)}^{\cdot}, \quad (2')$$

$$2Mn(IV)_{Mn(III)}^{\cdot} + O_O^{\times} \rightarrow 2Mn(III)_{Mn(III)}^{\times} + V_O^{\cdot\cdot} + 0.5O_2 \uparrow . \quad (6)$$

The enthalpy of formation has contributions from the oxidation of Mn^{3+} to Mn^{4+} and the formation of oxygen vacancies. The latter is accompanied by the reduction of Mn^{4+} to Mn^{3+}. Both oxygen vacancy formation and reduction of Mn^{4+} to Mn^{3+} are endothermic processes. The enthalpy of reaction (5) is the combined effect of these two concomitant factors and is denoted the enthalpy of reduction.

The enthalpy of reduction can be a function of substitution level (x) and oxygen deficiency (δ). However, studies of perovskites system [21,22] and perovskite-related La_2CuO_4 system [23] showed that the enthalpy of oxidation of a given substitution level is virtually independent of the amount of oxygen deficiency. Thus, the enthalpy of reduction at the substitution level of 0.25 can be estimated from the thermochemical data of the three samples with different oxygen contents as a first approximation. The enthalpy of reduction at $x = 0.25$ can be derived as the slope of the line of $\Delta H_{f,el}$ vs. $0.5V_O$ (Fig. 3):

$$\Delta H_{f,el} = (-1393.4 \pm 4.7) + (628.0 \pm 166.6)x \quad (7)$$

with x = moles of O_2

Thus, the enthalpy of reduction is 628.0 ± 166.6 kJ/mol O_2. This means an enthalpy of oxidation of -628.0 ± 166.6 kJ/mol O_2 associated with the reaction

$$Li_{1+x}Mn_{2-x}O_{4-\delta} + 0.5(\delta - \delta')O_2 \rightarrow Li_{1+x}Mn_{2-x}O_{4-\delta'} (\delta > \delta'). \quad (8)$$

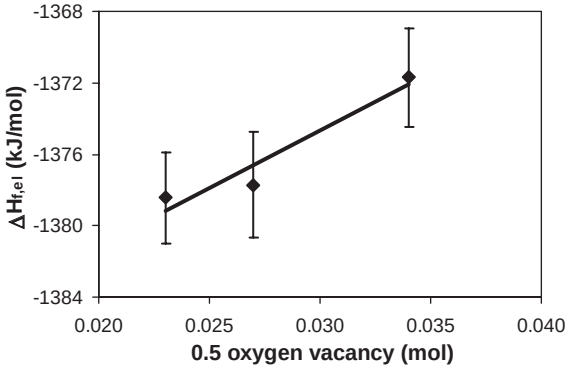

Fig. 3. Enthalpy of formation vs. 0.5 (moles of oxygen vacancies) at $x = 0.25$ in $Li_{1+x}Mn_{2-x}O_{4-\delta}$. The slope of the line represents the enthalpy of reduction ($\Delta H_{reduction}$ in kJ/mol O_2).

The enthalpy of reduction obtained has a large error. This is due to the closeness of the oxygen contents of the samples and the very few data points used for the linear approximation to obtain the enthalpy of reduction. Nevertheless, the data give a useful approximate value.

The enthalpy of formation from the elements for the stoichiometric sample ($Li_{1.25}Mn_{1.75}O_4$) can be extrapolated from the fitted line of $\Delta H_{f,el}$ vs. $0.5V_O$ ($x = 0$ in Eq. (7)) as -1393.4 ± 4.7 kJ/mol. The enthalpy of formation from oxides for $Li_{1.25}Mn_{1.75}O_4$ is then calculated as -119.9 ± 5.0 kJ/mol using the enthalpies of formation from the elements of the binary oxides (cycle 2 in Table 3).

The endothermic deviation of the enthalpy of formation from oxides in $Li_{1+x}Mn_{2-x}O_{4-\delta}$ at $x \geqslant 0.25$ is attributed to the large endothermic heat effect of reaction (5), i.e., the enthalpy of reduction. The stabilizing factor for the oxygen deficient compounds is the entropy (the entropy of oxidation, a typical value for transition metal oxides being about -92 J/((mol O) K) [24] and the configurational entropy). The negative entropy of oxidation compensates for the negative enthalpy of oxidation, and an intermediate state, containing both oxygen vacancies and Mn^{4+} (oxidized from Mn^{3+}), is the state of lowest free energy. The formation of oxygen vacancies may increase the configurational entropy and thus result in a more negative free energy.

4. Conclusions

$Li_{1+x}Mn_{2-x}O_4$ samples with high x values ($x \geqslant 0.25$) tend to be oxygen deficient with the AOS of manganese smaller than the maximum possible value. Synthesis conditions (temperature, oxygen partial pressure, cooling rate, heat treatment time) play important roles in the oxygen stoichiometry of the products and thus, the electrochemical properties of the electrode. The enthalpies of formation from constituent binary oxides at 298 K for $Li_{1+x}Mn_{2-x}O_4$ compounds with $0 \leqslant x \leqslant 1/3$ were determined by high-temperature oxide melt solution calorimetry. The enthalpy of formation from oxides becomes more exothermic with x in $Li_{1+x}Mn_{2-x}O_4$ for stoichiometric compounds ($x < 0.25$) and deviates from the trend endothermically for samples with oxygen deficiency ($x \geqslant 0.25$). This is attributed to the interplay of the enthalpy of oxidation of Mn^{3+} to Mn^{4+} and the enthalpy of oxygen vacancy formation, i.e., the enthalpies related to the two substitution mechanisms of lithium for manganese. For spinels with no oxygen vacancies, the oxidation of Mn^{3+} to Mn^{4+} is responsible for the charge-coupled substitution. For oxygen-deficient compounds, both mechanisms are operative.

Acknowledgments

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