Origin of 5 V Electrochemical Activity Observed in Non-Redox Reactive Divalent Cation Doped LiM\(_{0.5-x}\)Mn\(_{1.5+x}\)O\(_4\) (0 ≤ x ≤ 0.5) Cathode Materials

In Situ XRD and XANES Spectroscopy Studies

W. Wen, a,* B. Kumarasamy, a S. Mukerjee, a,** M. Auiat, b and Y. Ein-El b,**

aDepartment of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, USA
bDepartment of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

Divalent cation doped lithium Mn spinel with Zn and Mg as cathode materials for a lithium battery are investigated and partial reversible behavior is observed at the 5 V region. The electrochemical charge and discharge potential profiles of the Zn-doped materials indicate a close relationship between the lattice energy and lattice parameters in the Zn-doped spinel system. Lithium ions extracted from octahedral sites at the 5 V plateau during the charge cycle are partially reinserted back into the tetrahedral sites during the discharge step, which contributes to the partial reversible 5 V behavior. The significant findings reported here are that the strong tetrahedral site preference of divalent nonreactive cations such as Zn and Mg force Li cations onto octahedral sites in these materials, thus resulting in electroactivity at 5 V. In situ X-ray absorption spectroscopy measurements show that the Mn K edge is shifted to higher energy at the 4 V plateau during charge cycle and remains unchanged at the 5 V plateau. In situ Zn K-edge X-ray absorption near-edge structure measurements reveal that the valence state of zinc ions is unchanged at the 5 V plateau region. In situ Mn K-edge extended X-ray absorption fine structure studies suggest that O\(^{2-}\) ions in the Zn-spinel lattice are partially oxidized to O\(^{3-}\) at the 5 V plateau during the anodic process and O\(^{3-}\) ions are reduced back to O\(^{2-}\) during the cathodic process at the 5 V plateau. The oscillations of the lattice parameters observed at the 5 V plateau region during the anodic charge step are attributed to chemical instability of O\(^{2-}\) ions.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1997160] All rights reserved.

Manuscript submitted February 15, 2005; revised manuscript received April 29, 2005. Available electronically August 8, 2005.
valence state of +2 from group IIB (12), which cannot be further oxidized, on the overall material electrochemistry of a doped Mn spinel compound.

Zn substituted spinel material has been investigated by the $^1$Li solid-state nuclear magnetic resonance (NMR) method and some lithium ions were found to occupy octahedral sites, in contrast to their normal tetrahedral site occupancy in a pristine LiMn$_2$O$_4$.\textsuperscript{24} Particularly, a Zn vs Li ratio of 1 and a Mn vs Li ratio of 3 in the tetrahedral and octahedral sites, respectively, are reported in the literature for LiZn$_{0.5}$Mn$_{1.5}$O$_4$ composition.\textsuperscript{25} This suggests that Zn ions occupy tetrahedral sites in the crystal, thus forcing some fraction of lithium ions into the octahedral sites. Synchrotron X-ray diffraction (XRD) and neutron diffraction patterns of this material have been refined as a cubic structure with a space group $P$2$_1$3.\textsuperscript{26}

The crystal structure of this material is dependent on the use of different synthetic routes. Cation ordering in the octahedral sites with a space group $P4_3$2$\overline{1}$ is reported for samples quenched from 600°C and a disordered phase with a space group $Fd\overline{3}m$ if quenched from 750°C.

Recently, we reported in a short communication an unexpected 5 V behavior of low doped Zn substituted Mn spinel material of the type LiZn$_{0.5}$Mn$_{1.5}$O$_4$.\textsuperscript{20} Here, we fully report on the synthesis and electrochemical behavior of a series of low doped Zn substituted Mn spinel materials of the type LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$ ($0 \leq x \leq 0.5$) and on the origin of the observed 5 V behavior. The detailed mechanism has been investigated using in situ X-ray absorption near-edge structure (XANES) and XRD methods.

### Experimental

Samples with the general composition of LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$ ($0 \leq x \leq 0.5$) with $x = 0.05, 0.35, 0.325, 0.3, 0.25, 0.15,$ and 0.0, and LiMg$_{0.5-x}$Mn$_{1.5}$O$_4$ with an $x$ value of 0.0, 0.25, and 0.35 were prepared from the acetate salts (Li acetate, Mn acetate, and Zn and Mg acetate, Fluka) using a low-temperature sol-gel technique, described in detail elsewhere.\textsuperscript{11,12,13} Ex situ X-ray diffraction patterns of the synthesized powdered materials were recorded with the use of a Philips X'pert Diffractometer (PW3040/60). Evaluation and examination of powder grain size and morphology were conducted with the use of a high-resolution scanning electron microscope (Hitachi S-4800).

Composite electrodes were prepared by casting (doctor blading) a slurry comprised of 80% LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$, 10% polypyrrolidinone binder with a fugitive solvent and LiC$_6$ black. Composite electrodes were prepared by casting the slurry on an aluminum substrate. Cells were tested in the potential limits of 3.3-5.4 V at a current density of 100 mA/g. Details of the electrochemical test setup are given in Ref. 11,12. Cells were tested in the potential limits of 3.3-5.4 V at a current density of 100 mA/g.

### Results and Discussion

Materials characterization.— Powder X-ray diffraction (XRD) studies.—XRD patterns of several LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$ powder materials are shown in Fig. 1a. XRD patterns obtained from the Zn-doped lithiated Mn-oxide materials are different from the pattern recorded from an undoped LiMn$_2$O$_4$ spinel (with a fcc spinel structure) due to the emergence of extra diffraction peaks. The XRD pattern for LiZn$_{0.5}$Mn$_{1.5}$O$_4$ is indexed (using a powder indexing module in the Cerius$^2$ program) as a cubic structure with a lattice parameter of 8.17 Å. The XRD pattern of a reference material, Zn$_2$MnO$_4$ which has been indexed as a tetragonal structure (due to the presence of highly Jahn-Teller active Mn$^{3+}$ ions) with Zn ions occupying the tetrahedral sites, is also shown in Fig. 1b. Further, the intensity of some diffraction peaks, which are not observed in the LiMn$_2$O$_4$ XRD pattern, such as 110, 200, and 210, increases as Zn content increases. This suggests the possibility of Zn ions occupying tetrahedral sites in the crystal lattice. LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$ materials with a Zn content of 0, 0.2, 0.25, 0.35, and 0.5 exhibit similar XRD patterns, thus suggesting the existence of similar crystal structure. The existence of additional diffraction peaks, observed in LiZn$_{0.5-x}$Mn$_{1.5}$O$_4$ ($0 \leq x \leq 0.5$) materials, have been indexed to a space group $P2_1$3, with a primitive cubic structure instead of a face-centered-cubic spinel structure. These are evidenced by the existence of 200 and 400 planes, and an undetectable 100 plane, which suggests the existence of a $2\overline{1}$ screw axis at the 100 plane. The intensity of the 110 peak increases as we move along from LiZn$_{0.5}$Mn$_{1.5}$O$_4$ to LiZn$_{0.25}$Mn$_{1.8}$O$_4$ powder material, while, as will be shown later, the electrochemical discharge capacity decreases from 100 mA h/g (recorded with LiZn$_{0.5}$Mn$_{1.5}$O$_4$) to almost 0 (recorded with LiZn$_{0.5}$Mn$_{1.5}$O$_4$).

![Figure 1](https://example.com/figure1.png)
tion from a centrosymmetric coordination environment. In other words, we expect to observe a large preedge feature once the coordination environment for the center ions is tetrahedral, due to the higher overlapping of the transition-metal d orbital with the coordination ions p orbital. The small magnitude of the preedge feature, observed in Fig. 2a, suggests that Mn ions are positioned in an octahedral coordination environment. However, the preedge features observed from Zn substituted materials are gradually modified: while a single preedge peak is observed in LiMn1.5Zn0.5O4, two preedge peaks are featured in LiMn2O4. This could be the result of a decrease in the concentration of octahedral lithium ions in the crystal lattice as Zn content decreases.

Fourier transformed EXAFS signals obtained from four powdered compounds, namely LiMn1.75Zn0.25O4, LiMn1.8Zn0.2O4, LiMn1.5Zn0.5O4, and LiMn2O4, are shown in Fig. 2a. All edges of these four compounds are 10 eV above the Mn foil K edge, due to the higher oxidation state of Mn ions. It is readily seen from Fig. 2a that the oxidation state of Mn ions increases as Zn content in the ceramic compound increases, as indicated by the positive shift in the Mn K edge to higher energy levels. This is expected on the basis of charge compensation and the assumption that Zn ions are in their +2 valence state. The preedge feature at ~6540 eV indicates the transition from 1x orbital to 3d orbital in Mn ions, which is formally dipole-forbidden but quadrupole-allowed. This could also be explained by the hybridization of Mn 3d and oxygen 2p orbitals in the local structure. The preedge feature seems to be at a similar position to the K edge of the Mn foil. It is a general rule that the intensity of the preedge feature would increase with any deviation from a centrosymmetric coordination environment. In other words, we expect to observe a large preedge feature once the coordination environment for the center ions is tetrahedral, due to the higher overlapping of the transition-metal d orbital with the coordination ions p orbital. The small magnitude of the preedge feature, observed in Fig. 2a, suggests that Mn ions are positioned in an octahedral coordination environment.

Figure 2. (a) XANES spectra obtained from LiZn0.5−xMn1.5+xO4 (−x) x = 0, (−→) x = 0.25, (−−−−) x = 0.3, (−−−) x = 0.5, and (−−−−−) Mn foil; (b) Fourier transformed EXAFS signal of LiZn0.5−xMn1.5+xO4 (−x) x = 0, (−→) x = 0.25, (−−−−−) x = 0.3, and (−−−) x = 0.5. Inset presents a full scale spectrum of Fourier transformed EXAFS signal obtained from LiMn1.5O4.

X-ray absorption spectroscopy (XAS).—The XANES spectra of three different Zn-doped Mn spinels, LiMn1.8Zn0.2O4, LiMn1.5Zn0.5O4, and LiMn2O4, are shown in Fig. 2a. All edges of these four compounds are 10 eV above the Mn foil K edge, due to the higher oxidation state of Mn ions. It is readily seen from Fig. 2a that the oxidation state of Mn ions increases as Zn content in the ceramic compound increases, as indicated by the positive shift in the Mn K edge to higher energy levels. This is expected on the basis of charge compensation and the assumption that Zn ions are in their +2 valence state. The preedge feature at ~6540 eV indicates the transition from 1x orbital to 3d orbital in Mn ions, which is formally dipole-forbidden but quadrupole-allowed. This could also be explained by the hybridization of Mn 3d and oxygen 2p orbitals in the local structure. The preedge feature seems to be at a similar position to the K edge of the Mn foil. It is a general rule that the intensity of the preedge feature would increase with any deviation from a centrosymmetric coordination environment. In other words, we expect to observe a large preedge feature once the coordination environment for the center ions is tetrahedral, due to the higher overlapping of the transition-metal d orbital with the coordination ions p orbital. The small magnitude of the preedge feature, observed in Fig. 2a, suggests that Mn ions are positioned in an octahedral coordination environment.

Figure 3. High-resolution SEM micrographs obtained from three materials with different Zn composition of (a,b) x = 0.5; (c,d) x = 0.25; and (e,f) x = 0.0 in LiZn0.5−xMn1.5+xO4.
respectively. All three materials have a truncated octahedral structure (tetradecahedra), having six squares and eight hexagons (Scheme 1a), with side lengths of 60-100 nm. Although there are two ways for cojoining two tetradecahedra units (scheme I b) and six possibilities for three tetradecahedra blocks to be linked, the SEM micrographs (Fig. 3b, d, and f) reveal that the truncated octahedrals are bonded via the hexagon facets. Observance of such well defined faceted structures is reported here for the first time for such a composition, to the best of our knowledge. These “single-crystal”-like structures are important in understanding intradomain interactions and grain fracture as a result of cycling.

**Electrochemical characterizations.—** Slow scan cyclic voltammetry (SSCV, scan rate of 20 μV/s) obtained from polarizing LiZn0.5−xMn1.5+xO4 composite electrode materials (x = 0.5, 0.35, 0.325, 0.3, 0.25, and 0.15) in ethylene carbonate-dimethyl carbonate electrolyte containing 1 M LiPF6 is presented in Fig. 4a-f. The two-step charge and discharge profiles in the 4 V region of the Zn-doped ceramic compounds were resolved, as can be readily seen from Fig. 4c-f, albeit with less resolution as compared to corresponding behavior for pristine LiMn2O4, shown in Fig. 4a. The 5 V behavior is clearly observed using the SSCV method (Fig. 4c-f), which also suggests that LiZn0.2Mn1.8O4 may have the largest discharge capacity at both the 4 and 5 V regions, on the basis of the integrated areas under the anodic and cathodic regions (Fig. 4d). The SSCV patterns and the electrochemical charge-discharge profiles of LiZn0.15Mn1.85O4 are similar to the undoped LiMn2O4 spinel material, as the two anodic and cathodic peaks in the 4 V region are sharply resolved (Fig. 4b) compared with the two broad peaks observed with the “highly” Zn-doped materials, namely LiMn1.75Zn0.25O4 and LiMn1.65Zn0.35O4 (Fig. 4e and f). In addition, the 5 V behavior is barely detected upon polarizing the low doped Zn material, LiZn0.15Mn1.85O4. This suggests that the material having a low Zn content, with x = 0.35 in LiZn0.5−xMn1.5+xO4, is a mixture of several phases, with the major phase being similar to the undoped pristine LiMn2O4.

It is also observed that the detected 5 V behavior recorded for the doped Zn materials is not completely reversible, as the 5 V peak in the cathodic back-scan is much smaller than the corresponding anodic peak. Surprisingly, small 5 V reversible behavior is also detected while polarizing LiMn2O4 composite electrode, as can be seen in Fig. 4a, inset, suggesting that Zn doping is not the origin of the 5 V behavior. However, the significant anodic peak in the SSCV’s obtained from Zn-doped Mn oxide materials indicates that Zn doping is needed to facilitate the 5 V behavior.

**Galvanostatic charge/discharge profiles.—** Figure 5 presents electrochemical charge (to a potential of 5.4 V) and discharge (to a potential of 3.3 V) profiles of five LiZn0.5−xMn1.5+xO4 materials,
The LiMn1.5Zn0.5O4 compound, rendered as a result of having all of the V and 4 V electrochemical activities are observed with all the Mn in the lattice is in an oxidation state of +4, a shift to higher valence Mn as the originator of the 5 V behavior for LiZn0.5Mn1.5O4 composite electrode can be ruled out. This argument can also be applied to the other compositions of LiZn0.5-xMn1.5+xO4.

In situ spectroscopy studies.—In situ X-ray diffraction studies.—In situ XRD studies carried out with LiMn1.8Zn0.2O4 composite electrode as a function of charge and discharge processes are shown in Fig. 7a and b. No new diffraction peaks emerged during the charge and discharge processes, suggesting the existence of only one phase throughout. All XRD peaks obtained from polarizing LiMn1.8Zn0.2O4 composite electrode are shifted to higher angles during the charge process (guided by the dashed vertical lines in Fig. 7), while they are shifted to lower angles in the corresponding discharge process, as the lithium ions are extracted and reinserted into the crystal lattice, respectively. This suggests a decrease in the lattice parameter during the charge process as lithium ions are
extracted from the lattice, and an increase in the lattice parameters during the followed discharge process as lithium ions are reinserted back into the lattice.

A plot representing the lattice parameter values vs the specific capacity is shown in Fig. 8. Surprisingly, the profile of this plot is similar to the electrochemical charge and discharge curves (Fig. 5). The electrochemical potential of a cell is determined by the Gibbs free energy of the overall electrochemical reactions, which could be calculated from the Born-Harber cycle, yielding eventually the crystal lattice energy. However, the cell potential is modified not only via the amount of lithium ions inside the crystal lattice, but also by the specific site in which the lithium ion resides. Both can alter the lattice parameter profile in the charge cycle, presented in Fig. 8, which possess higher lattice energy than the tetrahedral lithium ions attributed to the extraction of lithium ions from octahedral sites.

The changes in the lattice parameter during the discharge step can also be fitted into four regions, albeit with lower resolution, as presented in Fig. 8. It is also worth noticing that the slopes of the lattice parameter change during the discharge process are significantly steeper than the slopes observed during the charging step. Again, the lattice parameter behavior within each specific potential window is also similar to the discharge profile presented in Fig. 5. This further demonstrates that the potential profile is well correlated with corresponding changes in the lattice parameters. Because the lattice energy and hence the Li extraction potential are related to the lattice parameter, the higher potential activity at 5 V region could be attributed to the extraction of lithium ions from octahedral sites which possess higher lattice energy than the tetrahedral lithium ions in the crystal lattice. The data represented in Fig. 8 suggest that a compound is more readily susceptible to structural changes when lithium ions are extracted from tetrahedral sites as compared to octahedral sites.

In situ XANES measurements.—In situ Zn K-edge XANES spectra obtained during the charge cycle are shown in Fig. 9. No shifts toward higher energies are observed in the zinc K-edge XANES spectra at the 5 V region during the charge step; such a shift is expected for any positive change in Zn valence states. No preedge feature due to a 3d10 configuration of the Zn2+ ion is observed, as well. The preedge feature presents the transition from 1s orbital to 3d orbital, which is dipole-forbidden but quadrupole-allowed. The absence of a preedge feature in the fully charged state suggests that no Zn2+ ions exist in the ceramic matrix; otherwise, a preedge feature should be expected for a 3d0 configuration.

The intensity of the preedge is expected to be high for tetrahedral Zn2+ ions. This is consistent with the existence of 5 V behavior in LiMn2O4. It is thus concluded that the origin of the 5 V behavior in a LiZn0.55Mn1.5O4 material system is different from that of other transition-metal substituted spinel materials such as Cu12,22 and Ni16,17, where charge compensation due to valence change involving the transition metals completely accounts for the 5 V behavior.

In situ Mn K-edge XANES profiles obtained during charge in the 4 V region are shown in Fig. 10a. The Mn K-edge is shifted to a higher energy level at the 4 V region, indicating an increase in Mn oxidation state, in order to compensate for the extraction of lithium ions from the crystal lattice. However, the corresponding XANES spectra obtained during charge at the 5 V plateau exhibit no shifts in the main Mn K-edge peak, as shown in Fig. 10b. A close examination of the preedge region of these spectra reveals a continuous enhancement of intensity in both the 4 and 5 V regions. Since these preedge features emanate as a result of a hybridization ρ-d state enabling quadrupole-allowed transitions, an increase in preedge peak intensity suggests an increased distortion of the Mn-O coordination in both the 4 and 5 V regions. It can be conjectured that in the 4 V region, the presence of Zn in tetrahedral sites forces some Li ions into octahedral positions, creating an environment in which Mn-O distortions could occur. This is supported somewhat by previous studies on chemical intercalation of LiMn2O4 and a Li-rich analog Li0.5Mn1.5O4.31 One of the explanations of the changes in the preedge features, especially in the 5 V region (where the main peak does not change), could be due to the oxidation of the O2− ions to O− ions in the 5 V region. The fully charged state is thus correlated to a locally distorted octahedral coordination environment near the Mn4+ ions.

---

**Figure 8.** A plot of lattice parameter (Å) vs specific capacity (mAh/g) values obtained during first charge and discharge steps of LiMn1.8Zn0.2O4 composite electrode.

**Figure 9.** In situ Zn K-edge spectra obtained during charge step at the 5 V region from LiMn1.8Zn0.2O4 composite electrode enabling quadrupole-allowed state with Zn2+ ions existing in the ceramic matrix; otherwise, a preedge feature should be expected for a 3d0 configuration.

**Figure 10.** a) Mn K-edge XANES profiles obtained during charge in the 4 V region, indicating an increase in Mn oxidation state, in order to compensate for the extraction of lithium ions from the crystal lattice. b) The Mn K-edge is shifted to a higher energy level at the 4 V region, indicating an increase in Mn oxidation state.
In situ XANES spectra at the 5 and 4 V regions in the discharge step are shown in Fig. 11a and b, respectively. A similar reversible change is also observed in the preedge feature. This behavior observed in the 5 V region with a discharge capacity of (---) 7.7 mA h/g (4.79 V), (----) 15.4 mA h/g (4.45 V), and (-----) 23.2 mA h/g (4.23 V). The preedge is shown in the inset. (♦) Mn foil, (●) 7.7 mA h/g (4.79 V), (○) 15.4 mA h/g (4.45 V), and (■) 23.2 mA h/g (4.23 V); and (b) at the 4 V region with a discharge capacity of (---) 52.8 mA h/g (4.03 V), (----) 61.3 mA h/g (3.98 V), (-----) 92.2 mA h/g (3.73 V), (-----) at fully discharged state (3.3 V), and (---) a Mn reference foil. The preedge is shown in the inset. (♦) Mn foil, (●) 52.8 mA h/g (4.03 V), (○) 61.3 mA h/g (3.98 V), (■) 92.2 mA h/g (3.73 V), and (□) fully discharged state (3.3 V).

The Fourier transforms of the EXAFS at the Mn K edge are shown in Fig. 12 and 13, representing in situ spectra for charge and discharge of LiMn$_{1.8}$Zn$_{0.2}$O$_4$. These EXAFS spectra when correlated with crystallographic features represent the Mn-O interactions of the first coordination shell at approximately 1.8 Å (without phase correction) and the Mn-Mn interactions of the second coordination shell reflecting the six octahedral Mn atoms (see the inset). Previous reports on the intercalation and deintercalation of Li in LiMn$_2$O$_4$ (chemically rendered) have indicated that removal of Li from the lattice causes a decrease in both the Mn-O and Mn-Mn distances, in good agreement with X-ray crystallographic data, while this was also shown to be completely reversible.

Typically, the amplitude of the Fourier transform of the EXAFS signal is effected directly by the change in coordination number and inversely by the Debye-Waller factor. The Debye-Waller factor is, however, composed of both static and dynamic (thermal disorder) terms. The latter reflects the extent of interatomic dislocations, while the former represents a measure of sample purity. An earlier report on the effect of charge and discharge in the context of LiMn$_2$O$_4$ shows that deintercalation of Li during charge from the spinel structure causes the amplitude of the Fourier transform to increase. This is also shown to be reversible, hence a concomitant decrease in the significant interactions due to the phenomenon of forward focusing, which accounts for the appearance of peaks in the radial coordinate distances of 4-5 Å and at 8 Å.

The Fourier transforms of the EXAFS at the Mn K edge are shown in Fig. 12 and 13, representing in situ spectra for charge and discharge of LiMn$_{1.8}$Zn$_{0.2}$O$_4$. These EXAFS spectra when correlated with crystallographic features represent the Mn-O interactions of the first coordination shell at approximately 1.8 Å (without phase correction) and the Mn-Mn interactions of the second coordination shell reflecting the six octahedral Mn atoms (see the inset). Previous reports on the intercalation and deintercalation of Li in LiMn$_2$O$_4$ (chemically rendered) have indicated that removal of Li from the lattice causes a decrease in both the Mn-O and Mn-Mn distances, in good agreement with X-ray crystallographic data, while this was also shown to be completely reversible.

Typically, the amplitude of the Fourier transform of the EXAFS signal is effected directly by the change in coordination number and inversely by the Debye-Waller factor. The Debye-Waller factor is, however, composed of both static and dynamic (thermal disorder) terms. The latter reflects the extent of interatomic dislocations, while the former represents a measure of sample purity. An earlier report on the effect of charge and discharge in the context of LiMn$_2$O$_4$ shows that deintercalation of Li during charge from the spinel structure causes the amplitude of the Fourier transform to increase. This is also shown to be reversible, hence a concomitant decrease in the
amplitude is observed during intercalation as a consequence of electrochemical discharge. This change in the amplitude of the Fourier transform has been correlated primarily to the change in the Debye-Waller factor as evidenced by a lowering of the magnitude of the Mn-O Fourier transform during charge related to a lowering of the Debye-Waller factor is shown in Fig. 2. In Fig. 3a, such behavior in the 5 V region can be accounted for on the basis of greater order in the lattice due to an increase in the Debye-Waller factor linked to thermal disorder, hence an increase of the amplitude of the Fourier transforms as a function of charge in the 4 V region. Comparison of the results presented in Fig. 12 and 13 with previous reports shows that the extent of changes in the magnitude of the Fourier transforms as a function of charge (Fig. 12a) and discharge (Fig. 13a) is relatively small for the Zn substituted sample as compared to the nondoped pure LiMn2O4 spinel. This is shown in terms of the comparison presented in Fig. 2 and is in agreement with the correlation with Mn oxidation state changes as a function of Zn substitution.

However, comparison of the corresponding magnitudes in the Fourier transforms of the Mn K-edge EXAFS spectra in the 5 V region exhibits a reverse trend, albeit small. This reverse trend comprised of an increase in the Debye-Waller factor as evidenced by a lowering of the magnitude of the Mn-O Fourier transform during charge (Fig. 12b) and the corresponding reverse effect during discharge related to a lowering of the Debye-Waller factor is shown in Fig. 13a. Such behavior in the 5 V region can be accounted for on the basis of a decrease in the ionic characteristics of Mn-O interaction as a consequence of a partial change of O2− ions to O− ions, which would cause an increase in the Debye-Waller factor as a function of charge of the Mn-O Fourier transforms as a function of charge in the 4 V region. Removal of Li during charge from the lattice in the 4 V region is shown in Fig. 12a. As expected, there is an increase in the amplitude of the Mn-O Fourier transforms at the 5 V region with a charge capacity of (—) 7.7 mA h/g (4.97 V), (—) 15.4 mA h/g (4.45 V), and (-----) 23.2 mA h/g (4.23 V).
result of a decrease in the Mn-O interactions. The fully charged material could be described using a formula of $[\text{Zn}^{2+}_{0.25}][\text{Mn}^{3+}_{0.5}][\text{O}_{2}^{2-}]$, and the average oxidation state of the oxygen ions is $\sim$1.9. The reversibility of this effect is manifested in the reverse trends seen in Fig. 13a. The presence of unstable O$^{-}$ in the oxygen ion is $-1.9$. The reversibility of this effect is manifested in the reverse trends seen in Fig. 13a. The presence of unstable O$^{-}$ in the lattice during charge in the 5 V region is expected to be accompanied by electrolyte oxidation.

Secondary reactions during the upper potential charge step, due to the presence of unstable monovalent oxygen ions at high potentials, could result in disproportionate reactions, according to the following set of equations

$$2\text{O}^{-} + 2\text{Mn}^{3+} \rightarrow \text{O}_2 + 2\text{Mn}^{4+}$$  \hspace{1cm} [1]

$$\text{O}^{-} + \text{(electrolyte)} \rightarrow \text{O}^{2-} + \text{(electrolyte)}^{+}$$  \hspace{1cm} [2]

In addition, under the extreme oxidizing potentials it is more likely to expect that a major by-product of the alkyl carbonate electrolyte oxidation would be protons. The produced protons at the electrode surface can initiate a cation exchange for Li ions in the electrode, as was proposed by Robertson et al. in exploring the electrochemical behavior of Li$_2$MnO$_3$. Thus, the rapid degradation in the observed capacity can be accounted for by two major processes occurring upon charging to the extremely high potential: oxygen loss and proton/Li ion exchange. The coordination number of the Mn ions is expected to decrease due to the oxygen evolution as described in Eq. 2 and will also contribute to the decrease of the magnitude of the Mn-O interaction in the Fourier transformed EXAFS signals.

The electrochemical behavior of LiMg$_{0.5-x}$Mn$_{1.5+x}$O$_4$—In order to evaluate the influence of non-Redox divalent cation introduced into the spinel matrix on the electrochemical activity of the Mn spinel materials at the 5 V region and to establish that the nonactive redox divalent cation forces some Li ions to reside in octahedral sites and in return the nonactive divalent cation resides in the original lithium tetrahedral sites, we also studied and evaluated lithiated Mn spinels doped materials with magnesium bearing a general formulation of LiMg$_{0.5-x}$Mn$_{1.5+x}$O$_4$ ($0.0 \leq x \leq 0.5$). LiMg$_{0.5-x}$Mn$_{1.5+x}$O$_4$ ($0.0 \leq x \leq 0.5$) materials were synthesized from the acetate salts as outlined in the Experimental section. The XRD patterns obtained from LiMg$_{0.5-x}$Mn$_{1.5+x}$O$_4$ ($x = 0.35$, 0.25, and 0.5) and LiZn$_{0.25}$Mn$_{1.75}$O$_4$ are shown in Fig. 14, I, II, III, and IV, respectively. It is noted that some new diffraction peaks (marked by asterisks in Fig. 14) appear in the spectra of the heavily Mg-doped materials, which are also present at almost similar positions to that of LiZn$_{0.25}$Mn$_{1.75}$O$_4$. Similar results are also reported in the literature and LiMg$_{0.5}$Mn$_{1.5}$O$_4$ is refined to a primitive cubic structure with a space group of P4$_3$32.

The electrochemical behavior recorded from polarizing the Mg-doped spinel materials is shown in Fig. 15a (slow scan cyclic voltammetry) and 15b (first galvanostatic charge and discharge between the potential limits of 3.3 and 5.4 V). This figure also presents a comparison of the electrochemical activity recorded from electrochemically polarizing doped Mg and Zn materials. As can be seen, a 5 V activity is also detected with the low doped Mg materials. The pronounced 5 V activity was detected to be with the LiMg$_{0.5}$Mn$_{1.5}$O$_4$ composition. Thus, the doping of the Mn spinel with nonreactive divalent cation causes the appearance of a 5 V activity. Magnesium as an additive in lithiated Mn spinel oxide deserves more scientific attention in light of these recent results. Thus,
extending our view on the role of non-Redox divalent cation in the Mn oxide spinel matrix has been demonstrated by doping Mg instead of Zn.

Conclusions

Partial reversible behavior of Li2Zn0.5-Mn1.5O4 group materials is observed at the 5 V region. As seen from in situ XRD spectroscopy studies, the diffraction peaks are shifted to a higher angle in the charge process and shifted backwards during the discharge cycle, while lithium ions are extracted from and reinserted into the crystal lattice, respectively. The lattice parameters vs discharge capacity plot resembles the electrochemical charge and discharge potential profiles and implicate a close relationship between lattice energy and lattice parameters in the Zn-doped spinel system. Lithium ions extracted at 5 V during the charge process are partially reinserted back into the tetrahedral sites during the discharge step, which probably contributes to the partial reversible 5 V behavior. The significant findings reported here are that the strong tetrahedral site preference of a divalent nonreactive cation such as Zn and Mg forces the Li cation onto octahedral sites in these materials, thus causing electroactivity at the 5 V region from the displaced Li in the 10d sites of the spinel. In situ XAS measurements show that the Mn K edge is shifted to high energy at the 4 V region during the charge cycle and remains unchanged at the 5 V region. In situ Mn K-edge EXAFS studies suggest that O2− ions in the Zn-spinel lattice are being partially oxidized to O− at the 5 V plateau during the anodic process and that some of the unstable O− ions are being reduced back to O2− during cathodic process at 5 V. The oscillations of the lattice parameters observed at the 5 V region during the anodic charge step are attributed to the chemical instability of O− ions, leading to electrochemical disproportion reactions.

Acknowledgments

This work was supported by the Miami Energy Research Foundation, grant no. 2003446, at the Research Foundation of the Technion-Israel Institute of Technology, and by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division, U.S. DOE under contract no. DE-AC02-98CH10886. The financial support from the Department of Energy, Materials Science Division for building and supporting the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY) is deeply appreciated. The authors thank N. Hakim and W. Fowle for their assistance in SEM studies.

Northeastern University assisted in meeting the publication costs of this article.

References

34. K. Kanamura, J. Power Sources, 81-82, 123 (1999).