Zn-doped Mn spinel was investigated for its unique 5 V reversible Li intercalation. Only at a certain Zn doping, LiZn0.25Mn1.75O4, lithium ions can be extracted at 5 V, while at high Zn doping of LiZn0.5Mn1.5O4 no reversible capacity was observed. Electrochemical extraction of lithium ions during charge at 5 V is partially reversible. The two Zn doped compositions (x = 0.25 and 0.5 in LiZn1−xMnxO4) have a single phase cubic spinel structure, possessing a primitive cubic atomic arrangement, in contrast to the face centered cubic LiMn0.5O4 spinel. All materials synthesized have a tetrahedra grain structure, bonded via the hexagon facets.

One highly interesting phenomenon associated with such doping is still regarded as a prospective cathode material for the next generation of lithium batteries. It has a face-centered cubic (FCC) spinel structure with lithium and Mn ions occupying the tetrahedral sites and octahedral sites, respectively. The theoretical specific capacity of this material is 148.2 mAh/g, with the characteristic, Mn 3+ oxidation state and minimize Jahn-Teller distortion.3,4 It is normally believed that the nonstoichiometric Li1−xMnxO4 has a high phase transition series is an important dopant element because it allows for better modeling of the behavior at elevated potentials. The filled d-shells of Zn enforce that as a consequence of charge compensation all Mn associated with Zn would be in the +4 valence state.

Experimental Samples with the general composition of LiZn1−xMnxO4 with x = 0, 0.25, and 0.5, were prepared from the acetate salts (Li acetate, Mn acetate, and Zn acetate, Fluka) using 7 Li solid state nuclear magnetic resonance (NMR).18 It suggests that Zn ions occupy tetrahedral positions, forcing some fraction of lithium ions into octahedral sites. However, these studies report on a single material composition, such as LiZn0.25Mn1.75O4, cycled up to 5 V, while other compositions of LiZn1−xMnxO4 remain unexamined both in terms of composition and potential window of charge/discharge.

In this short communication we report, for the first time, 5 V activity of Zn-doped Mn spinel material. The observed behavior is investigated with Zn substitution in the range LiZn1−xMnxO4, where x in the range 0 ≤ x ≤ 0.5. Zn being at the end of the first row transition series is an important dopant element because it allows for better modeling of the behavior at elevated potentials. The filled d-shells of Zn enforce that as a consequence of charge compensation all Mn associated with Zn would be in the +4 valence state.

Results and Discussion Materials characterization XRD measurements.---Figure 1 presents XRD patterns of three Zn-doped materials with Zn composition of x = 0.0, 0.25, and 0.5 in LiZn1−xMnxO4 (Fig. 1a-c, respectively). Nearly phase-pure Zn doped materials exhibited XRD patterns which were somewhat different from the diffraction pattern obtained from LiMn0.5O4, wherein a significantly higher number of diffraction peaks are observed in the former. The existence of a contaminant phase, with insignificant concentration, most probably

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due to the formation of ZnMn$_2$O$_4$ spinel (peaks positioned at 2 theta of 29.3° and 33.1°, marked in Fig 1b and c) is observed in the Zn doped powder materials. The intensity of some diffraction peaks which are not observed in the pristine LiMn$_2$O$_4$ XRD pattern, such as 110, 200, and 210, increases as the Zn content increases. This suggests that Zn ions may be occupying tetrahedral sites in the crystal lattice. LiZn$_{0.5}$Mn$_{1.5}$O$_4$ was indexed as a cubic structure with a lattice parameter of 8.17 Å, using powder indexing module in the Cerius$^2$ program. Furthermore, the Zn doped spinels with Zn content of 0.25 and 0.5 have similar XRD diffraction patterns, which suggest that their crystal structures are similar. The patterns for Zn-doped spinel materials were indexed to provide for a primitive cubic gest that their crystal structures are similar. The patterns for Zn-doped spinel materials were indexed to provide for a primitive cubic structure compared with face centered cubic LiMn$_2$O$_4$ spinel structure. Moreover, the existence of the 200 and 400 planes, and the absence of the 100 plane in the spectra may suggest the existence of a 21 screw axis at the 100 plane. Thus, the Zn substituted Mn spinel compounds belong to a P2$_1$3 space group. Hence, referring to the composition of LiZn$_{0.5}$Mn$_{2-x}$O$_4$ (with $x = 0.25$ and 0.5) as Zn doped Mn-spinels is incorrect and we henceforth refer to them as cubic Zn-modified LiMn$_2$O$_4$.

High-resolution scanning electron microscopy (HRSEM).—Figure 2 presents HRSEM images obtained from three samples of composition; LiZn$_{0.5}$Mn$_{2-x}$O$_4$ with $x = 0.0$, 0.25, and 0.5 (Fig. 2a, c, and e, respectively). All three materials have a truncated octahedral structure (tetradecahedra), having six squares and eight hexagons, with side lengths of 60-100 nm. Although there are two ways for co-joining two tetradecahedra units and 6 possibilities for three tetradecahedra blocks to be linked, the SEM micrographs (Fig. 2b, 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 to the best of our knowledge. These “single crystal” like structures are important in understanding intra-domain interactions and grain fracture as a result of cycling.

Electrochemical characterization. Slow scan cyclic voltammetry (SSCV).—Figure 3 shows SSCV of three samples with and without Zn-doping with Zn composition of $x = 0.0$, 0.25, and 0.5 in LiZn$_{0.5}$Mn$_{2-x}$O$_4$ (Fig. 3a-c, respectively). The two-step charge and discharge profile at 4 V region for $x = 0.25$ in LiZn$_{0.5}$Mn$_{2-x}$O$_4$ is well resolved as evident from Fig. 3b, albeit with a lower resolution as compared to the corresponding behavior for LiMn$_2$O$_4$ (Fig. 3a). The 5 V behavior is clearly observed for the LiZn$_{0.5}$Mn$_{2-x}$O$_4$ composition containing $x = 0.25$. However, no electrochemical activity is observed for the $x = 0.5$ in composition (LiZn$_{0.5}$Mn$_{2-x}$O$_4$).

Figure 1. XRD pattern (Cu Kα) for LiZn$_x$Mn$_{2-x}$O$_4$ powders, where $x$ = (a) 0, (b) 0.25, and (c) 0.5.

Figure 2. HRSEMs obtained from three Zn-doped materials with Zn composition of (a and b) $x = 0.0$; (c and d) $x = 0.25$ and (e and f) $x = 0.5$ in LiZn$_x$Mn$_{2-x}$O$_4$.

Figure 3. SSCV (20 μV/s) of three Zn-doped materials with Zn composition of $x = (a) 0.0$, (b) 0.25, and (c) 0.5 in LiZn$_x$Mn$_{2-x}$O$_4$. Li metal served as anode and reference electrodes.
Chromopotentiometric studies.—Three totally different types of electrochemical behavior are observed for the three LiZn$_{x}$Mn$_{2-x}$O$_4$ materials compositions, where $x = 0.0, 0.25$, and 0.5, as evident from Fig. 4. The Zn-doped material with Zn content of 0.25 exhibits two potential plateaus, which are located at 4 and 5 V, separated by a potential jump between 4.3 and 5 V. These two regions can also be seen in the discharge step, although the discharge capacity at 5 V is much smaller (50 mAh/g) as compared to the corresponding charge capacity (50 mAh/g), pointing to a poor reversibility and a possible electrolyte oxidation at 5 V. Nevertheless, the 5 V electrochemical activity is still observed (although reduced discharge capacity is being recorded at each cycle) at the following consecutive 3 cycles, as shown in the inset in Fig. 4. It is also observed that the specific discharge capacity at 4 V region increases with decrease in the Zn content in the ceramic compounds (almost no capacity at $x = 0.5$ to 50 mAh/g at $x = 0.25$ and 120 mAh/g at $x = 0$ in LiZn$_{0.25}$Mn$_{1.75}$O$_4$), which can be correlated to a decrease in the content of Mn$^{4+}$ ions in the crystal lattice. This is manifest in the extremely small capacity, of less than 5 mAh/g, for LiMn$_{1.75}$Zn$_{0.25}$O$_4$ material, having a nominal Mn oxidation state of +4. Furthermore, the 5 V behavior is completely absent. Thus, it is believed that the oxidation of Mn ions from a $+4$ state to a higher oxidation state is not the origin for the 5 V behavior observed with the specific composition of LiZn$_{0.25}$Mn$_{1.75}$O$_4$. The characteristic well-known two-step charge and discharge profiles, around 4 V region, typical for LiMn$_2$O$_4$, are also seen for the Zn-doped material with a composition of 0.25, albeit with a much smaller resolution. The existence of two step behavior with a lower resolution as compared to those typically observed for nondoped Mn spinel suggests a different intercalation environment due to Zn doping. This is supported by our XRD data where Zn doping causes a transition to a primitive cubic structure from a FCC spinel. Taking into a consideration that all zinc ions reside in 8a lithium tetrahedral sites, while some Li cations reside also in the octahedral 16d site, yielding a material formulated as [Li$_{0.75}$Zn$_{0.25}$]$_{8a}$[Mn$_{1.75}$(+4)Mn$_{0.25}$(+3)]$_{16d}$O$_4$, it is expected that at the 4 V region the overall theoretical capacity would be $\sim 70$ mAh/g, while the theoretical capacity at the 5 V, related to the extraction of Li from octahedral sites would be $\sim 35$ mAh/g. The experimental discharge capacities obtained both at the 4 V (50 mAh/g) and at the 5 V (25 mAh/g) regions are in good agreement with the theoretical calculations.

Zinc, cadmium, and mercury belong to Group II B (12) elements, having two s electrons outside filled d shells. These elements follow Cu, Ag, and Au in their electronic structures. Whereas in Cu, Ag, and Au, the filled d shells fairly readily lose one or two d electrons to yield ions or complexes in the II and III oxidation states, this was never reported or anticipated from Group II B (12) elements.\(^{19}\) The high potential activity of the low doped Zn spinel material cannot be attributed to an alteration in Zn ion valance state from a +2 state to a higher state, as was previously demonstrated with copper doped Mn spinels.\(^{3,4}\)

At the same time, the research group headed by Yoshio\(^{45}\) reported that the coexistence of both oxygen and lithium excess in the spinel matrix is a necessary condition for the 5 V anodic peak observed during SSCV. It was stated also that the intensity of the anodic peak observed at 5 V during SSCV increases as lithium content increases. We assume at this stage that Zn ions are forcing Li ions into 16d sites. It is thus suggested that the high anodic peak at 5 V region is related to the extraction of lithium ions from octahedral sites which possess higher lattice energy than the tetrahedral lithium ions.

**Conclusions**

Zinc doping into LiMn$_2$O$_4$ materials give rise to the formation of a primitive cubic structure, in contrast to the FCC LiMn$_2$O$_4$ spinel structure. A partially reversible electrochemical activity at 5 V was recorded with a low doped ($x = 0.25$) Zn substituted LiZn$_{0.75}$Mn$_{1.25}$O$_4$. As expected, almost no electrochemical activity was recorded with the highly doped ($x = 0.5$) Zn substituted analog. On one hand, zinc doping cannot be regarded as the origin of the 5 V electrochemical behavior, and on the other hand, Zn doping is proven to be necessary to facilitate the 5 V behavior.

The full version of the paper will provide detailed structural characteristics of the changes in the LiMn$_2$O$_4$ on Zn substitution. Zn doping is distinct from analogous doping with Cu, Cr, and other transition elements,\(^{19,12}\) where the original spinel framework was maintained to significant levels of doping. The significant findings reported in this short communication are that the strong tetrahedral site preference of divalent Zn cation is forcing Li cation onto octahedral sites in this material, thus causing electroactivity at 5 V from the displaced Li in the 16d sites of the spinel. This application of divalent doping of a nonredox active element, such as Zn in these high-substituted compositions in cubic LiMn$_2$O$_4$, has not been reported previously. Doping with $s^{2\ldots}$ elements such as Zn seems to have unique characteristics, wherein Mn-oxygen framework is influenced, unlike the effect of charge compensation observed with other transition metal dopants (such as Cr, Cu etc.). The effect of such changes in Mn-O coordination may shed some insights into understanding the overall 5 V behavior of undoped Mn-Spinel. The full version of this paper will present in detail the changes in the Mn-oxygen framework due to Zn substitution at high and low potentials (below 3 V). This will include synchrotron based in situ XRD, refinement of the structure by Rietvild analysis and XANES as well as electrochemical mapping of more Zn substituted Mn spinel compounds ($0.5 < x < 0$ in LiZn$_{0.75}$Mn$_{1.25}$O$_4$).

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