NaV$_{1.25}$Ti$_{0.75}$O$_4$: A Potential Post-Spinel Cathode Material for Mg Batteries

Xiaoqi Sun,† Lauren Blanc,† Gene M. Nolis,‡ Patrick Bonnick,† Jordi Cabana,†‡ and Linda F. Nazar*†‡

†Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
‡Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States

Supporting Information

ABSTRACT: Rechargeable Mg batteries are promising candidates for high energy density storage in theory, when a Mg metal anode is combined with an oxide cathode material. Despite the widely observed sluggish Mg$^{2+}$ diffusion in most oxide lattices, recent first-principles calculations predicted low diffusion barriers in the calcium ferrite (CF)-type post-spinel structures. In the present work, we experimentally examine the prospect of CF-type NaV$_{1.25}$Ti$_{0.75}$O$_4$ as a Mg cathode. The Na$^+$ ions, which lie in the ion migration pathway, need to be removed or exchanged with Mg$^{2+}$ to allow Mg$^{2+}$ de/intercalation. Partial desodiation was achieved through chemical and electrochemical methods, as proven by X-ray diffraction and X-ray absorption spectroscopy, but deep desodiation was accompanied by partial amorphization of the material. Mg$^{2+}$ ion exchange at moderate temperature (80 °C) resulted in the formation of Na$_{0.19}$Mg$_{0.41}$V$_{1.25}$Ti$_{0.75}$O$_4$; however, phase transformation was observed when higher temperatures were applied to attempt complete ion exchange. Such phenomena point to the instability of the CF lattice when the tunnel is empty or occupied by a small ion (Mg$^{2+}$). Thus, while the low migration barrier predicted by computation is partly based on the relative nonaccessibility, hindering this post-spinel’s application as an electrode material.

INTRODUCTION

Rechargeable Mg batteries show potential as high energy density storage systems. The Mg metal anode provides high volumetric capacity (3833 mA h mL$^{-1}$) and low redox potential (~2.37 V vs SHE), while long-term application, good safety, and low price are ensured by its limited dendritic growth during electrochemical deposition, its stability under ambient conditions, and a high abundance on earth. However, the divalent transition-metal oxide that overcomes these barriers is very challenging but at the same time necessary to advance the field.

First-principles calculations predict that the calcium ferrite (CF) structure (Figure 1 inset), which belongs to the post spinel structural family, allows relatively facile Mg$^{2+}$ diffusion. Mg$^{2+}$ migration barriers below 400 meV were calculated for the CF MgMn$_2$O$_4$ and desodiated NaV$_{1.25}$Ti$_{0.75}$O$_4$ materials.9,10 However, the former, along with many other post spinel materials, can be synthesized only under high pressure (a few Gpa),11–13 thus limiting accessibility from both a research laboratory and practical application point of view. NaV$_{1.25}$Ti$_{0.75}$O$_4$ on the other hand, can be obtained by conventional solid state synthesis at ambient pressure.14

Despite its relatively low predicted voltage of 1.5 V (vs Mg),10 it offers an easily accessed platform to experimentally investigate Mg$^{2+}$ diffusion in the CF structure. Herein, we examine the possibility of utilizing CF-type tunnel-structured NaV$_{1.25}$Ti$_{0.75}$O$_4$ obtained through a solid state synthesis method as a cathode material for Mg batteries. To induce Mg$^{2+}$ de/intercalation, the Na$^+$ cations in the tunnels were either extracted or exchanged with Mg$^{2+}$ ion through transition-metal oxide that overcomes these barriers is very challenging but at the same time necessary to advance the field.
chemical or electrochemical methods. Although the Na+ could be partially removed, our results showed a strong driving force toward structural degradation of the lattice upon full desodiation, demonstrating the instability of the CF phase when the tunnels are empty. Mg insertion in partially desodiated materials (either by chemical or electrochemical means) showed some (albeit limited) reversible capacity, suggesting Mg2+ mobility within the CF lattice. Thus, the approach to prepare metastable materials with low migration energy barriers shows potential in the search for Mg intercalation cathode candidates but must be balanced with targeting end members that are just on the edge of thermodynamic stability.

**EXPERIMENTAL SECTION**

Material Synthesis, Chemical Oxidation, and Mg Ion Exchange Reactions. NaV$_{1.25}$Ti$_{0.75}$O$_4$ was obtained from a small molar ratio, and the mixture was pelletized and heated at 600 °C for 1 h, and cooled naturally in the furnace. The tube was then opened in air, and water was added to transfer the powder to a funnel. The product was filtered and washed with water and ethanol.

**Materials Characterization.** X-ray diffraction (XRD) analysis was carried out on a PANalytical Empyrean diffractometer with Cu Kα radiation in Debye–Sherrer geometry. The sample was mixed with standard silicon (325 mesh, Sigma-Aldrich, 99%) and sealed in a 0.3 mm capillary to evaluate the crystalline fraction (Table S2). Rietveld refinement was performed using the FullProf suite. Scale factor, zero point, background, lattice parameters, fractional coordinates, and thermal parameters were sequentially refined. Vanadium and titanium have very similar X-ray scattering factors and cannot be distinguished by XRD. Thus, the occupancies were fixed at values reported in the initial reference from neutron diffraction. Trying to refine Na occupancy and thermal parameter in the chemically oxidized and Mg ion exchanged materials resulted in unstable values, so the thermal parameter was fixed as the pristine NaV$_{1.25}$Ti$_{0.75}$O$_4$, and the occupancy was refined.

The morphologies and elemental ratios of the materials were studied with a Zeiss Ultra field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX) detector. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo VG Scientific ESCALab 250 instrument. Spectra were processed with Gaussian–Lorentzian functions and a Shirley-type background with CasaXPS software and referenced to adventitious carbon at 285.0 eV. This report describes the SEM and EDX

Electrochemical Studies. Cathodes were prepared by mixing the pristine material with Super P and polyvinylene fluoride (PVDF, Sigma-Aldrich, average Mw ~ 354 000) at 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5%) and casting the slurry on stainless steel foil. An electrolyte comprised of 0.5 M Mg(Cl$_2$)$_2$ in tetraglyme$^{16}$ and a Mg metal anode were used for Mg cells, while an electrolyte comprised of 1 M NaClO$_4$ in PC with 2 vol % FEC and a Na metal anode were used for Na cells. Coin cells (2325) were assembled for cycling studies. Electrochemical studies were performed with a VMP3 potentiostat/galvanostat (Biologic) with cells held in a thermostated oven at designated temperatures.

In Situ XRD. The cathode slurry was cast on a glassy carbon electrode and assembled in a homemade in situ cell with 1 M NaClO$_4$ in PC with 2 vol % FEC electrolyte and Na metal anode. The cell was cycled at 5 mA g$^{-1}$ current density at room temperature, with XRD scans recorded operando. Each scan was half-hour long, corresponding to 2.5 mAh g$^{-1}$ capacity or ΔX = 0.0174 in NaV$_{1.25}$Ti$_{0.75}$O$_4$. Lattice parameters were extracted by Le Bail fitting$^{17}$ using the FullProf suite.

X-ray Absorption Spectroscopy (XAS). X-ray absorption spectroscopy measurements were conducted at beamline 6.3.1.2, Advanced Light Source, Lawrence Berkeley National Laboratory. Spectra were collected simultaneously in both the total-electron yield (TEY) and total-fluorescence yield (TFY) modes to make direct
surface to bulk comparisons. Data were obtained at a spectral resolution of ~0.2 eV with a 2 s dwell time. At least 2 scans were performed on each sample at each absorption edge, and scans were averaged to maximize the signal-to-noise ratio. V L2,3- and O K-edges were collected simultaneously at 505–600 eV, and Ti L2,3-edges were scanned at 445–480 eV. The current corresponding to I0 in electron yield was unstable at the energy of the Ti L2,3-edges. Because I0 did not change in the short time frame between samples, the measured yields of the spectra were not divided by it.

Results and Discussion

NaV$_{1.25}$Ti$_{0.75}$O$_4$ was synthesized following the previously reported procedure, with minor modifications (see Experimental Section for details). The material was at least 93 wt % crystalline as determined by comparison with a standard, and the crystal structure was confirmed by Rietveld refinement (Figure 1 and Tables S1a and 2). SEM images show that the crystallites are about one micrometer in dimension (Figure 1 inset). For the material to function as a Mg cathode, the Na$^+$ ions in the structure must either be removed or exchanged with Mg$^{2+}$. We examined Na$^+$ extraction using chemical oxidation. Two different oxidizing agents, FeCl$_3$/water and I$_2$/ACN were employed, providing products that were labeled as chem-ox-1 and chem-ox-2, respectively. The XRD patterns of both materials show a clear shift in d-spacing and intensity change compared to the pristine material (Figure 2a) with chem-ox-2 showing a larger difference that is indicative of a higher degree of Na$^+$ extraction. The most significant decrease is in the b lattice parameter, as summarized in Table 1. Rietveld refinement reveals a decrease in Na occupancy in the chemically oxidized materials (Figures 2b and c and Tables S1b and c), demonstrating that Na$^+$ was indeed removed from the structure. The lowest Na$^+$ content of 0.25 was achieved in chem-ox-2; i.e., a formula of Na$_{0.25}$V$_{1.25}$Ti$_{0.75}$O$_4$, whereas chem-ox-1 yielded Na$_{0.34}$V$_{1.25}$Ti$_{0.75}$O$_4$. The change in the Na content is in accord with EDX results (Table 1).

While Na can be chemically extracted from NaV$_{1.25}$Ti$_{0.75}$O$_4$ upon deep desodiation, simultaneous amorphization occurs. The crystalline weight percentages for chem-ox-1 and chem-ox-2 were 99 and 64%, respectively, suggesting a crystalline Na$^+$ content of less than 0.25 in chem-ox-2; i.e., a formula of Na$_{0.25}$V$_{1.25}$Ti$_{0.75}$O$_4$, whereas chem-ox-1 yielded Na$_{0.34}$V$_{1.25}$Ti$_{0.75}$O$_4$. The change in the Na content is in accord with EDX results (Table 1).

Chemistry of Materials

Figure 2. (a) XRD patterns in a selected range to show shifts in d-spacing, (b and c) Rietveld refinement fits with standard Si (34 wt % for chem-ox-1 and 17 wt % for chem-ox-2) addition, and (d) SEM images of the two chemically oxidized samples. (Black crosses, experimental data; red lines, fitted data; blue line, difference map between observed and calculated data; green ticks, the Pmnb CF phase; magenta ticks, the Fd$ar{3}$m Si phase. The different particle size in chem-ox-2 is a result of slightly different synthesis conditions being used to generate the pristine materials.)

(600 vs 400 meV). Even at an elevated temperature of 90 °C, the Na$^+$ content at the end of charge is about 0.44 as revealed by EDX. Electrolyte decomposition can take place below 4 V at such temperatures, adding slightly to the total capacity (Figure 3d).

The standard addition method to evaluate the weight percent of a crystalline phase in a cathode material using ex situ XRD data would result in large error due to the low cathode mass (a few milligrams), while reliable Rietveld refinement is not possible with in situ laboratory-XRD data due to the thinness of the electrode. Nevertheless, a rough estimation of any change in crystallinity on charging can still be made from in situ XRD peak areas. The total peak area of the charged material is about 93% of the pristine, showing that only minor amorphization, if any, of the electrochemically charged material takes place. This suggests that amorphization either only starts to take place at lower Na content and/or is primarily induced by the more

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DOI: 10.1021/acs.chemmater.7b03383
forcing potential provided by chemical oxidation ($I_2$ at elevated temperature), which is generally a less gentle oxidation method.

Table 1. Summary of Rietveld Refinement and Chemical Composition Results of the Desodiated and Magnesium Ion Exchanged Materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$x$(Na) (Rietveld x + Si std. addt'n)</th>
<th>$Xt$ wt % (Rietveld Si std. addt'n)</th>
<th>Overall $x$(Na)$y$(Mg)/$V_{1.25}Ti_{0.75}O_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>2.947</td>
<td>9.167</td>
<td>10.670</td>
<td>1 (fixed)</td>
<td>93(5)</td>
<td>0.87Na (EDX)</td>
</tr>
<tr>
<td>Chem-ox-1</td>
<td>2.937</td>
<td>8.954</td>
<td>10.649</td>
<td>0.36</td>
<td>99(5)</td>
<td>0.24Na (EDX)</td>
</tr>
<tr>
<td>Chem-ox-2</td>
<td>2.939</td>
<td>8.883</td>
<td>10.643</td>
<td>0.25</td>
<td>64(4)</td>
<td>0.14Na (EDX)</td>
</tr>
<tr>
<td>Echem-ox-RT</td>
<td>2.936</td>
<td>9.038</td>
<td>10.634</td>
<td></td>
<td></td>
<td>0.44Na (Echem)</td>
</tr>
<tr>
<td>Echem-ox-90 °C</td>
<td>2.933</td>
<td>8.996</td>
<td>10.649</td>
<td></td>
<td>0.02Na (Echem)</td>
<td>0.44Na (EDX)</td>
</tr>
<tr>
<td>Mg-ex</td>
<td>2.932</td>
<td>9.070</td>
<td>10.661</td>
<td>0.19 (Na)</td>
<td>92(5)</td>
<td>0.39Na, 0.22Mg (EDX)</td>
</tr>
</tbody>
</table>

Figure 3. (a–c) Lattice parameter evolution of Na$V_{1.25}Ti_{0.75}O_4$ during first charge examined in an in situ cell with a Na anode using an electrolyte comprised of 1 M NaClO$_4$ in PC with 2 vol % FEC. The electrochemical charge profiles of the corresponding cells (run at a current density of 5 mA g$^{-1}$ at room temperature) are also depicted. (d) Comparison of first charge profiles from cells running at room temperature and 90 °C, both at 5 mA g$^{-1}$.

Figure 4. X-ray near edge absorption spectroscopy (XANES) normalized electron yields for the materials examined in this study: (a) V $L_3$ and O $K$ edges between 513−522 eV, (b) Ti $L_2,3$ edge between 455−470 eV, and (c) V $L_3$ and O $K$ edges between 525−550 eV. XANES data for standards correspond to (1) VO$_2$, (2) V$_2$O$_5$, (3) TiO$_2$ anatase, and (4) pristine Na$V_{1.25}Ti_{0.75}O_4$. XANES data for Na$V_{1.25}Ti_{0.75}O_4$ subjected to various treatments are shown as follows: (5) chem-ox-1, (6) chem-ox-2, (7) electrochemically charged, and (8) chemically magnesiated. Full spectra are shown in the Supporting Information.
and S1, respectively. Electron yield signals correspond to the chemical state of the surface layer of the material, while fluorescence yield signals correspond to bulk properties. The trends discussed hereafter were very similar in both modes, indicating that surface and bulk undergo similar changes. The complete V L2,3 spectra can be found in Figure S2. The features correspond to transitions from transition-metal 2p3/2 (L3) and 2p1/2 (L2) states directly to the unoccupied 3d states, making them very sensitive to redox changes and local transition-metal coordination. The changes at the L3 edge, shown in Figure 4a, are representative of both edges. The spectrum of pristine NaV1.25Ti0.75O4 (#4, red) presents an intense feature at 518.3 eV with a shoulder at 517.1 eV and a tail to lower energies. The spectrum is located at energies significantly lower than those of VO2 (#1, black) and V2O5 (#2, gray), which show intense features around 519 eV, in agreement with literature reports. The slightly lower position of the center of gravity of VO2 compared to that of V2O5 is consistent with the lower formal oxidation state. The spectrum of NaV1.25Ti0.75O4 is close to V2O5 measured by Abbate, suggesting that V is in a majority (III) formal state in the compound as synthesized. This is in accord with previous magnetic susceptibility measurements of NaV1.25Ti0.75O4 that reported an average oxidation state of V3+, assuming a Ti(IV) valence. Our Ti 2p XPS data of the pristine material confirms the latter statement (Figure S3). The Ti L2,3-edge spectra of all NaV1.25Ti0.75O4 samples (Figure 4b) were consistent with a formal Ti(IV) state, indicating that redox takes place solely at the vanadium center. Slight variations in the symmetry of the coordination shell affect the multiplet splitting of the final 3d states. The L3 peaks between 455 and 462 eV are most sensitive to these changes in symmetry. The subtle differences between NaV1.25Ti0.75O4 (#4, red) and a standard spectrum for TiO2 (#3, olive) can therefore be ascribed to the specific geometric distortions of the octahedral environment of Ti(IV).

All O K-edge features originate from O 1s → O 2p transitions, where the states corresponding to O 2p orbitals hybridized with V and Ti 3d and 4s, p orbitals appear roughly below and above 535 eV, respectively (Figure 4c). The pre-edge features below this energy are again the most sensitive to redox changes. The O pre-edge of pristine NaV1.25Ti0.75O4 is composed of a broad, multicomponent signal starting at 529.6 eV and ending with a maximum at 531.9 eV. The shape, energy, and distribution of intensity were all different from VO2, V2O5, and TiO2, which show characteristic ts and e2 doublets around 530 and 532 eV, respectively, with the ts absorption event being the most intense of the two. The broad pre-edge features are representative of both edges. The spectrum is located at energies significantly lower than those of VO2 and TiO2, which show characteristic t2g and eg doublets around 530 and 532 eV, respectively (Figure 4c). The resulting overall line shape resembles the spectrum of VO2, indicating that chem-ox-2 was significantly more oxidized than chem-ox-1. This observation is consistent with the XRD analysis and suggests that the amorphous fraction resulting from the chemical treatments is significantly more oxidized than the crystalline oxide. The oxidation of the compound is accompanied by a subtle change in position of the Ti L3-edge spectra (e.g., around 460 and 465 eV, Figure 4b), indicative of changes in the local coordination of Ti(IV) due to the structural changes described by XRD. The formation of V(IV) in chem-ox-2 changed the hybridization with O, resulting in an increase of the ts feature at 530 eV in the pre-edge doublet (Figure 4c). The resulting O K-edge was closer to VO2. In the case of chem-ox-1, the pre-edge doublet was washed out, indicating a variety of V–O interactions at slightly different geometries. Its intensity increased with respect to the O 2p-V 4sp signals at the edge compared to the pristine state. Because XAS probes unoccupied electronic states, the increase in intensity is consistent with the decrease in electron occupancy of the O 2p-V 3d expected from oxidation. The changes at the V L3 and Ti L edges were small in Echem-ox-90 °C compared to the pristine state. However, the O K-edge spectrum was comparable to that of chem-ox-1, suggesting some oxidation of the compound. These trends agree with the XRD and EDX data.

The electrochemical behavior of both chemically and electrochemically desodiated materials was evaluated in Mg cells with a Mg monocarborane electrolyte (Mg(CB11H12)2 in tetraglyme) and Mg metal anode. At 60 °C, the chemically desodiated chem-ox-2 material (Na0.25V1.25Ti0.75O4) shows an initial sloping discharge curve at an average voltage of 1.5 V (Figure 5a), in good agreement with calculation. This trend continues up to a capacity of 50 mAh g−1, followed by a region of steeper voltage profile. A capacity of 80 mAh g−1 is reached at the end of discharge. The following charge retrieves only half of the initial capacity, and a large overpotential is observed.
showing moderate reversibility and kinetics of the process. The reversible capacity is retained on subsequent cycles, however. EDX revealed that 0.12(2) Mg\textsuperscript{2+} is present in the chem-ox-2 cathode at the end of the fifth discharge and demonstrates Mg intercalation takes place. The electrochemically desodiated material (Na\textsubscript{0.4}V\textsubscript{1.25}Ti\textsubscript{0.75}O\textsubscript{4}) exhibits poorer behavior upon Mg\textsuperscript{2+} intercalation; about twofold less capacity is reversible (Figure 5b). This may be due to its greater Na-ion content, which could affect Mg ion migration pathways.

The relatively poor electrochemistry of the chemically desodiated material (chem-ox-2) could result from the amorphous phase that is likely electrochemically inactive and resides on the surface. The electrochemically desodiated material, on the other hand, is still active as demonstrated by its low degree of amorphization (see discussion of Figure 3) as well as by its subsequent successful reversible cycling of sodium ions in a Na cell (Figure S4). Hence, we believe that the difficulty in inserting Mg\textsuperscript{2+} is due to the strong driving force toward structural degradation (in accord with calculations that

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**Figure 6.** (a) XRD of the Mg ion exchanged sample, showing a shift of XRD peaks. (b) Rietveld refinement fit the Mg ion exchanged sample with 17 wt % standard Si addition (black crosses, experimental data; red lines, fitted data; blue line, difference map between observed and calculated data; green ticks, the Pmnb CF phase; magenta ticks, the Fd3m Si phase; orange ticks, the R3c V\textsubscript{2}O\textsubscript{3} impurity phase, which also presents in the pristine material used in this ion exchange reaction due to slightly different synthesis conditions). Inset shows the SEM image.

**Figure 7.** XRD and SEM images of (a and c) low concentration and (b and d) high concentration CF in eutectic products showing MgTi\textsubscript{2}O\textsubscript{5} (red phase marks) and MgTiO\textsubscript{3} (orange phase markers) structures, respectively.
predict instability of the Mg-inserted lattice), which is not predicted to occur in the case of Na⁺ insertion.¹⁰

We also explored altering the strategy to directly exchange the Na⁺ ions with Mg²⁺. An ion exchange reaction was carried out by stirring the Na₁₀V₁₂.₅Ti₉₇.₅O₄ material in aqueous MgSO₄ at 80 °C. The XAS spectra of the Mg-ex exchanged were essentially the same as those in pristine NaV₁₂.₅Ti₉₇.₅O₄ except for a shift of the peak at 460.₅ eV to slightly lower energies (Figure 4). These similarities denote the preservation of the structure is formed (Figure 7b), which is the same as MgTiO₃ and NaV₁.₂₅Ti₀.₇₅O₄:eutectic were examined at 500 °C. This phase exhibits a tunnel Ti) is obtained as determined by XRD measurements (Figure 6a). X-rays cannot distinguish between Na and Mg due to their extremely similar scattering factors. Therefore, after initially refining the occupancy on the sodium site, we ensured charge balance was maintained in the final composition by assuming no oxidation state change on the transition metals arose during the ion exchange process (based on the XAS results), namely that the charge on that site (a combination of Na⁺ and Mg²⁺) was still close to zero. The refined Na and Mg occupancies (Table 1, Figure 6b, and Table S1d) yield a composition of Na₀.₁₉Mg₀.₄₁V₁.₂₅Ti₀.₇₅O₄ that is fully crystalline (see Table S1d for refinement details). A second ion-exchange process did not result in any change in either the Na/Mg composition or the crystallinity. This demonstrates that while some Mg²⁺ mobility indeed exists in the CF lattice, not all of the Na⁺ ions can be exchanged with Mg²⁺.

Alternatively, we carried out Mg ion exchange with a MgCl₂/KCl-1:2 eutectic which melts at 430 °C. Higher temperatures enhance ion diffusion in solid state lattices and would promote a deeper degree of ion exchange. Two different ratios of NaV₁₂.₅Ti₉₇.₅O₄ eutectic were examined at 500 °C (see Experimental Section for details), but both resulted in complete structural transformation. At a low CF ratio, MgM₂O₅ (M = V, Ti) is obtained as determined by XRD measurements (Figure 7a), which exhibits an XRD pattern identical to that of MgTi₂O₅ (ICSD no. 157236). This phase exhibits a tunnel structure similar to that of the CF phase, but the size of the tunnel is smaller owing to a different connectivity of the octahedral motifs (Figure 7a inset). This phase is presumably more thermodynamically stable at the higher temperatures employed in the reaction owing to the smaller size of the Mg²⁺ cation compared to Na⁺; hence, it is stabilized with shorter bonds. At a high CF ratio, a layered MgMo₃ (M = V, Ti) structure is formed (Figure 7b), which is the same as MgTiO₃ (ICSD no. 164766). We note that for both new phases, EDX shows that the same V:Ti ratio is preserved as in the starting NaV₁₂.₅Ti₉₇.₅O₄ phase. As both phases require a complete rearrangement of the CF structure, a dissolution—recrystallization process must be involved in the reactions in the eutectic melt. This is in agreement with the new morphologies of the products shown in the SEM images (Figures 7c and d) that are either square platelets (MgTi₂O₅) or submicrometer crystallites (MgTiO₃).

Overall, our experiments show that partial Na⁺ removal or Mg²⁺ exchange in the CF-NaV₁₂.₅Ti₉₇.₅O₄ material can be achieved under certain conditions. The largest change in the unit cell of the structure in both cases is observed in the b lattice parameter, which is perpendicular to the 1D ion tunnel direction, while minor changes are evident in the a and c parameters. Concomitant partial amorphization/phase trans-formation takes place, due in part to the inhomogeneity of Na⁺/Mg²⁺ ion distribution throughout the sample. Compositions with a lower Na⁺ content and/or more Mg²⁺ are unfortunately prone to framework collapse driven by thermodynamics. A similar trend toward amorphization/conversion was observed previously in other oxide-based Mg cathodes, which strongly limits their electrochemical behavior.⁷

Such structural instability of the CF phase is in accord with first-principles calculation results published after the start of our experimental study. According to Ceder et al., the E_hull of the empty lattice approaches 80 meV/atom, while Mg²⁺ insertion results in even higher E_hull values.¹⁰ Such values demonstrate a strong thermodynamic driving force toward structural decomposition to more stable phases, resulting in the amorphization or transformation into the MgTi₂O₅ and MgTiO₃ structures that we observed experimentally. The structural instability, on the other hand, lowers the energy difference between the starting and transition point of ion hopping and promotes a lower barrier. In fact, we observed some Mg²⁺ mobility in the CF structure based either on the (albeit limited) electrochemical performance of the Mg cells or the fact that we were able to achieve partial ion exchange of Na⁺ for Mg²⁺. Nevertheless, stabilizing a structure over a wide compositional range is required for cathode materials, which was not successful for the CF phase studied.

■ CONCLUSIONS

In summary, we carried out experimental investigations of CF-type NaV₁₂.₅Ti₉₇.₅O₄ as a potential cathode material for Mg batteries. Upon deep Na⁺ removal, amorphization is observed, demonstrating the instability of the empty lattice, and very limited Mg intercalation was observed into the electrochemically desodiated lattice. Such results are in agreement with the high E_hull values suggested by first-principles calculation. The structural instability of end members helps lower the ion migration barrier; however, it is essential that (1) the end members can be kinetically stabilized and (2) not undergo a high penalty for Mg²⁺ desolvation at the interface. Finding this “sweet spot” is challenging but can be potentially achieved by searching for metastable phases that provide a low energy barrier for ion diffusion with structures selected for optimal stability of the end members.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b03383.

Refrined parameters and crystalline phase weight percentages for the pristine, desodiated, Mg ion exchanged NaV₁₂.₅Ti₉₇.₅O₄ samples; XAS of the pristine, desodiated, and Mg ion exchanged samples measured for various materials in the full energy range at the V L₃-, Ti L₃-, and O K-edges with total electron and fluorescence yields complete V L₃ spectra; Ti 2p XPS spectrum; charge/discharge profiles for Na-ion de/insertion in NaV₁₂.₅Ti₉₇.₅O₄ in a Na cell (PDF)

■ AUTHOR INFORMATION

Corresponding Author*
E-mail: lfnazar@uwaterloo.ca.
Chemistry of Materials

ORCID
Jordi Cabana: 0000-0002-2353-5986
Linda F. Nazar: 0000-0002-3314-8197

Author Contributions
X.S. and L.F.N. conceived the experiments and study. X.S. carried out the materials synthesis, electrochemical studies, and materials characterization/analysis with the help of L.B. G.N. and J.C. performed the XAS study and contributed its discussion to the text. P.B. participated in the dialogue on divalent cation intercalation. X.S. and L.F.N. wrote the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the United States Department of Energy (DOE), Office of Science, Basic Energy Sciences. NSERC is acknowledged by L.F.N. for a Canada Research Chair. This research used Science, Basic Energy Sciences. NSERC is acknowledged by J. Alloys Compd.

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