# Phase-Controlled Electrochemical Activity of Epitaxial Mg-Spinel Thin Films

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**Supporting Information** 

**ABSTRACT:** We report an approach to control the reversible electrochemical activity (i.e., extraction/insertion) of  $Mg^{2+}$  in a cathode host through the use of phase-pure epitaxially stabilized thin film structures. The epitaxially stabilized  $MgMn_2O_4$  (MMO) thin films in the distinct tetragonal and cubic phases are shown to exhibit dramatically different properties (in a nonaqueous electrolyte,  $Mg(TFSI)_2$  in propylene carbonate): tetragonal MMO shows negligible activity while the cubic MMO (normally found as polymorph at



high temperature or high pressure) exhibits reversible  $Mg^{2+}$  activity with associated changes in film structure and Mn oxidation state. These results demonstrate a novel strategy for identifying the factors that control multivalent cation mobility in next-generation battery materials.

**KEYWORDS:** phase-selective electrochemical activity, Mg-spinel, epitaxial phase stabilization, multivalent insertion, pulsed laser deposition

## INTRODUCTION

Lithium ion battery (LIB) technology represents the current state-of-the-art rechargeable batteries with high Columbic efficiency (>99.99%) and modest charge density (140 mAh/ g).<sup>1</sup> It is unlikely to meet the needs for transportation and the electricity grid that account for two-thirds of U.S. energy use,<sup>2</sup> For example, current all-electric vehicles have a  $\sim$ 80 mile range compared to the  $\sim$ 300 mile range associated with internal combustion engines. This recognition has driven substantial research into "beyond lithium ion battery" technologies<sup>3,4</sup> that seek to increase gravimetric or volumetric capacities or to substantially reduce costs. Multivalent (MV) battery systems<sup>5-8</sup> (that use di- or trivalent ions, e.g., Mg<sup>2+</sup> or Al<sup>3+</sup> as the charge carrier instead of Li<sup>+</sup>) represent one possible beyond lithium ion chemistry. They are theoretically able to deliver more than 2-fold improvements in energy capacity compared to LIBs.<sup>9,10</sup> Their expected low cost due to the use of naturally abundant source materials makes MV batteries an attractive prospect.<sup>11</sup> Yet there has been little improvement in multivalent systems since the first demonstration of a Mg rechargeable battery prototype, 15 years ago, using a Grignard electrolyte, Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub> in tetrahydrofuran, and Chevrel phases of the  $Mo_6T_8$  family (T = S, Se, or their combination) with a theoretical charge capacity of ~122 mAh/g.<sup>5</sup> This system is limited by multiple factors, including its modest capacity (smaller than the typical capacity of LIB cathodes (140 mAh/ $g^{1}$ ), its low voltage, as well as substantial safety issues associated with the electrolyte.<sup>12,13</sup> The search for an improved MV battery system has been impeded by the need to identify a suitable cathode material that addresses both the prohibitively high diffusional barriers that are expected for MV ion transport (limiting ion transport<sup>10</sup>) and the need for electrochemical stability in contact with relevant multivalent electrolytes (e.g., typically nonaqueous, non-Grignard electrolytes).

Here, we present a novel approach to explore and understand factors that control reversible electrochemical activity of a Mg cathode through the use of model epitaxial thin film cathodes. Specifically, the use of epitaxial stabilization allows the comparison of electrochemical activity for structurally distinct materials that are compositionally identical. We demonstrate this approach by studying Mg<sup>2+</sup> insertion and extraction from spinel oxides, AB<sub>2</sub>O<sub>4</sub>, which are attractive cathode materials because they have low cost, low toxicity, and good safety characteristics.<sup>14</sup> This choice is based on the success of Li-based spinel cathodes, such as LiMn<sub>2</sub>O<sub>4</sub> (LMO) and LiNi<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub>.<sup>15</sup> Mg spinels, e.g., MgMn<sub>2</sub>O<sub>4</sub> (MMO),

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might be expected to reversibly incorporate Mg<sup>2+</sup>, since it has a diameter that is similar to Li<sup>+</sup> (~86 pm and ~90 pm, respectively)<sup>16</sup> and MMO has a theoretical gravimetric capacity of ~270 mAh/g.<sup>10</sup> Unlike LMO, MMO adopts a tetragonal spinel structure in space group  $D_{4h}^{19}-I4_1/amd$  with a = b = 5.727 Å and c = 9.284 Å.<sup>17</sup> This structure is a partially inverted spinel with a majority of Mn(III) in the octahedral site as well as a fraction of Mn(IV) and Mn(II) in the octahedral and tetrahedral sites, respectively<sup>18</sup> (indicated as  $(A_{1-\lambda}B_{\lambda})$ - $[A_{\lambda/2}B_{1-\lambda/2}]_2O_4$  where  $\lambda$  is the inversion degree and the parentheses and brackets denote the tetrahedral and octahedral sites, respectively). Theoretical investigations of this tetragonal spinel<sup>10</sup> as a possible insertion host for multivalent ions suggest that its primary limitation as a MV cathode is due to its intrinsically sluggish diffusion of Mg2+, moving between the tetrahedral and octahedral sites (with barriers of ~600-800 meV), which is a common limitation for multivalent cathodes. A recent experimental study shows that the delithiated cubic phase  $\lambda$ -Mn<sub>2</sub>O<sub>4</sub> can be inserted by Mg<sup>2+</sup> in both aqueous and nonaqueous electrolytes. However, this insertion drives a phase transformation from cubic  $Mn_2O_4$  to tetragonal Mg $Mn_2O_4$ .<sup>19</sup> In comparison, the stable operation of Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> as a cathode in LIBs makes use only of the cubic phase (i.e., x < 1), as complications such as capacity fade become apparent for x > 1where LMO transitions to the tetragonal phase.<sup>20</sup> These comparisons suggest that one possible route to improving the electrochemical properties of MMO as a multivalent cathode is the stabilization of the cubic  $MgMn_2O_4$  (or  $Mn_2O_4$ ) host lattice.

To test this idea, we compare the electrochemical activity of Mg<sup>2+</sup> in two epitaxially stabilized polymorphs of MMO thin films: the tetragonal vs cubic spinel structures of MMO. While the former is the stable phase under ambient conditions, the latter is found as the stable bulk phase only at high temperature (>950 °C)<sup>17,21</sup> or high pressure (>15.6 GPa).<sup>22</sup> Phase-pure epitaxially stabilized MMO thin films are synthesized on conducting buffer layers so that the intrinsic relationships between cathode crystal structure and its electrochemical activity can be explored. Our results reveal that these two phases exhibit dramatically different electrochemical properties: while no significant insertion behavior is found during charge/ discharge cycles for tetragonal MMO films, reversible Mg<sup>2+</sup> insertion was observed in cubic MMO films under identical experimental conditions. This study provides a new rational strategy to evaluate the critical factors that control cation mobility in host electrodes that ultimately can be used for the identification of active materials in MV battery systems.

## EXPERIMENTAL METHODS

**Thin Film Growth.** High quality epitaxial thin films of the tetragonal ( $\rm MMO_T$ ) and cubic ( $\rm MMO_C$ ) phases were grown by pulsed laser deposition (PLD) on MgO(001) substrates with a thin conducting buffer layer. PLD enables the growth of metastable crystalline structures,<sup>23,24</sup> allowing for the exploration of materials with new properties and novel functionalities. By adjustment of growth conditions (i.e., the substrate temperature, gas pressure, and laser power), heterostructured thin films with sharp interfaces and smooth surfaces can be obtained at the atomic level,<sup>25</sup> and many parameters such as film phase, geometry, orientation, and strain can be controlled. In particular, a critical challenge in this work is the identification and synthesis of conductive buffer layers that enable the electrochemical characterization of MMO films but also retain their conductivity upon growth of the active MMO layers under the strongly oxidizing PLD growth conditions.

Electrochemical Measurement. MMO<sub>C</sub>/TiC/MgO(001) and  $MMO_T/La_{0.7}Sr_{0.3}FeO_3/MgO(001)$  thin films were glued onto stainless steel supports and electrically connected to a stainless steel foil by silver paste that was sealed by Hysol 9462 epoxy. A capacitive anode was prepared by mixing BP2000 carbon (Cabot Corp.) with 40 wt % polyvinylidene difluoride (PVDF) and n-methyl-2-pyrrolidinone to make a viscous slurry. This slurry was then coated onto 304 stainless steel foil with a loading of  $\sim 4 \text{ mg/cm}^2$  and then dried in a vacuum oven at 75 °C for at least 8 h. Electrodes with a 7/16 in. diameter were punched from the sheet for use in the coin cell. These thin film cathodes were assembled in coin cell holders for battery tests, using a 0.2 M magnesium bis(trifluoromethane)sulfonamide  $(Mg(TFSI)_2)$  in propylene carbonate (PC) electrolyte. Cyclic voltammetry (CV) measurements were performed at 1 mV/s scan rate using a CHI660E potentiostat. The charged (i.e., Mg-extracted) and discharged (i.e., Mg-inserted) states of these thin film cathodes were obtained after several CV cycles by holding the potential at 1 V for 14 h and at ~0 V for 5 h, respectively.

**X-ray Diffraction.** Thin film X-ray diffraction (XRD) was performed using a four-circle diffractometer (PANalytical X'Pert PRO and Rigaku Smartlab) in specular and off-specular configurations with Cu K $\alpha_1$  ( $\lambda = 1.5406$  Å) radiation. Further characterization was performed at sector 33-BM-C and 11-ID-D of the Advanced Photon Source (APS) in Argonne National Laboratory (ANL) using 20 keV (33-BM) and 15.5 keV (11-ID) X-rays with a beam size of 2.0 mm horizontally and 0.1 mm vertically and an incident flux of ~10<sup>10</sup> (at 33-BM) or 10<sup>11</sup> (at 11-ID) photons per second. Scattered X-rays were detected using a pixel array area detector (Dectris PILATUS 100K mode). The sample was held in a custom-designed chamber with slow helium gas flow to avoid any sample damage during the XRD measurements.

X-ray Absorption and X-ray Photoelectrospectroscopy. The Mn oxidation states of charged and discharged MMO thin films and a standard MnO<sub>2</sub> powder were measured by X-ray absorption near edge spectroscopy (XANES) experiments and X-ray photoelectron spectroscopy (XPS). XANES measurements were carried out at APS sector 20BM-B. The powder sample was measured in transmission mode, and the thin film samples were measured using fluorescence. The XPS spectra were collected at the Keck II facility of NUANCE at Northwestern University with an Omicron ESCA probe using monochromated Al K $\alpha$  X-rays. A low-energy electron flood gun was used to compensate the XPS induced surface charging effects. The carbon 1s line (284.8 eV) was used as the reference to calibrate the XP spectra.

## RESULTS AND DISCUSSION

1. Epitaxially Stabilized MMO<sub>c</sub> vs MMO<sub>T</sub> Films. Polished MgO(001) single crystal substrates (from MTI and CrysTec) were used as substrates for PLD growth. MgO was annealed at 1100 °C in air for 12 h to obtain atomically flat surfaces (Figure S2). High quality, phase pure, 70 nm epitaxial  $MMO_T$  and  $MMO_C$  films each can be stabilized on MgO(001) substrates using a careful choice of conductive buffer layer composition and thickness (i.e., 50 nm La<sub>0.7</sub>Sr<sub>0.3</sub>FeO<sub>3</sub> (LSFO) and 50 nm TiC, respectively). Atomic-force microscopy measurements showed that MMO thin films have smooth surfaces with root-mean-square roughness of 2 Å (Figure S2). Specular X-ray reflectivity measurements (Figure S3) for both MMO<sub>T</sub>/LSFO/MgO(001) and MMO<sub>C</sub>/TiC/MgO(001) confirmed the phase purity of MMO, LSFO, and TiC thin films. The MMO film structure and its epitaxial relationships with the substrate and buffer layers were revealed by XRD (Figure 1). When grown on LSFO/MgO(001), the MMO<sub>T</sub> phase is obtained (Figure 1a). The resulting epitaxial alignment of MMO<sub>T</sub>[001]//LSFO[001]//MgO[001] directions is observed by specular XRD, with  $c_{\text{tetragonal}} = 9.244$  Å. Together with offspecular XRD and in-plane  $\phi$  scans (Figure S4), the in-plane



Figure 1. (a) Specular X-ray diffraction of tetragonal  $MMO_T$  around MgO(002) as a function of the modulus of the momentum transfer vector  $q = 4\pi \sin(2\theta/2)/\lambda$ . (b) Schematic of the crystallographic rotational and epitaxial relationships among MMO<sub>T</sub>, LSFO, and MgO, as well as MMO<sub>C</sub>, TiC, and MgO. Radial X-ray diffraction spectra of cubic  $MMO_{C}$  (c) near the MgO(002) and (d) MgO(202) Bragg peaks (in specular and nonspecular geometries, respectively). The solid lines are used to indicate the location of film and substrate Bragg peaks. The (004) peak positions of bulk MMO<sub>C</sub> (c = 8.600 Å) and bulk cubic spinel  $\lambda$ -Mn<sub>2</sub>O<sub>4</sub>(004) (c = 8.081 Å) are also denoted in (c) to indicate the expected diffraction peak positions for fully intercalated/ deintercalated MMO (in the absence of epitaxial stabilization). The small arrow in (c) shows changes in the lattice due to Mg<sup>2+</sup> extraction. In all cases, the XR data use the following color codes: black, asdeposited buffer layer (TiC or LSFO); red, as-deposited MMO on buffer layer; blue/green, charged and discharged states, respectively.

epitaxy is confirmed as MMO<sub>T</sub>[001]//LSFO[001]//MgO-[001] directions with  $a_{\text{tetragonal}} = 5.722$  Å. This tetragonal MMO<sub>T</sub> film has a 45° in-plane rotation with respect to LSFO and MgO substrates. (A schematic of the crystallographic alignment of the MMO films and MgO substrate is shown in Figure 1b.) In contrast, the cubic phase  $(MMO_C)$  was obtained when grown on TiC buffer layers (Figure 1c and Figure 1d). The following epitaxial relationships are observed:  $MMO_{C}[001] / / TiC[001] / / MgO[001]$  and  $MMO_{C}[100] / /$ TiC[100]//MgO[100] (see detailed explanation in Figure S5 and Supporting Information). The measured lattice constants of MMO<sub>C</sub>,  $a_{cubic} = 8.440$  Å and  $c_{cubic} = 8.339$  Å, show a nearly perfect lateral lattice match (within experimental uncertainties) to the TiC film (a = 4.224 Å, c = 4.218 Å) and the MgO substrate (*a* = 4.212 Å), namely,  $a_{\rm MMO} \approx 2^* a_{\rm TiC} \approx 2 a_{\rm MgO}$ . This suggests that the strain of forming a MMO film that is fully commensurate with its TiC buffer layer stabilizes the high T/P cubic MMO phase that has not previously been observed at ambient conditions.<sup>17,21,22</sup>

This controlled growth of tetragonal and cubic phases of MMO can be understood by the different strains induced by the two buffer layers (TiC and LSFO). Although LSFO and TiC are both cubic phases, the TiC buffer layer on MgO(001) has a lattice constant 4.218 Å, while LSFO has a lattice constant 3.931 Å. Compared to the bulk lattice constants of 8.6 Å for MMO<sub>C</sub><sup>[1]</sup> and 5.727 Å for MMO<sub>T</sub>, the in-plane strain induced by TiC,  $(a_{\rm MMO} - 2a_{\rm TiC})/(2a_{\rm TiC}) = 1.94\%$ , is much less than the strain if MMO<sub>T</sub> is grown on TiC,  $(\sqrt{2} a_{\rm MMO} - 2a_{\rm TiC})/(2a_{\rm TiC}) =$ 

-3.99%. However, to grow MMO on LSFO, the tetragonal phase has an advantage due to the smaller in-plane strain,  $(\sqrt{2} a_{\rm MMO} - 2a_{\rm LSFO})/(2a_{\rm LSFO}) = 3.02\%$ , as compared to that of MMO<sub>C</sub> on LSFO,  $(a_{\rm MMO} - 2a_{\rm LSFO})/(2a_{\rm LSFO}) = 9.39\%$ . Therefore, we conclude that epitaxial strain is a dominant factor to control and stabilize the different MMO phases in thin film form. Additionally, the buffer layer provides sufficient electrical conductivity to enable electrochemical measurements (<500 kΩ resistance measured within the plane of the film).

**2. Electrochemical Response of MMO\_T vs MMO\_C.** The electrochemical properties of the  $MMO_T$  and  $MMO_C$  phases were tested in coin cells using a  $Mg(TFSI)_2/PC$  electrolyte. Representative CV curves are shown in Figure 2a. Little or no



Figure 2. (a) Cyclic voltammetry (CV) of tetragonal  $MMO_T$  (pink) and cubic  $MMO_C$  (purple) thin film coin cells at 1 mV/s scan rate with BP2000 carbon on stainless steel as the anode and with 0.2 M Mg(TFSI)<sub>2</sub> in PC as the electrolyte. The bottom axis is the measured voltage versus carbon, and the top axis is the estimated Mg/Mg<sup>2+</sup> voltage. The carbon voltage was converted to Mg/Mg<sup>2+</sup> voltage by measuring its open circuit voltage versus a Ca reference electrode, which was calibrated in the same electrolyte using the ferrocene couple. (b) CV data for cycling tests of the MMOC at 1 mV/s scan rate. The redox peaks gradually decrease indicating capacity fade, but the redox peaks are still visible after 38 cycles.

significant electrochemical current is observed for  $MMO_T$ , which is similar to the background CV curves of the epoxy on stainless steel reference (Figure S7). In contrast,  $MMO_C$  shows substantial redox activity. On the basis of the integrated charge from CV curves and the known thickness of the  $MMO_C$  film, the charge capacity is estimated to be 250 mAh/g (in the second cycle), which is comparable to the MMO theoretical

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value of 270 mAh/g.<sup>10</sup> These redox peaks gradually faded with increasing cycle number; electrochemical activity can still be observed even after 38 cycles (with a capacity of 70 mAh/g), as shown in Figure 2b. The decrease could be due to the degradation of the film and the low Columbic efficiency (~65%) that is observed when using the Mg(TFSI)<sub>2</sub>/PC electrolyte. It is evident from these results that MMO<sub>C</sub> (the high temperature/pressure phase) exhibits substantially improved electrochemical performance compared to MMO<sub>T</sub>.

3. Characterizations and Discussion for Mg2+ Insertion/Extraction. Evidence that these observed redox reactions are due to changes in Mg<sup>2+</sup> stoichiometry (i.e., removal and insertion of Mg) is obtained by characterizing MMO<sub>T</sub> and MMO<sub>C</sub> samples through multiple structural and spectroscopic approaches. Specular XRD of MMO<sub>T</sub> in the asdeposited and charged states (Figure 1) shows no significant changes (e.g., in the peak position or width), consistent with the negligible electrochemical currents that were observed. In contrast, the  $MMO_{C}$  (004) lattice spacing (as measured by the (004) and (008) Bragg peak position) exhibits small but significant shifts between the charged and discharged states (Figure 1c and Figure S6). This reversible change in the MMO<sub>C</sub> lattice constant,  $\Delta c_{cubic} = 0.01$  Å, is a direct indication of structure changes associated with the extraction of Mg<sup>2+</sup> from the  $MMO_C$  lattice. (For reference, the (004) peak positions of MMO<sub>C</sub> (c = 8.600 Å)<sup>26</sup> and cubic spinel  $\lambda$ -Mn<sub>2</sub>O<sub>4</sub>(004) (c = 8.081 Å)<sup>19</sup> are also marked in Figure 1b; also, the change in LiMn<sub>2</sub>O<sub>4</sub> lattice constant is ~0.1 Å<sup>19</sup> when lithium is fully removed.) Note there is no significant change of  $MMO_{C}$  (404) peak position, as shown in Figure 1d. This could be due to no change of MMO<sub>C</sub> in-plane lattice constant from its epitaxial confinement by the substrate, thus negligible change of (404) *d*-spacing (discharged,  $d_{404} = 2.966$  Å; charged,  $d_{404} = 2.964$  Å).

The activity of  $MMO_C$  was further demonstrated by observing the associated changes to the Mn oxidation state. X-ray absorption near edge spectroscopy (XANES) measurements at the Mn K absorption edge (Figure 3) reveal systematic shifts of the Mn K edge energies (*E*) following the trend  $E(MnO_2) > E(MMO_C \text{ charged}) > E(MMO_C \text{ dis$  $charged})$ , with an observed edge shift of ~1.7 eV. This observation is consistent with the expected trend for Mn oxidation states, which is Mn(III) for Mg<sub>1</sub>Mn<sub>2</sub>O<sub>4</sub> and Mn(IV)



Figure 3. Mn K edge X-ray absorption near edge spectroscopy (XANES) of the charged and discharged cubic  $MMO_C$  thin films and a  $MnO_2$  reference powder. The small arrow indicates the edge shift (~1.7 eV) associated with the chemical state changes due to  $Mg^{2+}$  extraction.

for  $Mg_0Mn_2O_4$ . These observations confirm that the charged  $MMO_C$  has an average Mn oxidation state that is, on average, between III and IV, demonstrating at least partial magnesium extraction.

The relative stoichiometry of the different Mn oxidation states was obtained by surface sensitive X-ray photoelectron spectroscopy (XPS), further supporting the XANES findings. Figure 4a shows a survey scan of the charged and discharged MMO<sub>C</sub>. The change of Mg KLL peak intensity is indicative of Mg content. The composition analysis shows that discharged MMO<sub>C</sub> has relative stoichiometry of Mg/Mn  $\approx 1:2$  (i.e., the



**Figure 4.** (a) X-ray photoelectron spectra (XPS) survey scan of charged and discharged  $MMO_C$  thin films. The inset shows the change of Mg KLL signal, indicating the change of Mg content for the charged and discharged  $MMO_C$  states. (b) Mn 2p ( $2p_{1/2}$  and  $2p_{3/2}$  peaks at binding energies of ~654 and 642 eV) XPS of charged and discharged  $MMO_C$  thin films and a  $MnO_2$  reference powder. The peak shifts indicate that Mn in the charged  $MMO_C$  has an oxidation state between Mn(III) and Mn(IV). (c) A fit of the Mn  $2p_{3/2}$  peak shape for charged  $MMO_C$  shows a mixture of Mn(III) and Mn(IV).

nominal value of MgMn<sub>2</sub>O<sub>4</sub>), while charged MMO<sub>C</sub> has Mg/ Mn  $\approx$  1:3. Mg insertion and extraction are further supported by expected changes to the Mn 2p spectra of the charged and discharged MMO<sub>C</sub> (Figure 4b) showing that the Mn 2p<sub>3/2</sub> binding energy of charged MMO<sub>C</sub> lies between that of discharged MMO<sub>C</sub> and the MnO<sub>2</sub> powder standard, fully consistent with XANES results. These Mn 2p<sub>3/2</sub> spectra can be analyzed quantitatively according to the multiplet theory<sup>27</sup> (Figure 4b, Table 1, Figure S8) for the three samples.

Table 1. XPS Determination of Chemical States of Mn of Charged (Mg-Extracted) and Discharged (Mg-Inserted)  $MMO_C$  Films and a  $MnO_2$  Reference Powder<sup>a</sup>

chemical state	2+	3+	4+
MnO <sub>2</sub> powder			100%
$\mathrm{MMO}_{\mathrm{C}}$ charged	$0.1\% \pm 0.071\%$	$73.1\% \pm 2.0\%$	$26.8\% \pm 4.2\%$
$\mathrm{MMO}_{\mathrm{C}}$ discharged	15.9% ± 3.7%	84.0% ± 3.2%	$0.1\% \pm 1.1\%$
<sup><i>a</i></sup> The errors are obta analysis software.	ained using a Mor	nte Carlo method	from CasaXPS

Discharged  $MMO_C$  is predominantly (84%) Mn(III), as expected, with 16% Mn(II), while charged  $MMO_C$  has 27% Mn(IV) and 73% Mn(III). Together, the XRD, XPS, and XANES analyses consistently and quantitatively demonstrate reversible electrochemical extraction and insertion of Mg in  $MMO_C$ , with a net Mg activity that is ~33% of that theoretically available in the  $MMO_C$  lattice. (This reduced capacity with respect to the initial cycles seen in Figure 2b is due to the loss of capacity of the film after ~40 cycles.)

The above results show that the use of epitaxially stabilized crystalline thin films fabricated on conducting layers is a powerful approach to identify factors that control the electrochemical activities of multivalent cathode materials. These results demonstrate that the electrochemical activities of epitaxially stabilized  $\rm MMO_T$  and  $\rm MMO_C$  films are dramatically and surprisingly distinct. The tetragonal  $\rm MMO_T$  film is electrochemically inactive for  $\rm Mg^{2+}$  insertion. In contrast, the stabilized cubic  $\rm MMO_C$  exhibits reversible electrochemical activity. No theoretical calculations are yet available to evaluate the intrinsic  $\rm Mg^{2+}$  diffusion barriers in  $\rm MMO_C$ .

The present results suggest that this differential phaseselective electrochemical activity may be attributed to an unexpectedly low Mg<sup>2+</sup> diffusion barrier in MMO<sub>C</sub> films, which addresses, in principle, a key limitation of MMO as a multivalent cathode. This observation can be understood on the basis of the crystal chemistry of these materials. Tetragonal  $MMO_T$  is known to be a partially inverted spinel ( $\lambda \approx 0$ ) with distorted oxygen octahedra due to the Mn(III) electronic configuration,  $t_{2g}^{-3}$ - $e_g^{-1}$ , which induces the Jahn–Teller (J-T) distortion.<sup>28</sup> Mn is found in the octahedral site, while Mg<sup>2+</sup> occupies the tetrahedral site.<sup>17,21</sup> It appears that these structural constraints, coupled with the epitaxial stabilization of this phase, may combine to effectively limit the diffusivity of Mg within the MMO<sub>T</sub> film. In contrast, the cubic MMO<sub>C</sub> polymorph is a highly inverted spinel ( $\lambda \approx 0.45$ ),<sup>21</sup> in which Mn(III) Jahn-Teller lattice ions are displaced from the octahedral sites by Mn(IV), with the remaining Mn(II) located in tetrahedral sites<sup>18,29,30</sup> and with  $Mg^{2+}$  in both the tetrahedral and octahedral sites. While these differences in MMO<sub>T</sub> and MMO<sub>C</sub> structures are well understood, the mechanistic understanding that enables Mg diffusion in the MMO<sub>C</sub> films is not. Nevertheless, the increased structural complexity of MMO<sub>C</sub> opens up multiple potential mechanisms for increasing  $Mg^{2+}$  mobility. For example, site mixing due to the high degree of inversion in MMO<sub>C</sub> could create percolation pathways in the 3D spinel structure with diffusion barriers that may be lower than those available in the tetragonal phase. Also, the relative site energetics between the stable ion site and its transition state during diffusion has been identified as a key design parameter for multivalent ion mobility.<sup>31</sup> It is also possible that the more complex Mn lattice site distribution within the MMO<sub>C</sub> films may influence the Mg<sup>2+</sup> diffusion barrier, as is known for the analogous example in  $\rm LiMn_2O_4$  , where the  $\rm Li^+$  diffusion barrier can be significantly reduced at sites with neighboring Mn(III) and Mn(IV) species $^{32,33}$  or by Mn mobility suggested in LiMn<sub>2</sub>O<sub>4</sub> through molecular dynamics simulations<sup>34</sup> and firstprinciple calculations.<sup>35</sup> Regardless of the actual mechanism for increased Mg<sup>2+</sup> mobility, our results reveal that diffusional barriers calculated within the context of elementary cation site diffusion in a ideal oxide lattice as a search criterion in high throughput screening of potential multivalent electrodes may overestimate the actual barriers and artificially reduce the range of potential electrode materials.<sup>31</sup> Our work also suggests that the disordered local structure due to cation site mixing in spinel hosts could be ultilized to develop advanced battery with higher energy density.

#### CONCLUSIONS

In summary, we have demonstrated a new strategy to control the electrochemical activity of a model multivalent cathode material by epitaxial stabilization, in this case, using the tetragonal vs cubic polymorphs of the spinel MgMn<sub>2</sub>O<sub>4</sub> (MMO). The electrochemical response of the phase pure PLD-grown MMO thin films reveals that the cubic phase MMO<sub>C</sub> films exhibit reversible Mg<sup>2+</sup> electrochemical activity in  $Mg(TFSI)_2/PC$ , while the tetragonal phase MMO<sub>T</sub> films do not. These results demonstrate how epitaxial phase control can stabilize spinel oxides during charge/discharge cycles and highlights how the structural polymorphs can exhibit qualitatively different activities. While the results for MMO<sub>T</sub> are consistent with the large diffusional barriers calculated by theory,<sup>10</sup> the results for MMO<sub>C</sub> suggest that consideration of more complex diffusional pathways may be needed. The present results demonstrate that host phase stabilization during the electrochemical insertion of multivalent cation may be critical for identifying new materials for high-voltage rechargeable multivalent battery systems.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09346.

Details about the sample preparation, PLD growth, coin cell assembling, additional electrochemical tests, and additional XRD characterizations (PDF)

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#### Notes

The authors declare no competing financial interest.

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