Accelerated Kinetics Revealing Metastable Pathways of Magnesiation-Induced Transformations in MnO₂ Polymorphs
Takuya Hatakeyama,* Hongyi Li, Norihiko L. Okamoto, Kohei Shimokawa, Tomoya Kawaguchi, Hiroshi Tanimura, Susumu Imashuku, Maximilian Fichtner, and Tetsu Ichitsubo*

ABSTRACT: The intrinsic potential of manganese dioxides, considered high capacity cathodes of rechargeable magnesium batteries, was clearly exposed under conditions where the Mg migration kinetics are sufficiently enhanced. It has been reported to date that magnesium insertion into MnO₂ is substantially confined to the surfaces of MnO₂ particles due to its sluggish kinetics at room temperature, which leads to local overmagnesiation conditions causing conversion reactions etc. To unveil its ergodic or metastable phase transformation pathways of MnO₂ polymorphs (α, β, γ, δ, and λ) during magnesiation, this study employed intermediate temperature electrochemical experiments (at 150 °C) using heat tolerant ionic liquid electrolytes. Regardless of its original polymorphic structure, each MnO₂ polymorph was found to transform into a Mg including spinel and then to a rocksalt like phase by magnesiation. Given this tendency of transformation, the defect spinel λ MnO₂ phase possessing the coherent framework of spinel/rocksalt structures is expected to follow a topotactic transformation pathway, but thermally unstable λ MnO₂ underwent spontaneous reduction into Mn₃O₄ before magnesiation in an electrolyte. Instead, α MnO₂ was found to be robust enough among MnO₂ polymorphs to exhibit reversible magnesium intercalation at 150 °C under limiting capacity conditions. This result highlights that reversible magnesium intercalation in oxide cathodes is feasible for structures that are kinetically resistant to irreversible transformation pathways to spinel and rocksalt structures.

1. INTRODUCTION
Rechargeable magnesium batteries (RMBs) that employ magnesium metal anodes are potential alternatives to currently available Li based batteries.¹⁻³ The major advantages of Mg metal are its natural abundance in the earth’s crust compared to Li, the high volumetric capacity, and the dendrite free deposition upon charging.⁴ Therefore, constructing RMBs can potentially save material costs compared to Li ion batteries (LIBs) and offer a long term option for battery technology in general. The Mg metal anode yields an ideal capacity (volumetric, 3833 mAh/cm³; gravimetric, 2205 mAh/g) much higher than that of graphite (746 mAh/cm³, 370 mAh/g) and comparable to that of Li metal (2062 mAh/cm³, 3860 mAh/g). Moreover, magnesium tends to be plated rather smoothly during its electrodeposition,⁴ thereby ensuring safe operation in contrast to Li metal that easily forms dendrites.

Development of RMBs has, however, been impeded by a lack of promising cathode materials. Our group substantiated that spinel type oxides such as MgₓCo₂O₄ (X = Co, Mn, etc.) can accommodate sufficient Mg ions via spinel to rocksalt transition, in which rocksalt type Mgₓ₂O₄ is formed through electrochemical magnesiation at elevated temperatures.⁵ Since spinel and rocksalt structures can coherently share a common anion sublattice (assigned by 32e sites of space group #227), Mg intercalation/deintercalation reversibly proceeds through semicoherent phase transformation between spinel and rocksalt phases. In this mechanism, Mg ions inserted into 16c vacant sites of a spinel structure “push out” Mg ions located at 8a tetrahedral sites to 16c octahedral sites, and a rocksalt phase is eventually formed by disordering of Mg and X (X = Co, Mn, etc.) located at octahedral sites (16c and 16d, respectively). Although the phase transformation between spinel and rocksalt makes Mg insertion obviously appreciable, this somewhat complicated process impedes capacity retention.

To overcome this problem, we recently proposed defect spinel
type ZnMnO3 as a new cathode material for RMBs that can enable prolonged capacity retention.6 Because ZnMnO3 originally includes cation defects at 16d sites, Mg insertion into ZnMnO3 does not any longer require the push out process that would hinder reversion. Since ZnMnO3 can be regarded as a mixture of ZnO and MnO2, the structure stability of magnesiated MnO2 deserves to be investigated for further progress of the RMB cathode materials.

The advantages of MnO2 cathodes are (1) a high voltage derived from the valence change of Mn4+/3+, (2) a large gravimetric capacity of 616 mAh/g using also a Mn3+/2+ redox reaction (based on the mass of MnO2), and (3) a wide choice from various polymorphic crystal structures. As is well known, MnO2 has various polymorphs, so that it offers a wide choice of crystal structures such as α (hollandite, space group: I4/m), β (pyrolusite, P42/mnm), R (ramsdellite, Pnma), γ (mixture of β and R), δ (birnessite, C2/m), and λ (spinel, Fd3m). As to the Li intercalation into MnO2 phases, Thackeray deeply investigated, considered, and summarized their lithiation behaviors in a review paper.7 The feasibility of the Mn4+/3+ redox reaction has been proven with electrochemical insertion of two Li’s into spinel λ MnO2 to form spinel Li2MnO4 (4.2–3.5 V vs Li+/Li) and subsequently spinel Li1.5MnO4 (2.8 V vs Li+/Li).8,9 Additionally, further electrochemical lithiation of spinel (λ) Li1+xMnO4 allows the Mn3+/2+ redox reaction to form layered Li1+xMnO4 (around 1.2 V vs Li+/Li).7

The feasibility of magnesiation in MnO2 polymorphs has been examined by many researchers. Among the different polymorphs, especially λ type (spinel type) MnO2 has been intensively investigated with respect to the ability of Mg intercalation due to its structural similarity to LiMnO2. In our previous studies,7,10 Mg intercalation in tetragonal spinel MgMn2O4 was demonstrated in ionic liquid heated up to 150 °C. The demagnesiation process of spinel MgMn2O4 proceeds through a two phase reaction between tetragonal spinel MgMn2O4 and cubic spinel Mg1−xMn1+xO (based on inductivity coupled plasma, ICP, optical emission spectrometry) confirmed that Li and K content in the bulk composition were reduced by the solution treatment up to λ Li0.1MnO2 and δ K0.1MnO2, respectively.

2. RESULTS

2.1. Fabrication and Sample Characterization of Pristine MnO2 Polymorphs. To experimentally investigate phase change behavior of magnesiated MnO2 polymorphs, we prepared α, β, γ, δ, and λ MnO2. Here, we substituted the γ phase (mixture of 2 × 2 and 1 × 1 domains for the R phase (2 × 2 structure) because a pure R phase without a 1 × 1 domain is difficult to obtain from laboratory synthesis. α, β, and γ MnO2 were synthesized through the hydrothermal method; λ MnO2 was produced from spinel Li2MnO4 through chemical extraction of Li using HCl solution, and δ MnO2 was prepared from KMnO4 by thermal decomposition and washing with distilled water. Although the host structures of α MnO2, and δ MnO2 were not completely emptied, compositional analysis (based on inductivity coupled plasma, ICP, optical emission spectrometry) confirmed that Li and K content in the bulk composition were reduced by the solution treatment up to λ Li0.1MnO2 and δ K0.1MnO2, respectively.

X-ray diffraction patterns of prepared MnO2 polymorphs (Figure 1) generally agree well with the respective reference patterns. γ MnO2 is known to consist of the R MnO2 (2 × 1) structure, including microdomains of β MnO2 (1 × 1) units.59 The difference between experimental diffraction pattern of γ MnO2 and the calculated diffraction pattern of R MnO2 can be attributed to the presence of β MnO2 (1 × 1) microdomains. An XRD simulation that takes microdomains into account (Figure S1) indicated that the prepared γ MnO2 comprised approximately 80 vol % of the ramsdellite (R) domains separated by 20 vol % of pyrolusite (β) domains. Furthermore, the oxidation of manganese in λ (Li)MnO2 was suggested by the initial electrode potential (see Figure 2a later) to be higher than that of LiMn2O4 (ca. 3.0 V vs Li) and also the shrinkage of the lattice constant (the pristine LiMn2O4 shows a = 8.24 Å, whereas the Li extracted λ MnO2 immersed in an HCl solution has a smaller one, a = 8.05 Å). These properties of
structures are indexed based on space group symmetry measurements (Figure S2) and galvanostatic discharge (Figure Various MnO2 Polymorphs at 150 °C. As shown in Figure 2a, α-MnO2, shows a discharge capacity of 280 mAh/g (~0.45 Mg per MnO2). In the present experiments on α-MnO2, Li contamination can be thoroughly neglected since Li could not be detected in the ICP analysis as seen in Table 1. The XRD patterns in Figure 2b indicate that a high degree of magnesiation up to 280 mAh/g induces transformation of α-MnO2 (I4/m) into a “rocksalt like” single phase even far below the rocksalt composition. This intriguing behavior is observed also in γ-MnO2 and is discussed in a later section.

Before the transformation to the rocksalt-like phase occurs, the XRD peaks of the magnesiated α-MnO2 shift to lower angles compared to pristine α-MnO2. The most important characteristic feature in the XRD profile change is a decrease in the intensities of 110 and 200 diffraction peaks relative to that of the 130 diffraction peak. Figure 3a shows the Rietveld analysis for the pristine α-MnO2 and the intensity simulation profiles for various Mg sites using the Debye–Waller parameter obtained by the fitting process for the pristine sample (see Table S2). The above experimental trend can be interpreted by assuming that the inserted Mg ions are located at or around the center position of the 2 × 2 tunnel of α-MnO2 (2a, 2b, or 8h in I4/m) as demonstrated in Figure 3b and Figure S7. Thus, it is indicated that α-MnO2 topotactically accommodates Mg up to 220 mAh/g (~0.36 Mg per MnO2) via solid solution mechanism.

2.2.1. α-MnO2. After being soaked for 44 h in the electrolyte, as is seen in Figure 2c, a small new diffraction peak around 12.0° appeared; it could not be identified due to lack of other distinct peaks. Nevertheless, this phase is surely robust even at 150 °C.

Since β-MnO2 is the most dense and is well known as the most stable phase among the polymorphs, it is expected that Mg insertion may not be possible. However, β-MnO2 shows a fairly large capacity of 170 mAh/g (~0.28 Mg per MnO2) at 150 °C (Figure 2a). The X-ray diffraction measurement upon magnesiation also indicates the appearance of a secondary phase coexisting with pristine β-MnO2. Here, it should be noted that we also have to take account of Li insertion. As shown in Table 1, about 19% of the capacity is contributed by the Li insertion, while most of the carrier ions could be regarded as Mg ions. As far as we know, it is the first report on Mg insertion into (or reaction with) β-MnO2. There are two possible reasons why Mg insertion can be attained in this experiment: (i) facilitated kinetics of Mg insertion at elevated temperature (150 °C) and (ii) the concerted interaction with monovalent mobile Li ions and divalent sluggish Mg ions.

The Li reference was used to overcome the problem of the Li extracted Mn2O4 are in very good agreement with the previous results.30

2.2. Accelerated Electrochemical Mg Insertion into Various MnO2 Polymorphs at 150 °C and Their Transformation Behaviors. Electrochemical properties of MnO2 polymorphs were examined by cyclic voltammetry measurements (Figure S2) and galvanostatic discharge (Figure 2). The experiments were conducted with a three electrode beaker cell heated up to 150 °C to enhance Mg insertion kinetics that are usually sluggish at room temperature. We employed an ionic liquid electrolyte Mg(TFSA)2/CS-TFSA (molar ratio Mg/CS = 1/9) that exhibits low volatility even at 150 °C. Note here that the electrode potential was measured against a Li metal electrode separated from a Mg electrolyte; this setup has already been examined in our previous works. The redox potential of Mg2+/Mg was determined to be about 0.5 V versus Li+/Li in the Mg–Cs ionic liquid electrolyte.5,6,31 The Li reference was used to overcome the problem of the passivation of the Mg metal electrode with the TFSA anion so that accurate redox potentials cannot be measured by using a conventional Mg ribbon reference. In a very condensed Mg electrolyte like this ionic liquid, the Li contamination from the reference electrode can be neglected in most cases.

Phase transformation behavior of magnesiated MnO2 polymorphs was investigated using XRD measurement after electrochemical magnesiation at 150 °C. As shown in Figure 2a, MnO2 electrodes were galvanostatically discharged up to 2.0 V vs Li+/Li (about 1.5 V vs Mg2+/Mg) after a preliminary charge to remove residual ions within MnO2 structures. Figure 2b–f show the XRD profiles for each discharge amount and corresponding structures. As seen in Table 1, an increase in the Mg concentration after discharge was confirmed by ICP analysis. Even though the ionic liquid electrolyte contains more Cs+ ions (Mg/Cs = 1:9), the Cs concentration in the discharged MnO2 electrode is negligible compared to the Mg concentration. The CV profile (Figure S3) in Cs-TFSA electrolyte not containing Mg(TFSA)2 also suggests that a reaction involving Cs is not dominant in the case of Mg(TFSA)2/Cs-TFSA electrolyte. We tried to employ a Mg(TFSA)2/PP13TFSA electrolyte for magnesiation (see Table S1 and Figure S4); however, the Mg content of the MnO2 electrode after discharge was much smaller than what was expected based on discharge capacity. This is presumably due to side reactions such as electrolyte decomposition and proton insertion in the PP13 based electrolyte. We therefore chose the Mg(TFSA)2/Cs-TFSA electrolyte that reasonably allows magnesiation.
leading to reduction of the activation energy of migration and consequently facilitating the Mg migration.32

The main peaks of the secondary phase appearing at 8.5° and 16.4° can be assigned to tetragonal spinel Mn₃O₄ with Mg included (I41/amd); a deeper degree of magnesiation would be needed to clarify the detailed structure of the secondary phase. Here, it is emphasized that even the most stable β MnO₂ cannot retain its structure, that is, the two phase reaction occurs with Mg insertion.

2.2.3. γ-MnO₂. As seen in Figure 2a, γ MnO₂ seemingly exhibits a considerably large discharge capacity of 320 mAh/g (~0.5 Mg per MnO₂) among the MnO₂ polymorphs. However, Figure 2d shows that the magnesiated γ MnO₂ undergoes a two step irreversible phase transformation to spinel MgMn₂O₄ (λ MnO₂MnO₂) and eventually rocksalt like (Mg, Mn)₂O₂; this is similar to the cases for α MnO₂ and for β MnO₂. Thus, a large degree of magnesiation into MnO₂ polymorphs eventually results in the formation of a spinel type

Figure 2. Phase transformations of MnO₂ polymorphs caused by magnesiation at 150 °C. (a) Initial discharge curve of MnO₂ polymorphs in a 10 mol % Mg(TFSA)₂/90 mol % CsTFSA electrolyte at a rate of 10 mA/g. (b–f) X ray diffraction patterns of magnesiated α, β, γ, δ, and λ MnO₂. Magnesiation induced phase change was caused by discharge. Spontaneous phase change of unstable MnO₂ polymorphs was caused by isothermal treatment at 150 °C for 44 h in the electrolyte.
structure and then finally a rocksalt structure, regardless of the initial polymorphic structure of MnO₂.

After being soaked at 150 °C for 44 h in the electrolyte, γ-MnO₂ showed only little change in the XRD pattern. Thus, the γ-type structure is robust even at elevated temperatures. The XRD pattern of γ-MnO₂ can be seen up to 100 mAh/g (∼0.16 Mg per MnO₂), suggesting that γ-MnO₂ allows topotactic insertion of Mg to some extent. Upon further magnesiation, γ-MnO₂ starts to transform to a tetragonal spinel structure before 200 mAh/g (∼0.32 Mg per MnO₂) is yielded. The XRD patterns of γ-MnO₂ discharged up to 200 mAh/g and 250 mAh/g (∼0.35 (91%) Mg per MnO₂, respectively) are in accord with those of tetragonal spinel structured Mn₃O₄ and MgMn₂O₄. After further magnesiation up to 320 mAh/g (∼0.52 Mg per MnO₂), the XRD patterns eventually are very similar to those of rocksalt MgO and MnO.

Interestingly, the XRD pattern of γ-MnO₂ discharged up to 320 mAh/g (∼0.52 Mg per MnO₂) corresponds to that of a rocksalt like structure. As already stated, this is similar to the case of α MnO₂, in that this discharge capacity is only half (or, for α MnO₂, less than) that required to form rocksalt type MgO + MnO or MgMnO₂ (616 mAh/g). As demonstrated in the XRD simulations in Figure 4, the rocksalt like XRD pattern can be realized, when 16d (octahedral, Mn) and 16c (octahedral, vacancy) sites becomes equivalent by mixing and disordering. Even if some cations partly remain at 8a (tetrahedral, Mg) and/or 8b (tetrahedral, vacancy), namely, even if the structure still has a component of spinel structure, mixing and disordering of 16d and 16c makes the diffraction pattern rocksalt like.

Such an off-stoichiometric disordered rocksalt was also observed in our previous study, where a stoichiometric spinel MgCo₂O₄ (= Mg₀.₅CoO₂) transforms into a defect rocksalt Mg₀.₅CoO₂ under electron irradiation. The rocksalt like phase shows significantly broad diffraction peaks compared to those of the original α MnO₂ and γ MnO₂ phases. In addition, the lattice constants of the rocksalt like phase (a = 4.41 Å and a = 4.36 Å in the cases of α MnO₂ and γ MnO₂, respectively) estimated from XRD peaks in Figure 2b and d are between those of MgO (a = 4.22 Å) and MnO (a = 4.44 Å). These two characteristics suggest that the rocksalt like phase is substan

Table 1. Compositions of MnO₂ Electrodes Discharged in a Mg(TFSA)₂/CsTFSA Electrolyte at 150 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>discharge capacity (mAh/g)</th>
<th>Mg/Mn (based on capacity)</th>
<th>Mg/Mn (ICP)</th>
<th>Li/Mn (ICP)</th>
<th>Cs/Mn (ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MnO₂</td>
<td>100</td>
<td>0.16</td>
<td>0.11</td>
<td>&lt;0.015</td>
<td>0.007</td>
</tr>
<tr>
<td>α-MnO₂</td>
<td>150</td>
<td>0.24</td>
<td>0.15</td>
<td>&lt;0.012</td>
<td>0.006</td>
</tr>
<tr>
<td>α-MnO₂</td>
<td>220</td>
<td>0.36</td>
<td>0.19</td>
<td>&lt;0.014</td>
<td>0.006</td>
</tr>
<tr>
<td>α-MnO₂</td>
<td>280</td>
<td>0.45</td>
<td>0.36</td>
<td>&lt;0.013</td>
<td>0.005</td>
</tr>
<tr>
<td>β-MnO₂</td>
<td>170</td>
<td>0.28</td>
<td>0.18 (81%)</td>
<td>0.083</td>
<td>0.003</td>
</tr>
<tr>
<td>γ-MnO₂</td>
<td>100</td>
<td>0.16</td>
<td>0.13</td>
<td>&lt;0.012</td>
<td>0.003</td>
</tr>
<tr>
<td>γ-MnO₂</td>
<td>200</td>
<td>0.32</td>
<td>0.22</td>
<td>&lt;0.016</td>
<td>0.005</td>
</tr>
<tr>
<td>γ-MnO₂</td>
<td>250</td>
<td>0.41</td>
<td>0.25</td>
<td>&lt;0.012</td>
<td>0.003</td>
</tr>
<tr>
<td>γ-MnO₂</td>
<td>320</td>
<td>0.52</td>
<td>0.35 (91%)</td>
<td>0.070</td>
<td>0.004</td>
</tr>
<tr>
<td>δ-K₂₆MnO₂</td>
<td>150</td>
<td>0.24</td>
<td>0.15</td>
<td>&lt;0.020</td>
<td>0.012</td>
</tr>
<tr>
<td>λ-MnO₂</td>
<td>190</td>
<td>0.31</td>
<td>0.18</td>
<td>&lt;0.027</td>
<td>&lt;0.006</td>
</tr>
</tbody>
</table>

aMg/Mn based on capacity is equal to a discharge capacity divided by a theoretical capacity of 616 mAh/g. bThe values in parentheses denote the degree of contribution of respective carriers to the capacities. cThe inequality sign “<” means that the element was not detected; ICP analyses gave the nominal value “< 0.001 mg” for such an element.
tially strained due to the inherent lattice mismatch between the MgO component and MnO component (lattice mismatch of 5.2%, i.e., strain of 2.6%).

It is known that the phase transformation of γ MnO₂ into a spinel structure occurs not only via magnesiation but also via lithiation. According to Thackeray et al.,₃⁴ lithium insertion into γ MnO₂ at 80 °C using mild reducing agent preserves its framework structure up to a composition of Li₁₀₀₀MnO₂. However, an electrochemically lithiated γ Li₁₀₀₀MnO₂ readily transforms to the spinel type Li₁₀₀₀MnO₄ when being heated to 300 °C. Similarly, magnesiation at 150 °C produces a spinel structure with a composition of Mg₁₀₀₀₀−δMnO₂. These phenomena verify that cation inserted manganese dioxide eventually favors a spinel structure.

2.2.4. δ-MnO₂. Figure 2a lets us assume that δ MnO₂ allows a certain amount of magnesiation, but this is not the case. Actually, δ MnO₂ thermally decomposed into spinel Mn₃O₄ just after being soaked for 44 h in the electrolyte heated to 150 °C (Figure 2e). This spontaneous reduction (oxygen release) at 150 °C indicates that the δ type structure is quite unstable under oxygen free conditions at 150 °C. δ MnO₂ eventually transforms into a rocksalt structure (Mg inserted Mn₃O₄) upon discharge. The magnesiation capacity (150 mAh/g) required to form rocksalt structure is much smaller than that of other polymorphs such as α MnO₂ and γ MnO₂. This is because rocksalt phases can be readily formed from spinel structures via magnesiation; the spinel Mn₃O₄ transforms into rocksalt MgMn₃O₄ through a push out process proposed in our previous paper.⁵

In contrast to the present result, several previous works¹⁸,¹⁹ have shown excellent reversible Mg aquo ion intercalation/deintercalation cycles in an aqueous electrolyte. It is considered that δ MnO₂ is stabilized at an ambient temperature by the crystal water absorbed inside the structure. In this study, δ MnO₂ was discharged in the full absence of water using ionic liquid electrolyte at an elevated temperature (150 °C). This sharp contrast between aqueous and nonaqueous systems supports crystal water playing a crucial role in reversible insertion/extraction of magnesium and also in stabilization of the δ frame structure, which has been mentioned in the relevant literature.¹⁸,¹⁹

2.2.5. λ-MnO₂. According to the DFT calculation in Figure 8a, λ MnO₂ (i.e., 8a defect spinel structure) is the most unstable at high electrode potentials. As well as δ MnO₂, λ MnO₂ is quite unstable and transforms into spinel Mn₃O₄ by just being soaked in the electrolyte at 150 °C (Figure 2f). This transformation of λ MnO₂ can be explained by a spontaneous reduction with oxygen release in the inner atmosphere. Given that the energy difference between MnO₂ polymorphs is quite small (200 meV in Figure 8a), the chemical driving force of the reduction reaction (MnO₂ = 1/3Mn₃O₄ + 1/3O₂) is substantially similar for all of the polymorphs. However, spontaneous reduction was not observed for α MnO₂, β MnO₂, and γ MnO₂. This indicates that the kinetics of spontaneous reduction are considerably fast in λ MnO₂ and δ MnO₂ compared to in the other polymorphs. The spinel Mn₃O₄ formed by the thermal decomposition from λ MnO₂ is further reduced by magnesiation, leading to the formation of a rocksalt phase.

As well as δ MnO₂, the feasibility of magnesium insertion in λ MnO₂ has been reported mainly using aqueous solutions such as a Mg(NO₃)₂/water system in several studies.¹¹⁻¹⁶ In the absence of water, however, it is empirically known that magnesiation capacity is severely limited.¹⁴,³⁵ In this study, we intended to reveal a possible phase transformation path of pure λ MnO₂ in nonaqueous system at elevated temperatures, but this approach was found difficult due to the inherent instability of the λ MnO₂ phase before magnesiation. Although we will discuss this later, this means that the λ MnO₂ phase must be somehow stabilized by a certain treatment, as demonstrated in our previous study⁶ (ZnMnO₃: ZnO stabilized λ MnO₂), toward practical applications, where the λ MnO₂ phase can hold and magnesiation kinetics are reasonable at elevated temperatures.

2.3. Summary of Phase-Transformation Pathways during Magnesiation at 150 °C. Figure 5 illustrates the transformation pathways of the respective MnO₂ polymorphs experimentally observed in the electrochemical tests done at 150 °C.

"Semi-topotactic" means that the oxide ion sublattice remains unchanged during the phase transformation between spinel and rocksalt structures.

1. Sufficiently magnesiated α MnO₂ and γ MnO₂ tend to transform to rocksalt type structures without any phase separation. However, the α MnO₂ framework is rather
robust to some extent of magnesiation to allow topotactic insertion.

2. At elevated temperatures, even the most stable $\beta$ MnO$_2$ can allow a reaction with Mg to some extent, forming the secondary phase of the spinel structure.

3. In terms of the complete topotactic insertion, the framework of $\lambda$ MnO$_2$ (8a defect spinel type) would be the best structure, but it is the most unstable phase among the polymorphs. In addition, not only $\lambda$ MnO$_2$ but also $\delta$ MnO$_2$ is decomposed to spinel type Mn$_3$O$_4$, by just being soaked in an electrolyte elevated at 150 °C under oxygen free conditions.

2.4. Reversibility of Mg Intercalation in $\alpha$-MnO$_2$. In this section, we focus on the reversibility of intercalation/deintercalation of Mg into/from $\alpha$ MnO$_2$; see Figure 6. In the charge process, Mg deintercalation from Mg$_x$MnO$_2$ is inevitably accompanied by electrolyte oxidation, due to the large overpotentials.$^{17}$ Hence, we examined the reversibility of Mg intercalation/deintercalation on $\alpha$ MnO$_2$ in a few cycles, by using Mg(TFSA)$_2$/CsTFSA ionic liquid that exhibits a wide

Figure 6. Magnesiation cycles of $\alpha$ MnO$_2$ in a Mg(TFSA)$_2$/CsTFSA electrolyte at 150 °C. (a) Charge/discharge profiles with a cutoff capacity of 200 mAh/g and (b) corresponding X-ray diffraction patterns. (c) Charge/discharge profiles with a cutoff capacity of 100 mAh/g and (d) corresponding X-ray diffraction patterns, (e, f), X-ray photoelectron spectra (XPS), and X-ray absorption fine structure (XANES) measured for various magnesiated and demagnesiated $\alpha$ MnO$_2$. 
electrochemical window. The beaker cell was sufficiently filled with excess electrolyte (6.0 g of electrolyte for 2 mg of α MnO₂) so that the electrochemical cycle can proceed even if the electrolyte is partly oxidized during demagnesiation.

One and half cycles of magnesiation and demagnesiation within a capacity of 200 mAh/g (Figure 6a) already yield a rocksalt structure from α MnO₂ (Figure 6b). After the first magnesiation of 200 mAh/g, the α type structure is still observed in the diffraction pattern, although the broad diffraction peaks imply that the magnesiated α type structure was distorted. The crystallinity of α MnO₂ is then recovered by charging up to 200 mAh/g. While the slight peak shift toward higher angles implies that magnesium is extracted from α MnO₂, the crystal structure does not completely revert to the pristine state by charging, suggesting an incomplete extraction of inserted magnesium. Because the colorless electrolyte turned to light brown during charging, incomplete magnesium removal can be attributed to the oxidation of electrolytes competing with demagnesiation. Due to such an incomplete removal of Mg, the second magnesiation of 200 mAh/g leads to overmagnesiation and transformation of the α type structure into rocksalt structure.

To demonstrate a reversible magnesiation of α MnO₂, the discharge capacity was limited to 100 mAh/g. Since the charge capacity inevitably involves electrolyte oxidation during the demagnesiation process, the subsequent charge was excessively extended up to 250 mAh/g (Figure 6c) to completely extract the magnesium ions. As a consequence of excess charge and limited discharge, the α type structure is successfully preserved during one and half cycles (Figure 6d).

The fact that α type structure is maintained even after the second discharge of 100 mAh/g indicates that the inserted Mg ions are extracted by the excess charge. These results show that α MnO₂ allows reversible magnesiation under the following conditions: (i) limited discharge and (ii) overcharge. When magnesiation capacity reaches 200 mAh/g, the crystallinity of α MnO₂ is significantly lowered. Therefore, the limitation of discharge capacity can contribute to the reversible magnesiation/demagnesiation processes. Demagnesiation from α MnO₂ inevitably accompanies oxidation of electrolyte even in TFSA-based ionic liquid that shows an excellent resistance to decomposition after discharging 100 mAh/g and 200 mAh/g; Figure 6e (lower spectra). The Mn 2p_{3/2} spectrum gradually shifts to higher energy upon charging. This indicates the reversible oxidation of Mn via demagnesiation reaction. The corresponding decrease in the magnesium composition was also confirmed by energy dispersive X ray (EDX) spectroscopy (see Figure S8). Nevertheless, it should be noted that the Mn 2p_{3/2} spectra do not completely revert back to the pristine state (Mn^{3+}), which is probably due to the limited electrochemical window of the electrolyte.

Moreover, to obtain the bulk sample information on the valence change of Mn before/after magnesiation and demagnesiation, X ray absorption near edge structure (XANES) measurements have been performed at BL14B2, SPring 8. Figure 6f shows the XANES spectra near the Mn K edge energy with several reference spectra of the typical manganese oxides and Mn metal. After discharge (magnesiation of 100, 200, 280 mAh/g), each K edge profile shifts to lower energy, while the edge reverts to the higher energy side after charge (demagnesiation of 250 mAh/g after magnesiation of 100 and 200 mAh/g). As well as the XPS results, after magnesiation of 280 mAh/g, the K edge profile partially resembles the MnO spectrum, which means that the divalent Mn exists inside the bulk sample, even far below the rocksalt composition, which is corroborated by the XRD profile in Figure 2b. Thus, the tendency of the valence change measured by XANES is in very good agreement with the surface information on the Mn valence change by XPS.

To demonstrate the cyclability, a prolonged cycle test was performed in a more limited capacity condition. In this experiment, to compensate for the low efficiency of the demagnesiation reaction due to the competing electrolyte oxidation that can occur above about 4 V vs Li⁺/Li, the charge process was extended to 150 mAh/g, which is larger than the discharge capacity of 80 mAh/g. The cycle reversibility of magnesiation and demagnesiation is shown in Figure 7 (see also Figure S9 for XRD profile after the cycle test), which indicates that α MnO₂ is capable of exerting over 10 cycles of topotactic magnesiation and demagnesiation at an elevated discharge capacity of 80 mAh/g. The cycle test of α MnO₂ at 150 ºC under limited capacity conditions: 80 mAh/g discharge and 150 mAh/g charge.
Figure 8. Schematic illustration showing the two kinds of magnesiation pathways of α MnO2 particles at intermediate temperature and room temperature, where the latter pathway was based on the previous work by Arthur et al.25

3. DISCUSSION

In this section, we shall discuss the thermodynamic validity of these pathways in Figure 5. Using DFT calculations, we calculated the formation energies of the following five kinds of MnO2 polymorphs: α, β, R, δ, and λ. In addition, following the approach by Ling et al.,26 the formation energies of possible decomposition products (such as rocksalt MgO + bixbyite Mn2O4, rocksalt MgO + spinel Mn3O4, rocksalt MgO + rocksalt MnO) were calculated to compare with those of magnesiated MnO2 polymorphs. Based on the reaction of hcp Mg metal and λ MnO2 that is the most unstable structure between the polymorphs36 (as demonstrated in the present experiments, Figure 2), the formation energies of respective magnesiated polymorphs Mg0.5MnO2 at 0 K were obtained by the following equation:

$$
\Delta E_{\text{Mg,MnO}_2} = E_{\text{Mg,MnO}_2} - (xE_{\text{Mg}} + E_{\text{MnO}_2})
$$

where $\Delta E_{\text{Mg,MnO}_2}$ denotes the formation energy of Mg0.5MnO2 and $E_{\text{Mg,MnO}_2}$, $E_{\text{Mg}}$, and $E_{\text{MnO}_2}$ represent the internal energies of the respective compounds. The detailed calculation procedure for the structure determination is described in the Supporting Information (Figure S10).

Figure 9a (upper) shows the formation energy $\Delta E_{\text{Mg,MnO}_2}$ as a function of the Mg composition $x$ and also shows the energy gain by the phase decomposition with magnesiation. A typical plausible structure at each composition of Mg for each polymorph is also displayed in Figure 9a, which was obtained after relaxation from each initial structure (by a local minimum convergence without drastic structure change). Figure 9a (lower) gives the electrode potential versus Mg from the calculated formation energy. Since we suppose that the negative electrode is Mg metal, the voltage for Mg0.5MnO2 + $\Delta x$Mg = Mg$_{0.5+x}$MnO2 is given by $V = -(\Delta E_{\text{Mg,MnO}_2} - \Delta E_{\text{Mg,MnO}_2})/2\Delta x$.

It is indicated that possible magnesiated products are λ Mg0.5MnO2 (spinel MgMn$_2$O$_4$), spinel Mn$_3$O$_4$ + rocksalt MgO, rocksalt MgO + rocksalt MnO, and rocksalt MgMnO2. What is the most important here is that, between $x = 0$ and 0.5 in Mg$_0.5$MnO2, the ground state energy is attained for the two phase state of each polymorph MnO2 + λ Mg$_{0.5}$MnO2. The lowest formation energy for λ Mn$_{0.5}$MnO2 at $x = 0.5$ excludes the possibility of the conversion reaction, λ MnO2 + 1/2Mg = 1/2MgO (rocksalt) + 1/2Mn$_3$O$_4$ (bixbyite). This is also corroborated by the fact that the spinel type MgMn$_2$O$_4$ is also a stable natural mineral. Namely, the magnesiated MnO2 polymorphs (α, β, R, and δ MnO$_2$) other than λ MnO$_2$
Figure 9. (a) Upper: Formation energies of magnesiated MnO$_2$ polymorphs and possible decomposition products based on DFT calculation. The convex ground state hull of each polymorph was determined by calculating more than 100 possible Mg Va configurations (see Figure S7). The formation energies are shown with respect to energies of xMg and yMnO$_2$. The energies are given by the relaxed structures shown in the figure. Purple, orange, and red atoms represent Mn, Mg, and O, respectively. Possible Mg sites are shown as black dots in the structures at y = 0.0. (a) Lower: Computed voltage of magnesiation at 0 K as a function of Mg concentration. Red shadow area indicates the potential range upon magnesiation that would eventually transform to the most stable spinel type $\lambda$ Mg$_{0.5}$Mn$_{0.5}$O$_2$ after magnesiation, provided that the magnesium diffusion is sufficiently active. Especially, $\alpha$ Mg$_{0.5}$Mn$_{0.5}$O$_2$ is suggested from Figure 9a to be a less stable structure than other magnesiated polymorphs. Therefore, it deserves to be noted that the experimentally observed topotactic insertion in $\alpha$ Mg$_{0.5}$Mn$_{0.5}$O$_2$ (as shown in Figures 2b and 6) can take place while being retained metastably. That is, the substantial instability of $\alpha$ Mg$_{0.5}$Mn$_{0.5}$O$_2$ suggests that the topotactic pathway would inexorably disappear when thermodynamic equilibration is indeed achieved (probably, at much higher temperatures). Thus, the gradual structural breakdown into the spinel/rocksalt phase could be another factor that promotes irreversible cycling as well as electrolyte decomposition.

From the viewpoint of the DFT calculation, $\lambda$ MnO$_2$ (also $\delta$ MnO$_2$ and R MnO$_2$) can topotactically accommodate Mg up to x = 1, whereas $\alpha$ MnO$_2$ and $\beta$ MnO$_2$ undergo a nontopotactical structure change before x reaches 1. Therefore, the $\lambda$ MnO$_2$ framework is the best structure in terms of complete topotactical Mg insertion. However, practically $\lambda$ MnO$_2$ (and also $\delta$ MnO$_2$) cannot retain its host structure at elevated temperatures, e.g., 150 °C. Therefore, it is necessary to consider how to enhance the thermal stability for the two polymorphs. A plausible solution is ZnMnO$_3$, which is stabilized by mixing ZnO with $\lambda$ MnO$_2$.

Although we experimentally observed no further magnesia process in this work, we discuss the transformation behavior based on the results of the DFT calculation. At x = 0.66, the two phase state, 2/3MgO (rocksalt) + 1/3Mn$_3$O$_4$ (spinel), is in the lowest formation energy state; namely, even the most stable $\lambda$ MnO$_2$ could also be decomposed to these phases. In practice, however, unless the operation temperature is raised, this phase decomposition from $\lambda$ MnO$_2$ once formed would be kinetically hindered at low temperatures due to slow migration kinetics of Mg and Mn polyvalent cations.

At x = 1.0, although the ground state is a two phase state of MgO (rocksalt) + MnO (rocksalt), a tentative ordered rocksalt structure of MgMnO$_2$ occupied with Mg at 16c and Mn at 16d sites in Fd3m also shows a quasi close formation energy (only 18.5 meV per Mg$_{0.5}$Mn$_{0.5}$O higher in Figure 9a). Such close formation energies of MgMnO$_2$ and MgO + MnO imply that mixed Mg–Mn configurations in the cation sublattice of the rocksalt structure with the fixed fcc oxygen sublattice are achieved by small excess energies.

For a more accurate analysis, we also considered the mixing entropy effects on the phase stability of these phases. Figure 9b shows the free energy of the quasi binary system of MgO and MnO at various temperatures. The formation energy of ordered rocksalt Mg$_{0.5}$Mn$_{1-y}$O was estimated by the cluster expansion method; the validity of the evaluation is supported by the formation energies substantially equaling zero at y = 0 and y = 1. The blue curve in Figure 9b indicates that the ordered rocksalt at y = 0.5 yields an excess of only 32 meV/Mg$_{0.5}$Mn$_{0.5}$O higher in Figure 9a). Such close formation energies of MgMnO$_2$ and MgO + MnO imply that mixed Mg–Mn configurations in the cation sublattice of the rocksalt structure with the fixed fcc oxygen sublattice are achieved by small excess energies.
insertion into spinel $\lambda$ Mg$_{8/3}$MnO$_2$ forms a single phase disordered rocksalt MgMnO$_2$ (= Mg$_{8/3}$Mn$_{2/3}$O). Also, in the rocksalt like phases observed (even far below the rocksalt composition) in $\alpha$ MnO$_2$ and $\gamma$ MnO$_2$, the same argument would be applied; the phase separation would be retarded or hindered as shown in Figure 8.

The calculated electrode potentials upon magnesiation of MnO$_2$ at 0 K are shown in Figure 9a (lower). The electrode potential of magnesiation that transforms MnO$_2$ polymorphs into $\lambda$ Mg$_{8/3}$MnO$_2$ is around 2.8 V vs Mg$^{2+}$/Mg, being in agreement with our previous work.$^5$ This voltage is the highest among those for the topotactic magnesiation in $\alpha$, $\beta$, $\delta$, and $\gamma$ MnO$_2$, suggesting that a transformation to $\lambda$ Mg$_{8/3}$MnO$_2$ from each magnesiated polymorph other than $\lambda$ MnO$_2$ is thermodynamically favorable compared to the topotactic magnesiation for $\alpha$, $\beta$, $\delta$, and $\gamma$ MnO$_2$. Another conversion reaction to form $2/3$MgO + $1/3$Mn$_3$O$_4$ (spinel) also shows a higher voltage than that of the topotactic magnesiation reaction of $\alpha$ MnO$_2$ (and also $\gamma$ MnO$_2$), being consistent with the argument pointed out in the previous works.$^{25-27}$ This indicates that the former is likely in thermodynamics, and therefore, the topotactic reactions in $\alpha$ MnO$_2$ and $\gamma$ MnO$_2$ actually observed would occur “metastably”.

In terms of the high electrode potential and structure similarity before/after magnesiation, future research should aim to somehow stabilize $\lambda$ MnO$_2$ in order to obtain the best cathode performance. In contrast to the excellent phase stability of spinel MgMn$_2$O$_4$, the instability of the $\lambda$ MnO$_2$ phase hinders stable magnesiation cycling, especially at elevated temperatures. However, we substantiated that, for the topotactic magnesiation of metastable $\alpha$ MnO$_2$, the host framework does not always necessarily need to be thermodynamically stable but needs to be kinetically stable enough against irreversible phase transformations. On the basis of this recipe, it would be justified to find out certain chemical elements that kinetically prevent irreversible phase transformation of $\lambda$ MnO$_2$. Our recent work clearly demonstrated that chemical doping of Zn significantly stabilizes the defect spinel structure,$^9$ but this approach still needs further optimization in terms of capacity as a future work.

Finally, we remark on the enhancement of the magnesium insertion kinetics into MnO$_2$ polymorphs, which would be improved by controlling the crystal facets and surfaces of the active materials. As well as magnesium migration in an oxide framework, the desolvation process on the surface of the cathode materials seemingly limits the rate of magnesium insertion. Recently, Prendergast et al. suggested that desolvation kinetics of the magnesium complex (Mg TFSA$^+$ and Mg–Cl$^-$) on oxide cathodes is highly facilitated on a certain crystal facet of the cathode material (e.g., MoO$_3$).$^{40,41}$ They also established the advanced molecular dynamics free energy sampling technique that enables the prediction of the solvation structures of polyvalent cations having multiple stable structures.$^{40}$ This technique would be helpful for modification of MnO$_2$ cathodes and a search for compatible electrolytes.

4. CONCLUSIONS

This study has investigated the behavior of the magnesiation induced transformations of five MnO$_2$ polymorphs at an intermediate temperature. The polymorphs $\alpha$, $\beta$, $\gamma$ (R), $\delta$, and $\lambda$ type MnO$_2$ were electrochemically magnesiated at 150 °C, and their phase transformations were experimentally analyzed and interpreted in the light of the prediction of the ab initio calculation in density functional theory (DFT). The accelerated electrochemical tests have clearly indicated that there is a strong tendency for all the MnO$_2$ polymorphs to transform into spinel and then rocksalt phases upon magnesiation and/or thermal decomposition. It has been shown that only $\alpha$ MnO$_2$ is kinetically stable in terms of resistance against the spinel and/or rocksalt transformations and allows a significant Mg intercalation and deintercalation with no change of the framework.

The salient results can be summarized as follows:

(1) Although $\alpha$ MnO$_2$ eventually transforms into rocksalt when the discharge capacity reaches 270 mAh/g, $\alpha$ MnO$_2$ can allow Mg intercalation up to 150–220 mAh/g without transformations into spinel and rocksalt phases.

(2) Mg insertion into $\beta$ MnO$_2$ was demonstrated for the first time. Even the most stable polymorph $\beta$ MnO$_2$ can allow a reaction with Mg to some extent at elevated temperatures. $\beta$ MnO$_2$ would eventually transform to a spinel/rocksalt structure.

(3) $\gamma$ MnO$_2$ consisting of R type and $\beta$ type structures exhibits a high discharge capacity over 300 mAh/g, but this large capacity is attributed to an irreversible reaction, that is, transformation of the original framework $\gamma$ MnO$_2$ into spinel and eventually rocksalt phases.

(4) The fact that $\lambda$ MnO$_2$ and $\delta$ MnO$_2$ are thermally decomposed to the spinel Mn$_3$O$_4$ by being soaked in an electrolyte at 150 °C (without any electrochemical reactions) indicates that their structure stabilities are quite poor among the MnO$_2$ polymorphs. In contrast, it should be noted that the magnesiated $\lambda$ MnO$_2$ (i.e., spinel MgMn$_2$O$_4$) is the thermodynamically most stable phase.

(5) Thus, only $\alpha$ type structure can resist the strong driving force of the magnesiation induced transformation to spinel structure and subsequent rocksalt structure, especially at elevated temperatures.

(6) As indicated by the ab initio calculations, the conversion route to form spinel/rocksalt phases is thermodynamically more favorable than the topotactic intercalation even in $\alpha$ MnO$_2$. Therefore, the experimental fact that $\alpha$ MnO$_2$ allows Mg intercalation to a large extent, indicates that the $\alpha$ MnO$_2$ framework can be kinetically retained, and Mg intercalation is faster than conversion reactions in the $\alpha$ type structure.

(7) Although $\alpha$ MnO$_2$ yields a topotactic magnesiation capacity of about 200 mAh/g in the initial discharge, subsequent electrochemical cycling of 200 mAh/g eventually leads to forming rocksalt structure. This is because extraction of Mg in the charge process was insufficient within the electrochemical window of the ionic liquid. However, it was found that $\alpha$ MnO$_2$ can allow reversible magnesium intercalation/deintercalation at a certain limited capacity (e.g., 100 mAh/g). $\alpha$ MnO$_2$ needs to be carefully designed as a cathode material for RMBs, because irreversible phase changes take place when it is overdischarged.

(8) From theoretical viewpoints, $\lambda$ MnO$_2$ is expected to exhibit high magnesiation capacity through complete topotactic insertion of Mg without any change of its framework. Because $\lambda$ MnO$_2$, spinel Mg$_{8/3}$Mn$_{2/3}$O$_2$, and rocksalt MgMnO$_2$ share the common anion sublattice, $\lambda$ MnO$_2$ is expected to undergo coherent phase transformation over a wide range of Mg compositions. It would therefore be a key challenge to consider how to stabilize $\lambda$ MnO$_2$ that is unstable compared to other MnO$_2$ polymorphs.
5. METHODS

5.1. Experimental Method. α MnO2 and β MnO2 were produced by hydrothermal synthesis methods reported by Wang et al.42 For the synthesis of α MnO2, oxidizing agents, (NH4)2S2O8 and NH4SO4 were dissolved into a 0.67 mol/L MnSO4 aqueous solution at a molar ratio of MnSO4/(NH4)2S2O8/NH4SO4 = 1.0:1.0:1.875. The solution was transferred into a Teflon lined stainless steel autoclave and heated at 140 °C for 12 h. For the synthesis of β MnO2, (NH4)2S2O8 was dissolved into an aqueous solution of 1.0 mol/L MnSO4 mixed at a molar ratio of MnSO4/(NH4)2S2O8 = 1.0:1.0:1.875 and heated within a Teflon lined stainless steel autoclave at 180 °C for 6 h. Similarly, for γ MnO2, (NH4)2S2O8 was dissolved into 0.25 mol/L MnSO4 aqueous solution at a molar ratio of MnSO4/(NH4)2S2O8 = 1.0:1.0, and the resulting solution was heated in a Teflon lined stainless steel autoclave at 60 °C for 12 h.

λ MnO2 was produced by chemically extracting Li from spinel LiMn2O4. Spinel LiMn2O4 was prepared from α MnO2 and LiOH by heating the stoichiometric mixture at 480 °C for 10 h. The LiMn2O4 powder was immersed in 0.4 M HCl aqueous solution to extract Li. The powder was filtered and washed with distilled water several times followed by vacuum drying.

δ MnO2 was prepared following Gallot et al.43 KMnO4 crystalline powder was thermally decomposed at 700 °C in air. In order to remove soluble byproducts, the powder was washed with distilled water several times until a colorless solution was obtained. The remaining insoluble black powder was filtered and dried in a vacuum at 80 °C.

MnO2 electrodes were prepared by coating a slurry of 80 wt % MnO2, 10 wt % carbon black, and 10 wt % polyvinylidene difluoride dispersed in N methylpyrrolidone (NMP) on Al foil. The coated electrodes were then dried at 150 °C in a vacuum for 12 h. The loading of MnO2 on the electrode was 1.2–2.2 mg/cm².

Electrochemical measurements were performed using a three electrode beaker cell in an Ar filled glovebox. The beaker was filled with 6.0 g of electrolyte composed of 10 mol % Mg(TFS)2 (TFSA) represents (CF3SO2)N anion/bis(trifluoromethanesulfonyl)amide) and 90 mol % CsTFSA. This ionic liquid electrolyte has good thermal stability at 150 °C during the measurement.45,46 The addition of CsTFSA to Mg(TFS)2 allows adjustment of the melting temper ature of the binary ionic liquid. CsTFSA exhibits a lower melting temperature of pure Mg(TFS)2 is too high for using Li metal as a reference electrode (the melting point of Li metal is 180 °C), the melting temper ature of the binary ionic liquid was adjusted to be below 120 °C at a molar ratio of 90% CsTFSA/10% Mg(TFS)2.46,47

A Mg metal ribbon was used as the counter electrode. A glass tube Li reference electrode used in the beaker cell was prepared by immersing Li foil into 0.1 M LiTFSA/N,N diethyl N methyl N (2 methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide (DE METFSA). The reference electrode was electrically connected to the Mg(TFS)2/CsTFSA electrolyte with a liquid junction of a porous ceramic filter. The cyclic voltammetry measurements were performed at a scan rate of 1 mV/s. Magnesium induced phase change was caused by galvanostatic discharge performed at a rate of 10 mA/g in the electrolyte at 150 °C. Spontaneous phase change of unstable MnO2 polymorphs was induced by isothermal treatment at 150 °C for 44 h in the electrolyte. Electrochemical data were collected using a VMP3 potentiostat/galvanostat (Bio Logic SAS). The MnO2 electrodes were immersed in acetoneitrile to remove the remaining electrolyte before characterization.

The prepared MnO2 powders were characterized with a field emission scanning electron microscope (FE SEM, JEOL, JSM 7200F) operating at an accelerating voltage of 5 kV. X ray powder diffraction (XRD) analysis was performed using a Rigaku SmartLab diffractometer with Mo Ka radiation (λ = 0.70926 Å). The pristine powders were characterized with Bragg–Brentano geometry, and the electrode materials upon electrochemical treatment were characterized with Debye–Scherrer geometry after being sealed in a Lindeman glass capillary. The experimental diffraction patterns were compared to the simulation results calculated by the VESTA program.48 Simulation of XRD patterns of γ MnO2 was performed with the DIFFAx program49 following Chabre et al.50

XPS measurements were performed using an X ray photoelectron spectrometer (Fisons Instruments, S probe) for the electrode samples, and XANES measurements were conducted for the pelletized samples with BN powders at BL14B2, SPring 8.

5.2. Computational Method. The density functional theory (DFT) calculations were implemented with Projector Augmented Wave (PAW)50 potentials using Vienna Ab initio Software Package (VASP).51,52 The exchange correlation effects were described with Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).53 The plane wave cutoff energy was set at 520 eV. To obtain formation energies close to the experimental values in a wide range of Mn oxidation states, on site Coulomb interactions were corrected with the Hubbard U parameter of 3.9 eV following the literature.54,55 We relaxed ionic positions, lattice parameters, and angles until the energy converged to less than 10−4 eV per MnO2. The atom configurations were relaxed according to the conjugate gradient method. Although the formation energies of MnO2 depend on the magnetic structures, we confirmed that the energies vary within 0.05 eV per MnO2 of all polymorphs by calculating more than 20 possible magnetic structures. A possible Mg Va configuration of Mg3MnO4 was produced using the Alloy Theoretic Automated Toolkit (ATAT).56 The crystal structures were visualized using the VESTA program.58

AUTHOR INFORMATION

Corresponding Authors

Takuya Hatakeyama — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; Graduate School of Engineering, Tohoku University, Sendai 980 8579, Japan; orcid.org/0000 0003 4593 5929; Email: hatakeyama t@imr.tohoku.ac.jp

Tetsu Ichitsubo — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; orcid.org/0000 0002 1127 3034; Email: tichi@imr.tohoku.ac.jp

Authors

Hongyi Li — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; orcid.org/0000 0003 1890 3825

Norihiko L. Okamoto — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; orcid.org/0000 0003 0199 7271

Kohei Shimokawa — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; orcid.org/0000 3261 9679

Tomoya Kawaguchi — Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan; orcid.org/0000 0002 7600 4847
Maximilian Fichtner — Helmholtz Institute Ulm (HIU)  
Electrochemical Energy Storage, 89081 Ulm, Germany; Institute of Nanotechnology, Karlsruhe Institute of Technology, D 76021 Karlsruhe, Germany

Notes
The authors declare no competing financial interest.

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