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Kyoto University
Intercalation and Push-Out Process with Spinel-to-Rocksalt Transition on Mg Insertion into Spinel Oxides in Magnesium Batteries

Shinya Okamoto, Tetsu Ichitsubo,† Tomoya Kawaguchi, Yu Kumagai, Fumiyasu Oba, Shunsuke Yagi, Kohei Shimokawa, Natsumi Goto, Takayuki Doi, and Eiichiro Matsubara

On the basis of the similarity between spinel and rocksalt structures, it is shown that some spinel oxides (e.g., MgCo$_2$O$_4$, etc) can be cathode materials for Mg rechargeable batteries around 150 °C. The Mg insertion into spinel lattices occurs via “intercalation and push-out” process to form a rocksalt phase in the spinel mother phase. For example, by utilizing the valence change from Co(III) to Co(II) in MgCo$_2$O$_4$, Mg insertion occurs at a considerably high potential of about 2.9 V vs. Mg$^{2+}$/Mg, and similarly it occurs around 2.3 V vs. Mg$^{2+}$/Mg with the valence change from Mn(III) to Mn(II) in MgMn$_2$O$_4$, being comparable to the ab initio calculation. The feasibility of Mg insertion would depend on the phase stability of the counterpart rocksalt XO of MgO in Mg$_2$X$_2$O$_4$ or MgX$_3$O$_4$ (X = Co, Fe, Mn, and Cr). In addition, the normal spinel MgMn$_2$O$_4$ and MgCr$_2$O$_4$ can be demagnesiated to some extent owing to the robust host structure of Mg$_{1-x}$X$_2$O$_4$, where the Mg extraction/insertion potentials for MgMn$_2$O$_4$ and MgCr$_2$O$_4$ are both about 3.4 V vs. Mg$^{2+}$/Mg. Especially, the former “intercalation and push-out” process would provide a safe and stable design of cathode materials for polyvalent cations.

1. Introduction

In terms of energy and environmental concerns, modern industrial society strongly demands high energy-density rechargeable storage batteries. Currently, lithium ion batteries (LIBs) are widely used for a lot of practical applications, and their energy density has been enlarged year by year, but its growing rate tends to be saturated recently. If lithium metal itself could be used as an anode material instead of carbonaceous materials currently used, LIBs would have shown significantly high energy densities, but this cannot be done due to the well-known fatal problem, “dendritic growth” of Li metal on charge that leads to dangerous short circuits. Therefore, in order to further enhance the energy density of storage batteries, we have to develop new type of metal-anode battery systems.

As an alternative to Li metal-anode battery, polyvalent-metal (Mg, Ca, Al, etc) storage batteries (PSBs) have recently attracted increased attention owing to their large capacities; for example, in the case of Mg, its capacity (ca. 2200 mAh g$^{-1}$) largely exceeds that for the current carbonaceous anode materials (ca. 370 mAh g$^{-1}$). Especially, it has been reported that Mg electrodeposition occurs with non-dendritic formation, therefore Mg metal can be expected to work as an anode material. Thus, the Mg rechargeable battery (MRB) field has been currently attracting much attention but growing up quite gradually. Namely, the MRB research is still a very challenging field and not established yet, and hence we have to make much effort to accomplish MRBs. For example, there are no appropriate electrolytes with wider electrochemical windows and without causing passivation on the Mg-electrode surface. Furthermore, despite that several candidates for the MRB cathode materials have been reported, there are few cathode materials for MRBs that can work at ambient temperature except for Chevrel compounds even though the Chevrel compounds are used, the electromotive force delivers about 1.0–1.2 V, and the energy density of Mg battery is less than 150 mWh g$^{-1}$ (currently 370 mWh g$^{-1}$ in electrode energy density of LiCoO$_2$ vs graphite). Therefore, unless more talented cathode materials that can accommodate...
polyvalent cations are sought out, PSBs would not be comparable to Li ion batteries in terms of the energy density. Thus, in order to change the energy storage paradigm, we have to seek cathode materials for polyvalent cations.

Here we focus Mg spinel oxides as candidates for cathode materials of MRBs. As shown in Figure 1, the lattice sites in the spinel structure are generally denoted as 8a, 16d (cation sites), and 32e (oxygen sites) in the Wyckoff position in the space group No. 227 ($Fd\bar{3}m$), while those in the rocksalt structure are denoted as 16c, 16d (cation sites) and 32e (oxygen sites) when it is assigned to the same space group. Thus, a spinel structure can be regarded as a rocksalt whose 16c sites are vacant and instead the 8a sites are usually occupied by cations. Therefore, it is expected that Mg cations can be inserted onto 16c vacant sites in the spinel lattice, as well as the Li insertion mechanism in spinel oxide materials.$^{[10,11]}$

In this work, with several spinel oxides MgCo$_2$O$_4$, MgMn$_2$O$_4$, MgFe$_2$O$_4$, MgCr$_2$O$_4$, and Co$_3$O$_4$, we demonstrate that some of spinel oxides can allow the insertion of Mg cations at high potentials (about 3 V vs. Mg$^{2+}$/Mg) via “intercalation and push-out” mechanism as shown in Figure 1. The electrochemical-test temperature was set at 150 °C in the present study by the following two reasons: i) the melting temperature (about 120 °C) of the CsTFSA based ionic liquids$^{[12,13]}$ used here and ii) the enhancement of Mg diffusion in the active materials. Actually, the future Mg battery is expected to be operated at moderately high temperatures in that Mg insertion and extraction can be facilitated at such temperatures. Finally, we discuss the feasibility of Mg insertion/extraction into/from the spinel oxides in terms of stabilities of the resultant rocksalt phases and the original spinel structure types.

2. Results and Discussion

2.1. Redox Behavior of Spinels Oxides

A typical construction of beaker cells used here is illustrated in Figure 2a (upper). In order to perform electrochemical tests around 150 °C, we used the CsTFSA-based ionic liquids reported by Hagiwara et al.,$^{[13]}$ which show excellent thermal stabilities around 200 °C. The electrodeposition of Mg hardly occurs in a Mg(TFSA)$_2$/CsTFSA binary ionic liquid, but the electrolytic dissociation of Mg(TFSA)$_2$ in the ionic liquid takes place, which is judged from the fact that the Mg cations can be inserted into the Chevrel compounds.$^{[14]}$ Besides, as demonstrated in the previous works,$^{[13,15]}$ hcp Mg metal can be electrodeposited in (Mg/Li/Cs)-TFSA ternary ionic liquids.

Figure 1. Schematic illustration showing the cation insertion process. The upper left structure is drawn in the usual spinel coordinate, whereas the right is depicted by setting a 32e site (Wyckoff position) for oxygen in the space group No. 227 as origin. After a Mg cation is inserted into a 16c site in the spinel (left lower) structure, the original cation located in its neighboring 8a site moves to an adjacent 16c site due to the repulsion between the cations.
Based on this fact, the virtual Mg redox potential is deduced by reducing the Li composition from the ternary ionic liquids. Thus, the potential conversion rule from the potential versus the reference electrode (RE) used in the present work to that versus Mg/Li/Mg was tentatively determined to be “0.5 V vs. Li+/Li in RE = 0 V vs. Mg2+/Mg”, as shown in Figure 2a (lower). Although, in addition to the electrodeposition/stripping phenomenon of Mg, the Li insertion into Mg metal matrix can be involved in the CV profiles, we have judged that the obtained CV profile shape is of typical electrodeposition/stripping phenomenon; see SI for details. Incidently, the anodic limit in the electrochemical window of the CsTFSA ionic liquid is about/below 4.5 V vs. Li+/Li in RE; see Figure S1, Supporting Information, for details.

Figure 2b shows the cyclic voltammogram (CV) obtained for MgCoO4. Usually, one would consider the conventional reaction, i.e., the reaction of Mg extraction from the host material, MgCoO4 ⇔ Mg1-xCoO4 + xMg2+ + 2e⁻. However, such a reaction may occur above 4.4 V vs. Li+/Li in RE, but this cation extraction from MgCoO4 appears to be difficult in terms of the structural stability and anodic limit of the electrochemical window of the binary ionic liquid. Apart from this usual deintercalation, it is clearly seen that direct Mg insertion can occur into the host MgCoO4 without a pre-charge process, and then the cation extraction is observed during a charge process; the equilibrium redox potential is about 2.9 V vs. Mg2+/Mg (3.4 V vs. Li+/Li in RE), which is in agreement with the ab initio calculation (3.0 V vs. Mg2+/Mg); see the later section on the ab initio calculation. Thus, the insertion/extraction of Mg cations are found to be drastically facilitated by elevating temperature.

After the electrochemical tests, we confirmed Mg insertion semi-quantitatively by the energy-dispersive X-ray (EDX) spectroscopy analysis (not presented here), and also we have performed the inductively coupled plasma (ICP) analysis after the electrochemical performance test for the Mg-Li rocking-chair type dual-salt battery.[16]

As candidates of cathode active materials for MRB systems, other spinel oxides, Co3O4, Mn3O4, Cr2O3, and Fe2O3, were also investigated. Figures 2c–f show cyclic voltammograms for these spinel oxides measured in the (Mg10/Cs90)-TFSA binary ionic liquid at 150 °C. The CV profile in Figure 2c of Co3O4 is very similar to that of MgCoO4, where the extraction of Co(II) cations is not observed during the anodic scan from the open circuit potential (OCP). The elemental analysis by EDX suggested that Mg cations were inserted into the spinel Co3O4 (note presented here). In contrast to MgCoO4, the extraction of Mg2+ ions from Mn3O4 is observed in Figure 2d during the first anodic scan from the OCP value, and two redox-peak couples corresponding to the insertion/extraction of Mg2+ ions are observed at around 3.4 V and 2.3 V vs. Mg2+/Mg; the former reaction would correspond to the valence change of Mn(IV) to Mn(III), whereas the latter would correspond to that of Mn(III) to Mn(II). According to the present ab initio calculations of the energy differences between MgMnO4 and demagnesiated-spinel Mn3O4 and between MgMnO4 and magnesiated-spinel (i.e., rocksalt) Mn3O4, the average redox potentials were estimated to be 2.9 V vs. Mg2+/Mg for the former and 1.8 V vs. Mg2+/Mg for the latter, being in fairly agreement with the experimental results.

As to the former reaction, the similar trend was observed in Figure 2e for MgCr2O4 that is, the valance change from Cr(IV) to

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**Figure 2.** a) Three-electrode beaker cell setup (upper): (Mg10/Cs90)-TFSA ionic liquid was used for the electrolyte, the cathode active material was used as the working electrode (WE), a Mg ribbon was counter electrode (CE), and Li metal immersed in a 0.5 M-LiTFSA/DEMETFSA electrolyte in a glass tube separated with a porous ceramic filter was used as the reference electrode (RE). Cyclic voltammogram (lower) measured at 150 °C in the ionic liquid of the mixture of Mg(TFSA)2, LiTFSA, and CsTFSA salts with various concentrations to extrapolate the virtual redox potential of Mg2+/Mg. Co3O4, Mn3O4, Cr2O3, and Fe2O3 were used as the working electrode (WE), a Mg ribbon was counter electrode (CE), and Li metal immersed in a 0.5 M-LiTFSA/DEMETFSA electrolyte in a glass tube separated with a porous ceramic filter was used as the reference electrode (RE). Cyclic voltammogram (lower) measured at 150 °C in the ionic liquid of the mixture of Mg(TFSA)2, LiTFSA, and CsTFSA salts with various concentrations to extrapolate the virtual redox potential of Mg2+/Mg. Co3O4, Mn3O4, Cr2O3, and Fe2O3 were used as the working electrode (WE), a Mg ribbon was counter electrode (CE), and Li metal immersed in a 0.5 M-LiTFSA/DEMETFSA electrolyte in a glass tube separated with a porous ceramic filter was used as the reference electrode (RE). Cyclic voltammogram (lower) measured at 150 °C in the ionic liquid of the mixture of Mg(TFSA)2, LiTFSA, and CsTFSA salts with various concentrations to extrapolate the virtual redox potential of Mg2+/Mg. Co3O4, Mn3O4, Cr2O3, and Fe2O3 were used as the working electrode (WE), a Mg ribbon was counter electrode (CE), and Li metal immersed in a 0.5 M-LiTFSA/DEMETFSA electrolyte in a glass tube separated with a porous ceramic filter was used as the reference electrode (RE). 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Cr(III) was observed, but in contrast, the valence change of Cr(III) to Cr(II) was hardly observed in this case. In the case of MgFe₂O₄, as well as the above materials, we confirmed that MgFe₂O₄ can be used as a cathode material for MRBs, but marked redox peaks were not observed in Figure 2f; as a trend, the current density for this material is considerably lower than those in the other spinels. However, the faint peaks probably correspond to the insertion and extraction of Mg cations into MgFe₂O₄; the insertion/extraction potential is about 2.7 V vs. Li⁺/Li in RE, being lower than the redox potential (about 3.4 V vs. Li⁺/Li) of Fe cations in the olivine LiFePO₄. This is further supported by the XRD and XANES measurements in the next section.

In the above cyclic voltammetry tests, the temperature was set at 150 °C. Here, we show the CV profiles of MgCo₂O₄ at relatively lower temperatures, by using the Mg(TFSA)₆/triglyme electrolyte, which was recently developed for MRBs. Since the electrolyte is in a liquid state at room temperature and the boiling point of triglyme is about 216 °C, we can conduct electrochemical tests in a relatively wide temperature range. Figure 2g shows the cyclic voltammograms measured for MgCo₂O₄ in a triglyme electrolyte containing 0.5 M Mg(TFSA)₆ at room temperature (RT) and 100 °C. The insertion of Mg²⁺ ions into the spinel MgCo₂O₄ was observed in each case (60 mAh g⁻¹ for RT and 105 mAh g⁻¹ for 100 °C) below 3.4 V vs. Li⁺/Li in RE. After the cathodic sweep to 1.5 V vs. Li⁺/Li in RE, the anodic current corresponding to the extraction of Mg²⁺ ions was markedly observed above 3.4 V vs. Li⁺/Li in RE, but it is found that the extraction of Mg²⁺ below 100 °C is considerably laborious within the electrochemical window of the triglyme. Thus, the triglyme electrolyte can be used for the evaluation of active materials at RT and/or higher temperatures.

2.2. Structure Analyses

We conducted structural analyses for mainly MgCo₂O₄ before/after Mg insertion/extraction tests to comprehend the cation-insertion mechanism. The analyses have been done for MgCo₂O₄, Co₃O₄, MgMn₂O₄, and MgFe₂O₄. As shown in XRD profiles in Figure 3a (left), after insertion of Mg cations by discharge of about 120 mAh g⁻¹, the active material contains two phases, i.e., spinel and rocksalt phases. Further insertion of Mg cations up to about 210 mAh g⁻¹ substantially forms a rocksalt single phase. The fact that the spinel phase disappears even at such an incomplete discharge amount less than the theoretical value (260 mAh g⁻¹) means that the rocksalt phase includes a certain amount of cation vacancies, that is, a solid-solution phase of off-stoichiometry exists. When charging after the discharge of 120 mAh g⁻¹, the structure completely reverts to the spinel structure. By measuring the corresponding XANES spectra around the Co K-edge in Figure 3a (right), we further ensure that a part of Co(III) cations in the spinel phase are reduced to Co(II) after discharge of about 120 mAh g⁻¹ and again oxidized to Co(III) after charge; compare to the XANES profiles of Co₃O₄ containing Co(II) and Co(III), CoO with only Co(II), and LiCoO₂ with only Co(III).

As well as MgCo₂O₄, we have also conducted XRD and XANES measurements for Co₃O₄ in Figure 3b, MgMn₂O₄ in Figure 3c, and MgFe₂O₄ in Figure 3d. As is expected easily, the Mg insertion/extraction behavior into/from Co₃O₄ in Figure 3b is very similar to that of MgCo₂O₄. Incidentally, a certain amount of Si was mixed to gain a sufficient sample volume in the capillary for the measurements. Namely, by the insertion of Mg cations (200 mAh g⁻¹), the rocksalt phase is formed in the spinel mother phase. Comparing to MgCo₂O₄, the spinel phase tends to remain in the case of such an incomplete discharge amount. On the other hand, we observe not only the Mg insertion into a pristine MgMn₂O₄ but also the Mg extraction from such a pristine MgMn₂O₄, as seen in Figure 3c. As to the insertion, broad XRD peaks coming from the rocksalt phase are also observed in this case, whereas several new peaks are detected after the Mg extraction from the host material. As is seen in corresponding XANES spectra (Mn K-edge), the white line of as-synthesized MgMn₂O₄ shifts to a lower energy after discharge.
and shifts to a higher energy after charge. These behaviors are consistent with those of the reference samples corresponding to the various valence states of Mn. Finally, although MgFe$_2$O$_4$ did not show an excellent cathode property in Figure 2f, we have investigated the structural and valence changes after Mg insertion. As found from Figure 3d, the XRD peak positions of MgFe$_2$O$_4$, FeO and MgO are very close, so that we cannot clearly see the peak shifts in the broad XRD profile of pristine MgFe$_2$O$_4$. However, after the Mg insertion, the XRD peaks tend to move to lower angles (probably due to the influence of FeO) and the white line (Fe K-edge) tends to shift lower. As seen in the XANES profiles of Fe$_2$O$_3$ and Fe$_2$O$_4$, there is only a little change in the respective white lines, and the present XANES profile change after Mg insertion is rather similar to this trend, unlike the Fe K-edge profile in the olivine LiFePO$_4$ structure.

As a representative of spinel oxide cathode materials for MRBs, the crystal structure parameters were determined by Rietveld refinement with the program RIETAN-FP[18] using the XRD profiles of the as-synthesized MgCo$_2$O$_4$ sample and one after partial discharge (120 mAh g$^{-1}$) in the Mg battery system that corresponds to Figure 3a. We mentioned before that the rocksalt phase would have vacancies after discharge, but we here assume that the discharged rocksalt structure does not have any vacancies. The cation ratio of the spinel structure was fixed at Mg/Co = 1/2, and no constraint was imposed on the cation ratio in the rocksalt structure, i.e., the discharge amount (120 mAh g$^{-1}$) was not taken into account for the Rietveld analysis. The fitting results and detailed parameters for crystal structures are shown in Figure S3 and Table S1, Supporting Information. From the Rietveld analysis, as-synthesized MgCo$_2$O$_4$ takes a disordered spinel structure with a degree of disorder of about 0.43, being consistent with our previous works.[7,19] In contrast, the partially discharged sample contains spinel and rocksalt phases, and the degree of disorder is slightly changed to about 0.37, and the site occupancies of Mg and Co cations in the rocksalt structure are 0.49 and 0.51, respectively. The volume fraction was determined to be spinel (27%) and rocksalt (73%) structures, indicating that about 70% of the discharge process proceeds in terms of the present structure analysis. Therefore, considering the fact that the discharge amount was less than half of the full capacity (120 mAh g$^{-1}$/260 mAh g$^{-1}$), we need to consider the presence of vacancies in the rocksalt crystal. Thus, the insertion of one Mg atom induces the spinel to rocksalt transition in a larger region than one unit cell of the rocksalt structure.

From the present structure analysis, the Mg cations are inserted into 16c sites in the spinel structure, and the original cations located at the 8a sites of the spinel structure are pushed out to the 16c sites, eventually to form a rocksalt structure. The Mg insertion mechanism, “intercalation and push-out” process, is close to the Li-insertion mechanism in spinel oxide materials.[10,11] Then, the Mg insertion into the MgCo$_2$O$_4$ spinel lattice is expressed as

$$\text{MgCo}_2\text{O}_4 + x(\text{Mg}^{2+} + 2e^-) \leftrightarrow (1-x)\text{MgCo}_2\text{O}_4 + x\text{Mg}_2\text{Co}_3\text{O}_4,$$

where Mg$_2$Co$_3$O$_4$ takes a rocksalt structure, and the rocksalt structure is formed via “intercalation and push-out” process in Figure 1, where the slight structural change or atomic rearrangement must be also accompanied by the cation insertion, which would be facilitated at moderate temperatures (about 100–150 °C). Thus, around the Mg-inserted 16c sites, the crystal lattice undergoes the spinel-to-rocksalt transition, thus the atomic-level two-phase equilibrium can be attained, and consequently this structural change would occur coherently, as seen in Figure 1, by which deterioration of the lattice structure would be significantly suppressed.

### 2.3. Cathode Performance Tests in MRB Systems

We have successfully obtained various evidences of the Mg insertion/extraction into/from the spinel oxides. Then, let us demonstrate the high potentials of these cathode materials by constant-current battery performance tests. In this Mg battery system using the (Mg10/Cs90)-TFSA ionic liquid, the Mg anode is readily passivated, so that its anodic dissolution comes to occur above 1.5 V vs. Li$^+$/Li in RE,[15] which leads to an unfortunate consequence that the cell voltage decreases with the passivation of the Mg anode. Thus, the electrode potential of the cathode material (i.e., working electrode potential) was monitored versus RE. Here, referring to the CV profiles in Figure 2, we have chosen two cathode materials, MgCo$_2$O$_4$ and MgMn$_2$O$_4$, for the cathode performance tests. Figure 4 shows the cathode performance test for MRBs, a) 1/10 C for MgCo$_2$O$_4$, and 1/20 C and 1/50 C for b) MgCo$_2$O$_4$ and for c) MgMn$_2$O$_4$.

As to the cathode material MgCo$_2$O$_4$, the battery test can also start from the discharge process. As shown in Figure 4a, a charge process cannot be sufficiently done due to the anodic limit (oxidation decomposition around/below 3.5 V vs. Mg$^{2+}$/Mg) of the electrochemical window of the electrolyte. Consequently, after the charge process, the discharge amount became smaller than the first one, but this is not the essential problem of the cathode material. Moreover, the cyclability is significantly affected by the thermal stability of the PVDF binder (in the composite active material) that cannot be endurable around 150 °C. To return to the subject, in the 1st discharge process, the converted working potential is shown to be 2–2.5 V vs. Mg$^{2+}$/Mg, which is much higher than that of the Chevrel compounds,[8] and the capacity amounts to about 120 mAh g$^{-1}$ above 2 V vs. Mg$^{2+}$/Mg and also amounts to 170 mAh g$^{-1}$ above 1 V vs. Mg$^{2+}$/Mg at a rate of 1/10 C.

At a slower C rate, we can obtain more excellent discharge behavior. Figure 4b,c compare the discharge (i.e., Mg insertion) behaviors of MgCo$_2$O$_4$ to MgMn$_2$O$_4$ at slower rates, 1/20 C and 1/50 C. As to MgMn$_2$O$_4$, the battery test was started from a charge process (over 200 mAh g$^{-1}$) including the oxidation decomposition of the electrolyte. In the case of 1/20 C, the MgCo$_2$O$_4$ cathode material shows a longer plateau region around 2.0–2.5 V vs. Mg$^{2+}$/Mg in the potential versus capacity curve, and the discharge amount reaches about 200 mAh g$^{-1}$. Even for a slower rate of 1/50 C, the capacity was substantially unchanged, indicating that a certain repulsive interaction associated with the push-out process is influenced on the Mg insertion process when the cation density is increased, which is a certain kind of freezing phenomenon like glass/jamming transition.

In contrast, the MgMn$_2$O$_4$ cathode material displays two stages (above 2.5 V vs. Mg$^{2+}$/Mg, 1.5–2.5 V vs. Mg$^{2+}$/Mg) in...
the discharge process, which are in accordance with the redox potentials observed in the CV profile for MgMn$_2$O$_4$ in Figure 2d. According to the XANES spectra in Figure 3c, the higher potential region corresponds to the Mn valence change from 4 to 3, whereas the lower potential region represents the valence change from 3 to 2. It is seen that a larger capacity (about 200 mAh g$^{-1}$) can be attained for a slower rate in MgMn$_2$O$_4$ $−$ $\text{Mg}^{2+}/\text{Mg}$, the influence of reduction decomposition of the TFSA anion comes to appear \cite{15}. However, even though the two kinds of valence changes are recognizable, the present test shows only about 150–200 mAh g$^{-1}$ for MgMn$_2$O$_4$. As before, one of the reasons for the gradual decrease in the potential is a strain effect due to the lattice mismatch of MgO and MnO rocksalt phases, which yields a considerable strain energy depending on the insertion amount of Mg cations.\cite{20,21} Nevertheless, the higher potential (over 2.5 V versus Mg$^{2+}/\text{Mg}$) of this cathode material would be a fascinating characteristics.

**2.4. Redox Potentials by Ab Initio Calculations**

Ab initio calculations were performed using GGA+$U$ in order to supplement the experimental findings. Although MgCo$_2$O$_4$ and MgFe$_2$O$_4$ are disordered spinels, we considered only normal spinel configurations as it is found in our recent study\cite{16} that the cation configuration in MgCo$_2$O$_4$ does not significantly affect the redox potential caused by the Mg insertion; see Supporting Information for details. We calculated the redox potentials of Mg$X_2$O$_4$ by Mg insertion as

$$V_{\text{insert}} = -\frac{1}{2e}[E(\text{Mg}_2X_2O_4) − E(\text{Mg}_2X_2O_4) − E(\text{Mg})].$$

(1)

where $E(A)$ denotes the total energy of phase $A$, $X$ = Cr, Mn, Fe, or Co, and $e$ is the elementary charge. The redox potential of Co$_3$O$_4$ by Mg insertion was also calculated as

$$V_{\text{insert}} = -\frac{1}{2e}[E(\text{Mg}Co_2O_4) − E(\text{Co}_3O_4) − E(\text{Mg})].$$

(2)

In each system, the most stable magnetic configuration was searched for within collinear configurations in the primitive-based unit cell and its total energy was used in the evaluation of the redox potentials. Rocksalt Mg$_2$X$_2$O$_4$ and MgCo$_2$O$_4$ models were created by displacing the Mg or Co cations located at the 8a sites to neighboring 16c sites and inserting Mg cations to the remaining 16c sites. On the other hand, the redox potential of Mg extraction was calculated as

$$V_{\text{extract}} = -\frac{1}{2e}[E(\text{Mg}_2X_2O_4) − E(\text{X}_2O_4) − E(Mg)].$$

(3)

The initial structures of the $X_2O_4$ phases were made by simply removing the 8a-site Mg cations. The calculated potential vs. Mg$^{2+}/\text{Mg}$ for the insertion/extraction of Mg cations into/from the host spinel structure are summarized in Table 1. The discrepancies between calculated and experimental redox potentials are within ca. 0.5 eV.

**2.5. Criteria on Mg Insertion and Extraction**

Here we discuss the feasibility of Mg insertion and cation extraction into/from the spinel oxides. Table 1 summarizes the experimental and calculation results and thermal stabilities of various rocksalt phases relevant to the resultant rocksalt phase. It is naturally expected that Mg$_2$Co$_2$O$_4$ and Mg$_2$Co$_2$O$_4$ of a random-solution type rocksalt phase can be formed for MgCo$_2$O$_4$ and Co$_3$O$_4$, since both of MgO and CoO have similar rocksalt structures and both phases are thermally stable in the ambient conditions. Similarly, since the rocksalt MnO is stable, Mg cations can easily be inserted into the MgMn$_2$O$_4$ host material. However,
since the lattice mismatch of MnO and MgO is fairly large (as seen in the ICSD profile in Figure 3), the Mg insertion may overcome the strain energy increase. In contrast, for example, in the case of MgCo$_2$O$_4$ and MgFe$_2$O$_4$, although the MgO phase is stable, the CrO and FeO phases are less stable in the ambient condition, resultingly to disproportionate to Cr and Cr$_2$O$_3$ from MgCr$_2$O$_4$. Especially, since Cr(III) is the 3$^+$ ion and Fe$_2$O$_4$ is difficult Mg extraction tends to occur in MgCo$_2$O$_4$, MgMn$_2$O$_4$, and MgCr$_2$O$_4$, toward Mg rechargeable batteries (MRBs). In some of the spinel oxides (MgCo$_2$O$_4$, Co$_3$O$_4$, MgMn$_2$O$_4$), the Mg insertion and extraction can be clearly observed, which is facilitated by elevating temperature (about 150 °C). From various viewpoints, for example, electrochemistry, structural analysis, and ab initio calculation, we have substantiated the eccentric mechanism on Mg insertion into spinel-oxide lattices, termed “intercalation & push-out” process. This Mg insertion into a spinel structure occurs with an atomic-level coherent phase transition, where dual-phase reaction of the spinel and rocksalt phases proceeds. For example, in the case of spinel MgCo$_2$O$_4$, Mg insertion occurs at a significantly high potential of about 2.9 V vs. Mg$^{2+}$/Mg, being consistent with ab initio calculation, and its capacity approximately amounts to 200 mAh g$^{-1}$ (theoretically 260 mAh g$^{-1}$). The feasibility of Mg insertion into spinel oxides would depend on the stability of both MgO and XO rocksalt phases in MgX$_2$O$_4$ or X$_3$O$_4$. In contrast, the normal spinel oxides, MgMn$_2$O$_4$ and MgCr$_2$O$_4$, can be demagnesiated to some extent, where the Mg insertion/extraction potentials of MgMn$_2$O$_4$ and MgCr$_2$O$_4$ are both about 3.4 V vs. Mg$^{2+}$/Mg.

Since the valence change from 4 to 3 can be utilized in the latter redox reaction, a relatively higher potential is delivered, while a relatively lower potential due to the valence change from 3 to 2 is utilized in the former redox reaction. Nevertheless, even though the former redox reaction is used, since the Mg-insertion potentials are as high as about 2–3 V vs. Mg$^{2+}$/Mg (for MgCo$_2$O$_4$), the electrode energy density experimentally amounts to about 400 mWh g$^{-1}$ (theoretically it would exceed 600 mWh g$^{-1}$). Thus, we are sure that the “intercalation and push-out” mechanism provides a new strategy for designing future cathode materials for polyvalent cations such as Mg cations. In addition, the spinel oxide cathode materials (e.g., MgCo$_2$O$_4$) can allow not only Mg-cation insertion but also Li-cation insertion, which enables us to design a new type of rechargeable battery, “rocking-chair type Mg-Li dual-salt battery”, which is discussed in our another paper.[16]

3. Conclusions

In conclusion, based on the structural similarity in spinel and rocksalt structures, we have investigated cathode properties of spinel oxides, MgCo$_2$O$_4$, MgMn$_2$O$_4$, MgFe$_2$O$_4$, MgCr$_2$O$_4$, and Co$_3$O$_4$, toward Mg rechargeable batteries (MRBs). In some of the spinel oxides (MgCo$_2$O$_4$, MgMn$_2$O$_4$), the Mg insertion and extraction can be clearly observed, which is facilitated by elevating temperature (about 150 °C). From various viewpoints, for example, electrochemistry, structural analysis, and ab initio calculation, we have substantiated the eccentric mechanism on Mg insertion into spinel-oxide lattices, termed “intercalation & push-out” process. This Mg insertion into a spinel structure occurs with an atomic-level coherent phase transition, where dual-phase reaction of the spinel and rocksalt phases proceeds. For example, in the case of spinel MgCo$_2$O$_4$, Mg insertion occurs at a significantly high potential of about 2.9 V vs. Mg$^{2+}$/Mg, being consistent with ab initio calculation, and its capacity approximately amounts to 200 mAh g$^{-1}$ (theoretically 260 mAh g$^{-1}$). The feasibility of Mg insertion into spinel oxides would depend on the stability of both MgO and XO rocksalt phases in MgX$_2$O$_4$ or X$_3$O$_4$. In contrast, the normal spinel oxides, MgMn$_2$O$_4$ and MgCr$_2$O$_4$, can be demagnesiated to some extent, where the Mg insertion/extraction potentials of MgMn$_2$O$_4$ and MgCr$_2$O$_4$ are both about 3.4 V vs. Mg$^{2+}$/Mg.

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4. Experimental Section

Sample Preparation: All spinel oxides were synthesized by the inverse co-precipitation method. Aqueous metallic nitrate salt solutions (0.1, 0.080 μM Mg(II), 0.160 μM X(II), X = Co, Mn, Cr, Fe) were prepared by dissolving Mg(NO₃)₂·6H₂O and X(NO₃)₂·3H₂O, etc., in deionized water. A sodium carbonate solution (0.2 L, 0.350 M Na₂CO₃) for pH control and precipitation was also prepared. These solutions were heated to 70–80 °C under vigorous stirring (500 rpm). The metallic nitrate salt solutions were added dropwise into the sodium carbonate precipitation solution. The resulting suspensions were stirred at 70–80 °C for 30 min and then filtered. The filtered precipitates (precursors) were rinsed with deionized water (300 cm³) at 80 °C to remove completely Na-containing by-products, and air-dried for 24 h at 80 °C. The precursors were followed by calcination in air at 350–750 °C for 2–24 h.

Electrochemical Tests: Each composite cathode was prepared by coating an Al plate collector with a mixture of the active material, carbon black (as conductive agents), and PVDF ( binder) in a weight ratio of 80:10:10. Mainly we used CsTfSA-based liquid electrolytes containing Mg(TfSA)₂ (and/or LiTfSA) salt established by Hagiwara et al.,[13] where TfSA is bis(trifluoromethanesulfonyl)amide, N(CF₃SO₂)₂. We and others used an 0.5 M LiMg(TfSA)₂/triglyme electrolyte established recently.[17] When the atomic percent of the cations in the mixed liquid ion is, for example, Mg/Gs = 10/90, the composition of the electrolyte is denoted as Mg(TfSA)/Cs(TfSA)-TfSA. A typical construction of beaker cells used here is illustrated in Figure 2a (upper), where a typical weight of the active materials was about 1 mg on 5 mm x 10 mm square and volume of electrolyte was about 2 ml. As a reference electrode, we used a Li ribbon instead of Mg ribbon to circumvent any passivation, which was immersed in a separated glass tube with a ceramic filter. The solvents used for the reference electrode were n,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)amide (DEMETSA) for CsTfSA-based mixed liquid ion and the same triglyme solvent for the 0.5 M Mg(TfSA)/triglyme electrolyte, and the solution for the reference electrode was LiTfSA in both cases. As shown in Figure 2a (lower), the redox potential of Mg²⁺/Mg couple in the (Mg10/ Cs90)-TfSA electrolyte was estimated to be about 0.5 V vs. Li⁺/Li in RE, where RE means the Li reference electrode in a glass tube separated by a ceramic filter. Moreover, the redox potential of Mg²⁺/Mg couple in the 0.5 M Mg(TfSA)₂ in triglyme electrolyte was estimated to be about 0.8 V vs. Li⁺/Li in RE (not presented here). All the electrochemical tests and beaker-cell construction were done with galvanostatic/potentiostatic apparatuses (Biologic, SP-300 and VSP-300) in the glove box whose dew point was below ~72 °C.

Structural Analysis: The structure and valence state of the active material were investigated by X-ray diffraction (XRD) and X-ray absorption near edge structure (XANES), respectively, at a synchrotron ACCMS at Kyoto University were used in this work. This achievement is commissioned by JST, MEXT of Japan, and the MEXT Elements Strategy Initiative to Form Core Research Center. Computing resources of ACCMS at Kyoto University were used in this work. This achievement is based on the significant work on the ionic liquids by Professor Hagiwara et al. (Kyoto University) at the Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING) project from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Supporting Information
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