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Supplementary information:
A new aspect of Chevrel compounds as positive electrodes for magnesium batteries

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Cyclic voltammogram by starting from $Cu_xMo_6S_8$ in Grignard-reagent/THF electrolyte

In order to reveal more clearly that Cu cations can be extracted from $Cu_2Mo_6S_8$ below $E_{Cu^{2+}/Cu}$($\approx$ 1.7 V), we have conducted cyclic voltammetry for a three-electrode cell (WE: $Cu_xMo_6S_8$, CE, RE: Mg ribbons) within the more limited narrow potential range, $0 - 1.6$ V vs. Mg/Mg^{2+}. First, the electrochemical cell was kept for about 24 h until the open circuit potential (OCP) decreases from about 1.9 V down to 1.58 V vs. Mg/Mg^{2+}, and subsequently the CV test was followed, the results of which is shown in Fig. S1; the charge/discharge amount per each anodic/cathodic scan was about 10-30 mAh/g in the present cyclic voltammetry. After 50 CV cycles, the CV test was quit at 0.5 V on the way in the final reduction process. From the subsequent EDX measurement, it was confirmed that the atomic ratio of Cu to Mo decreases by about 33% after 50 cycles. Since the redox potential of Cu is about 1.7 V vs. Mg/Mg^{2+}, some of Cu cations extracted from $Cu_xMo_6S_8$ is considered to be deposited on the electrode surface.

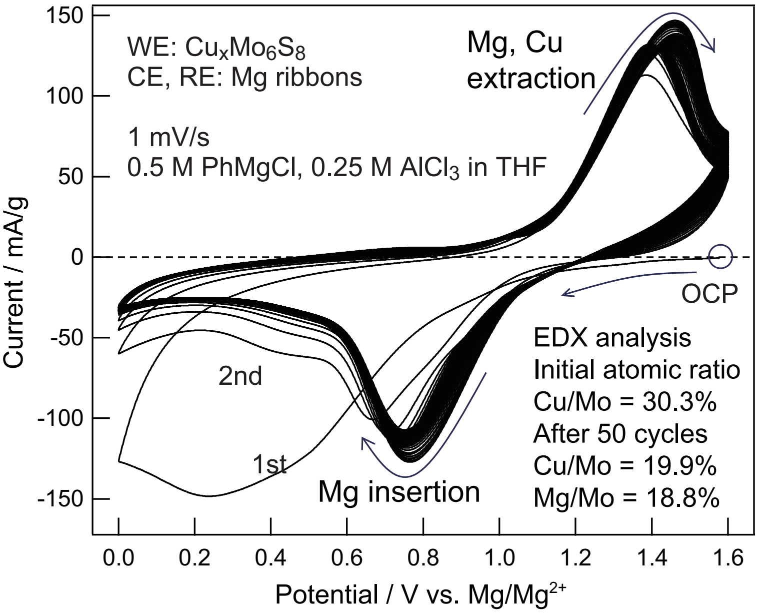

FIG. S1: Cyclic voltammogram measured at 1 mV s^{-1} in phenylmagnesium chloride/THF electrolyte with $AlCl_3$. The starting material of working electrode is $Cu_xMo_6S_8$. Mg-metal ribbons were used as the counter and quasi-reference electrodes. The composition of respective cations were measured by SEM-EDX qualitative analysis.

Anodic dissolution and cathodic deposition of Li and Mg in the triglyme electrolyte

Figure S2 shows cyclic voltammograms measured in triglyme electrolyte containing LiTFSA and Mg(TFSA)$_2$, where TFSA is bis(trifluorosulfonyl)amide, N(CF$_3$SO$_2$)$_2$$^-$. Especially, the electrolyte for a Mg battery was developed by the group of Professor Takeshi Abe in Kyoto University,[1] and Kitada et al.[2] have devised the electrolyte by including the ionic liquid such as PP13-TFSA (N-methyl-N-propylpiperidinium bis[(trifluoromethyl)sulfonyl]amide), and then we have followed up. As shown in Fig. S2(a), in the absence of Mg(TFSA)$_2$, the cathodic and anodic currents corresponding to the deposition and dissolution of Li metal are observed around about 0 V vs. Li/Li$^+$, which means that this electrolyte is adequate for Li batteries. To know about the difference in the redox potential between Li and Mg in the triglyme electrolyte, dual-salt electrolyte containing both LiTFSA and Mg(TFSA)$_2$ was used. In the dual salt electrolyte in Fig. S2(b) (Li/Mg cation ratio = 1.0), the cathodic and anodic currents corresponding to Mg deposition and dissolution are observed around about 0.85 V vs. Li/Li$^+$ in addition to the deposition and dissolution of Li. Thus, the redox potential of Mg/Mg^{2+} is about 0.85 V vs. Li/Li$^+$ in LiTFSA-Mg(TFSA)$_2$/triglyme electrolyte, if taking account that Mg activity is reduced by alloying with Li, it can be said that the present potential difference is close to the relation, i.e., about 0.7 V difference between Li/Li$^+$ and Mg/Mg^{2+}, in aqueous solution. Therefore, in the body text of the paper, we used the conventional value of 0.7 V for a rough standard.[3]

Figure S3 shows the cyclic voltammogram measured in 0.50 M Mg(TFSA)$_2$ triglyme electrolyte. As seen in Fig. S3, the anodic dissolution of deposited Mg occurs at about −0.4 V vs the Mg quasi-reference, and Mg metal is found to be slightly passivated in Mg(TFSA)$_2$ triglyme electrolyte. Thus, the real redox potential of Mg/Mg^{2+} redox couple is about −0.4 V versus the Mg quasi-reference electrode passivated in the electrolyte. Based on this, the upper axis of Fig. 5(c) in the body text is corrected for the real redox potential of Mg redox couple.

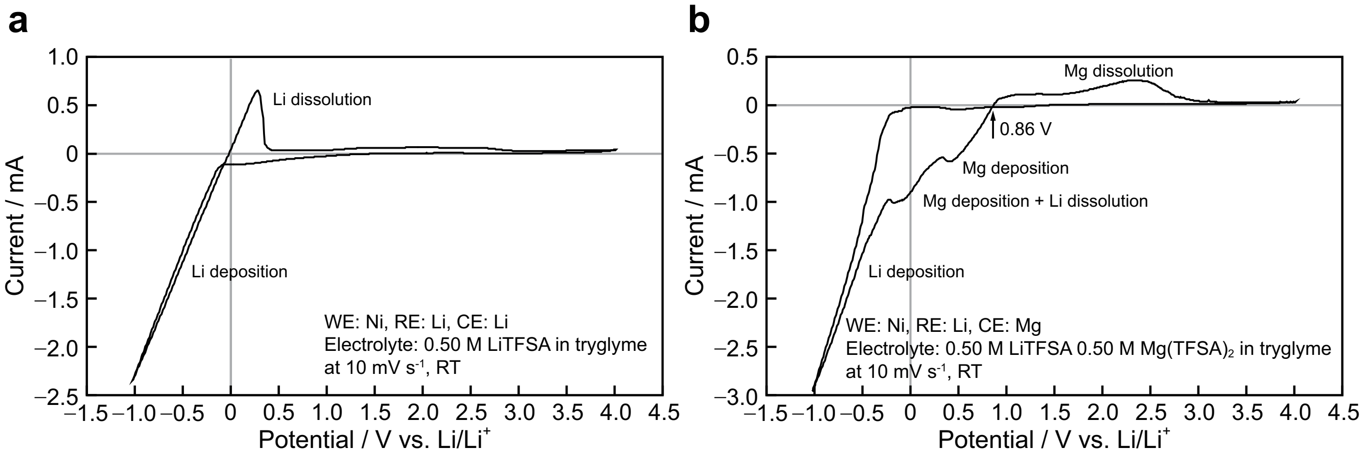

FIG. S2: Cyclic voltammogram measured at 10 mV s^{-1} in triglyme electrolyte containing (a) 0.50 M LiTFSA and (b) 0.50 M LiTFSA and 0.50 M Mg(TFSA)$_2$. Li metals were used as the counter and quasi-reference electrodes, and the Li quasi-reference electrode was isolated from the electrolyte with Vycor glass to prevent the displacement deposition of Mg on Li.

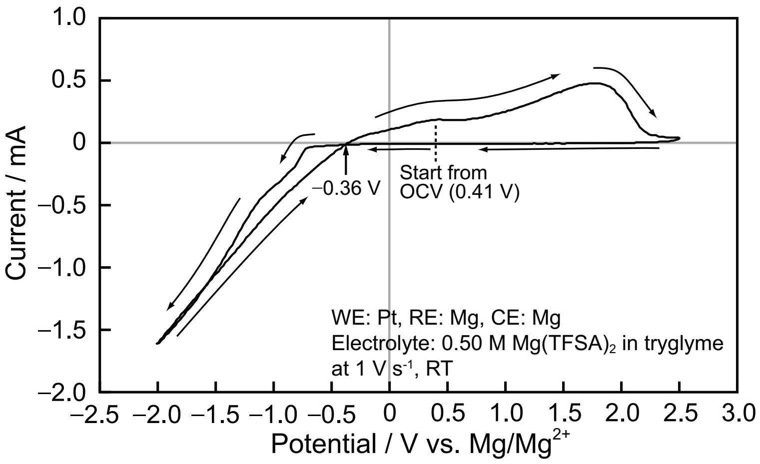

FIG. S3: Cyclic voltammogram measured at 1 V s^{-1} in triglyme electrolyte containing 0.50 M $Mg(TFSA)_2$.

Typical cyclic voltammogram of the Chevrel compound in the ionic liquid at elevated temperature

Figure S4 shows the cyclic voltammogram measured using $Cu_2Mo_6S_8$ as the working electrode in a ternary ionic liquid (CsTFSA : LiTFSA : $Mg(TFSA)_2$ = 8 : 1 : 1) at 5 mV s^{-1} and 180 °C. This ionic liquid was firstly developed by Hagiwara et al.,[4] and then the validity of the electrolyte was further confirmed by the authors' group.[5] About four pairs of redox peaks are observed in the CV: two pairs below the open circuit potential (OCP) and two above the OCP (about 3 V). Apparently, it is found that the first extraction of cations (Cu cations in this case) from the Chevrel crystal occurs at a voltage as high as 3.7 V vs. Li/Li$^+$. Among these cathodic peaks, the cathodic deposition of Cu (around 3.4 V vs. Li/Li$^+$) is also included, but the cation insertion of Mg or Li at the higher potential is found to be possible at the temperature, because the diffusion of cations are facile at 180 °C.

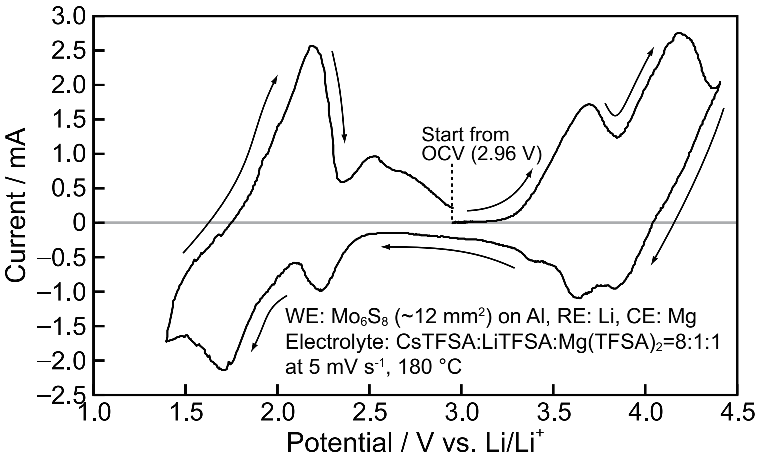

FIG. S4: Cyclic voltammogram of $Cu_2Mo_6S_8$ measured at 5 mV s^{-1} and 180 °C in ternary ionic liquid (CsTFSA : LiTFSA : $Mg(TFSA)_2$ = 8 : 1 : 1). Mg ribbon and Li metal were used as the counter and quasi-reference electrodes, respectively. Usually, Li quasi-reference electrode should be isolated from the electrolyte with Vycor glass to prevent the displacement deposition of Mg on Li, but since the Mg electrode in this electrolyte is slightly passivated and the exchange current density would be smaller than that of Li, the redox potential of the Li quasi reference remains virtually unchanged.

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[1] T. Abe, Private Communication.

[2] A. Kitada, Y. Kang, Y., Y. Uchimoto, & K. Murase, *J. Electrochem. Soc.*, 2014, **161**(3), D102–D106.

[3] Mg deposition is dominant by preceding the Li deposition. Because, in the SEM observation even after being kept at such a low potential as Li metal can be deposited, we have confirmed very smooth deposition of mainly Mg without dendritic formation of Li. Since Mg can dissolve Li in the solid state, it is expected that Mg-Li alloy can be formed at the electrodeposition. In this situation, we guess that the composition of the electrodeposited alloy consists mainly of Mg. Based on this, we have judged that the small convex peak around 0.3 V vs Li corresponds to the Li dissolution. Empirically, we know that the electrode potential difference between Li and Mg is about 0.7 V, and in the Mg-Li alloy the chemical potential of Mg is lowered compared to that of pure metal Mg. Hence, it is reasonable to judge that the anodic reaction around 0.86 V vs Li corresponds to the anodic dissolution of Mg(-Li) alloy.

[4] B. Gao, T. Nohira, R. Hagiwara, & Z. Wang, Molten Salts Chemistry and Technology, M. Gaune-Escard and G. M. Haarberg eds., *John Wiley & Sons, Ltd.* Chapt. 5.4, 2014.

[5] M. Oishi, T. Ichitsubo, S. Okamoto, S. Toyoda, E. Matsubara, T. Nohira & R. Hagiwara, *Journal of The Electrochemical Society*, 161, A943-947 (2014).