## **Supporting Information**

# Nanoscale Defluorination Mechanism and Solid Electrolyte Interphase of a MgF<sub>2</sub> Anode in Fluoride-Shuttle Batteries

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#### 1. Characterization of XRD and SEM of pristine MgF2 anode

To improve the electron conductivity of MgF<sub>2</sub> anode, a composite electrode of MgF<sub>2</sub> and Fe was prepared. MgF<sub>2</sub> and Fe powder were mixed at a weight ratio of 1:10 by mechanical milling at 600 rpm for 3 h. Figure S1 shows the backscattered electron scanning electron microscopy (BSE SEM) images of the pristine composite electrode of MgF<sub>2</sub> and Fe. The contrasts of BSE SEM image increase depending on the square of the atomic number Z, meaning that the contrast of Fe (Z = 26) is brighter than that of Mg (Z = 12) and F (Z = 9). The BSE SEM images of top surfaces of the MgF<sub>2</sub> anode (Figs. S1a and S1b) show that MgF<sub>2</sub> seems to partially cover the surface of the Fe particles.

The cross-sectional EBS SEM image of Fig. S1c shows exposed surfaces of the Fe particles. Then, it can also be confirmed in the magnified cross-sectional image of Fig. S1d that MgF<sub>2</sub> with Fe fine particles covers the Fe particles. The exposed surface of the Fe particles and the existence of fine Fe particles in the MgF<sub>2</sub> layer are preferable microstructures from the viewpoint of improving electron conductivity.



**Figure S1.** (a) BSE SEM image and (b) magnified image of top view of pristine MgF<sub>2</sub> anode. (c) BSE SEM image and (d) magnified image of cross-sectional view of the pristine MgF<sub>2</sub> anode.

The X-ray diffraction (XRD) pattern obtained from the pristine MgF<sub>2</sub> anode shows the reflection only from Fe particles, as shown in Fig. S2. This is because the reflection in XRD patterns for MgF<sub>2</sub> anode become broader due to the fine particles with below several nanometer sizes as a result of the mechanical milling. In addition, the high background in the pattern exists due to fluorescence from Fe using the wavelength (CuK<sub> $\alpha$ 1</sub>  $\lambda$  = 0.154059 nm) of the laboratory XRD (Empyrean, PANalytical B.V.).



**Figure S2.** XRD characterization of the MgF<sub>2</sub> anode. The topmost panel is an XRD pattern obtained from the pristine MgF<sub>2</sub> anode. The reference reflection lists of Fe with a space group Im-3m (a = b = c = 0.2886 nm, ICSD number 64795), MgF<sub>2</sub> with a space group of  $P4_2/mnm$  (a = b = 0.4621 nm, c = 0.3052, ICSD number 394) and Mg with a space group  $P6_3/mmc$  (a = b = 0.32088 nm, c = 0.52099, ICSD number 76259) show below experimental XRD patterns. hkl indices in the reference reflection list show only main reflections.

#### 2. Electrochemical testing of MgF<sub>2</sub> anode

Figure S3 shows the results of charge/discharge curves of the MgF<sub>2</sub> anode at room temperature in a halfcell test. The MgF<sub>2</sub> anode shows a capacity of 664 mAhg<sup>-1</sup> in the first charge (defluorination) process. This capacity is 77 % of the MgF<sub>2</sub> theoretical specific capacity, 860 mAhg<sup>-1</sup>. After first charge, the discharge (fluorination) capacity is 354 mAhg<sup>-1</sup>. Coulombic efficiency of the first cycle is around 53 %. The poor Coulombic efficiency is considered to be related to the formation MgF<sub>2</sub> on the Mg surface during discharge process (fluorination reaction). MgF<sub>2</sub> formed on the surface reduces the efficiency of the fluorination of Mg inside owing to its poor electronic conductivity. In addition, the Mg metal may have been fluorinated by F ions in the electrolyte due to self-discharge of the anode. In this case, the amount of Mg as the active anode material is reduced, resulting in a decrease in discharge capacity. Then, the MgF<sub>2</sub> formed by self-discharge on the Mg surface also interferes with internal fluorination reaction of Mg particles, as in the case of discharge. These reasons may be the cause of the poor Coulomb efficiency.

Here, the cut-off voltages in charge processes were set at -0.19 V. The cut-off voltages for the discharging processes were set to be different for the first three cycles, i.e., 1.54 V (first cycle), 1.74 V (second cycle) and 1.94 V (third cycle). Note that the difference of cut-off voltages in each discharge process is the result of examining the dependence of discharge capacity on potentials. Since this work mainly discusses the formation of Mg metal and SEI during electrochemical reduction process, essential results are not affected despite of the different cut-off voltages in the discharge cycles. In fact, although the capacities are deteriorated according to progressing the number of cycles, it can be seen that the profiles of charge curves do not change significantly within this range of cycles. Therefore, we regard that the defluorination in the 4th charge was appropriately performed.



**Figure S3.** (a) Schematic of three-electrode measurement system in this work. (b) Charge and discharge curves and (c) cycling performance of MgF<sub>2</sub> anode. The charge and discharge curves were obtained at room temperature in a half-cell test. The specific capacities were calculated from the weight of MgF<sub>2</sub>. The current density of charge and discharge were -34.4 mAg<sup>-1</sup> (0.04 C rate) and 17.2 mAg<sup>-1</sup> (0.02 C rate), respectively.

#### 3. SEM EDS analysis of MgF<sub>2</sub> anode before/after defluorination

Figure S4 shows the results of compositional analysis using SEM EDS for the MgF<sub>2</sub> anode before and after defluorination. The formation of Mg metals in defluorinated MgF<sub>2</sub> anode can be expected, but there is no clear difference between the pristine and defluorinated MgF<sub>2</sub> anodes in the SEM EDS results. This is because the signals of MgF<sub>2</sub> and Mg in the depth direction overlap due to the small region of formed Mg metal. In other words, it is difficult to analyze the diffuorinated MgF<sub>2</sub> anode by the SEM EDS method.



**Figure S4.** SEM images and SEM EDS analysis results of Mg-K and F-K in (a) pristine and (b) defluorinated MgF<sub>2</sub> anodes.

#### 4. Electron diffraction analysis of region of Mg metal formation

Relative plasmon intensity  $I_{rp}$  map of Fig. 3d clearly shows the distribution of Mg metal in defluorinated MgF<sub>2</sub> anode. Meanwhile, the reflection from Mg metal is not detected by the electron diffraction pattern of Fig. 1e. This is because the formed Mg metals exist as very fine particles with below several nanometer sizes. It is difficult to detect the reflection of Mg metal in electron diffraction patterns recorded from wide areas. Therefore, we investigated the selected area electron diffraction obtained from the regions with the large volume ratio of Mg metals as shown in Figs. S5a and S5b.

Figure S5c shows the result of the electron diffraction pattern obtained from the region in which the Mg metal is formed. The crystal structure of Mg is hexagonal with a space group  $P6_3/mmc$  (a = b = 0.32088 nm, c = 0.52099, ICSD number 76259). The highest intensities in the diffraction pattern of the hexagonal Mg are attributed to 011 reflections as shown in Fig. S2. The Mg 011 reflections are expected to appear in the electron diffraction pattern between the 011 and 111 reflections of MgF<sub>2</sub>. In order to improve the visibility of the 011 reflection of the hexagonal Mg, the relevant intensity region was extracted from an electron diffraction pattern as shown in Fig. S5d. The result clearly shows the bright parts derived from the 011 reflection of the hexagonal Mg.



**Figure S5.** (a) Annular dark-field (ADF) STEM image of the defluorinated MgF<sub>2</sub> anode. (b) A relative plasmon intensity  $I_{rp}$  map from the same region as **a**. (c) An electron diffraction pattern obtained from the circled region in (a) and (b). (d) Extracted intensities from electron diffraction pattern between 011 and 111 reflection of MgF<sub>2</sub> in (c). White arrows in (d) indicate the Mg 011 reflections.

### 5. STEM EDS analysis of MgF2 anode before/after defluorination

Figure S6 shows the results of compositional analysis of pristine and defluorinated  $MgF_2$  anode using STEM EDS. Compared to the relative plasmon intensity map (main text in Fig. 4), the STEM EDS method cannot clearly distinguish regions of Mg metal formation. This is because the signals of  $MgF_2$  and Mg are overlapped in depth directions. In the defluorinated  $MgF_2$  anode, it can be seen oxygen signals on its surface. An oxide was formed on the surface as a result of electrolyte decomposition.



**Figure S6.** ADF STEM images and EDS map of F-K (yellow), Mg-K (orange), Fe-K (green) and O-K (magenta) of (a) pristine and (b) defluorinated MgF<sub>2</sub> anode. Composite images in (a) and (b) comprising EDS data of Mg-K (orange), Fe-K (green) and O-K (magenta) to visualize the oxygen on MgF<sub>2</sub> surface. Scale bars, 100 nm.

### 6. BF STEM image of MgF2 anode after defluorination



**Figure S7**. (a) HAADF and (b) bright-field (BF) STEM images of defluorinated  $MgF_2$  anode corresponding to Fig. 4 in the main text. Solid, dotted and dashed lines indicate the interfaces between a Fe particle and defluorinated  $MgF_2$ , between defluorinated  $MgF_2$  and SEI, and between SEI and coated carbon layer, respectively. The regions inside the dotted-dashed line in (a) and (b) indicate the unreacted area.