Characterisation of Defluorination Reaction and Solid Electrolyte Interphase in Fluoride-Shuttle Battery Anode MgF2

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Article

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Abstract

Fluoride-shuttle batteries using fluoride ion transfer have been extensively investigated for producing post-lithium-ion batteries. One of the key issues hampering the development is the low capacity utilisation rate in anodes, causing a significant reduction in battery performance. To improve the utilisation rate, it is necessary to clarify the unexplained parts regarding the (de)fluorination behaviour to optimise the electrode design. Here, we demonstrated the characterisation of Mg metal formations and the solid electrolyte interphase (SEI) in defluorinated MgF$_2$ anode. Mg was mainly formed in the region with electron and F ion conductivities, implying that these conductivity paths must be efficiently increased to further improve the utilisation rate. Nanosized Mg metals were formed even in the region with poor electron conductivity, implying that an efficient (de)fluorination process could be achieved by designing the electrode configuration or/and elemental composition. The influence of SEI in battery performance have currently been neglected because the problems of low utilisation rate are more serious. However, as research progresses, the control of the SEI composition and its properties should be an important investigation to further improve fluoride-shuttle battery performances.

Introduction

Fluoride-shuttle battery, which utilises fluoride ion (F$^-$) transfer between electrodes, is one of the candidates as a next generation battery due to its potential to achieve higher energy density than the lithium-ion battery\textsuperscript{1,2}. The concept of this battery was reported in 1970s\textsuperscript{3,4}. Reddy and Fichtner in 2011\textsuperscript{2} demonstrated the first reversible cycling performance in an all-solid-state fluoride-shuttle battery even at elevated temperature, and it has attracted significant attention ever since\textsuperscript{5–12}. There are many types of metal/metal fluorides, thus making it possible to achieve a high voltage cell by exploring the suitable combinations of cathode and anode materials with an appropriate fluoride ion conductivity electrolyte. Then, in the defluorination process based on conversion reaction of metal/metal fluorides in the electrodes, multiple electron reactions can be promoted by moving single charged anions of F$^-$ in electrolyte. Therefore, theoretical energy density of fluoride-shuttle battery can be expected to be up to 5000 Wh/L\textsuperscript{1}.

However, fluoride-shuttle batteries require extensive research and development to improve their electrochemical performance for practical applications. One of the critical problems of the battery is its low-capacity utilisation rate or low utilisation of active materials\textsuperscript{2,13–15}. The most critical problem lies with the construction of the anode. This is because typical anode materials such as AlF$_3$, CaF$_2$, LaF$_3$ and MgF$_2$ have wide band gaps ($E_g$) of $\sim$10.8 eV\textsuperscript{16}, $\sim$11.8 eV\textsuperscript{17,18}, $\sim$10.5 eV\textsuperscript{19}, and $\sim$11.8 eV\textsuperscript{20}, respectively. The band gaps of the anodes are over twice as large as typical cathode materials, for example, $\sim$2 eV of CuF$_2$\textsuperscript{21,22} and $\sim$4 eV of BiF$_3$\textsuperscript{23,24}. The large band gap of anode materials results in poor electronic conductivity, making it difficult for F ions to exchange electrons at the interfaces between a metal and a metal fluoride inside active anodic materials during the (de)fluorination process. Since the formation enthalpy of a metal fluoride for an anode is essentially much lower than that of a metal\textsuperscript{25}, removal of F
ions from the metal fluorides of an active anode is more difficult compared to that of an active cathode. A nearly complete utilisation in the first discharge capacity (defluorination) has been reported in the case of a CuF$_2$ cathode using a liquid electrolyte$^8$ and a BiF$_3$ cathode using a solid electrolyte$^7$ at room temperature. Meanwhile, regardless of various efforts such as improving conductivity$^{14}$ and a compositied electrode (Mg-MgF$_2$)$^{15,26}$, the capacity utilisation rate of the active anode materials are currently very low. Therefore, the active anode material needs to be present in excess to the cathode active materials for electrochemical testing$^{2,5,8,14,15,26,27}$. In other words, the enhancement of the capacity utilisation rate in an anode can directly lead to the improvement of the energy density and the performance of fluoride-shuttle batteries. To improve the low utilisation rate of anode materials, it is necessary to understand the mechanisms of (de)fluorination reaction and optimise the electrode design. However, there is a lack of information regarding the (de)fluorination behaviour in anodes. Moreover, useful analyses of anode materials have not yet been established due to the nanoscale dimensions of particles and the low amount of reaction from the material.

In this study, imaging techniques using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were developed to analyse the MgF$_2$ anode, which is a promising anode material owing to its high theoretical capacity of 860 mAh g$^{-1}$, before/after electrochemical defluorination. Advanced STEM EELS imaging technique successfully visualised the distribution of Mg metal in the defluorinated MgF$_2$ anode. Furthermore, the interphase, i.e., solid electrolyte interphase (SEI) in the case of lithium-ion battery anode$^{28}$, was also confirmed in defluorinated MgF$_2$, on the surface or the interface between the electrolyte and the anode.

**Results**

*Electrochemical measurement of MgF$_2$ anodes.* Figure 1 shows the charge/discharge curves of the MgF$_2$ anode at room temperature in a half-cell test. The MgF$_2$ anode shows a capacity of 493 mAh g$^{-1}$ in the charge (defluorination) process. This capacity is 57 % of the MgF$_2$ theoretical specific capacity, 860 mAh g$^{-1}$. After charge, the discharge (fluorination) capacity is 271 mAh g$^{-1}$. Coulombic efficiency of the first cycle is around 55 %. This performance is not enough for practical use but is more favourable than previous reports$^{14,15,26}$.

Previously, most fluoride-shuttle batteries have been investigated using solid electrolytes. In such systems, degradation of cycling performance is mainly attributed to the loss of contact between an electrolyte and the active material. The interface dissociation is caused by the large volume change of active materials during (de)fluorination. MgF$_2$, used as the active anode material in the present study, exhibits a large volume shrinkage (−71 %) from MgF$_2$ ($V = 65.18$ Å$^3$) to Mg ($V = 46.46$ Å$^3$)). In contrast, liquid electrolytes proposed for fluoride-shuttle batteries$^{8,29–35}$ can maintain contact with active materials. Therefore, liquid electrolytes are considered to be one of the main reasons why the Coulombic efficiency reported in this study is better than those of previous reports using solid electrolytes$^{14,15,26}$.
In addition, the electrochemical performance of the present MgF$_2$ anode can be also explained by the configuration of additive Fe particles and MgF$_2$. The X-ray diffraction (XRD) pattern obtained from the pristine anode shows only the reflections from Fe particles (see Fig. S1). Reflections from MgF$_2$ do not appear because of their fine particle size, approximately several nanometers, as a result of mechanical milling process. The scanning electron microscopy (SEM) images (see Fig. S2) show that the nanosized MgF$_2$ covers the Fe particles. The exposed surface of the Fe particles and the existence of fine Fe particles in the MgF$_2$ layer are preferable microstructures from the viewpoint of improving electron conductivity. However, the utilisation of MgF$_2$ anode after electrochemical defluorination was still at 57%. This result indicates that the morphology of the composite anode in this study was not sufficient to enhance the exchange reaction of F ions between the anode and the liquid electrolyte.

**Characterisation of MgF$_2$ anodes before/after defluorination.** Compositional analysis using SEM and energy dispersive X-ray spectroscopy (EDS) was carried out to observe Mg metal distribution in the defluorinated MgF$_2$ anode. However, we did not observe clear changes in the MgF$_2$ active materials before/after defluorination (Fig. S3). The results indicate that the size of Mg metal formed by electrochemical defluorination is too small to be detected due to the overlapping of Mg metal and MgF$_2$. Therefore, in order to clarify the distribution of Mg metal in defluorinated MgF$_2$ anode, STEM observation and EELS analysis were performed.

Figures 2a and 2b show the high-angle annular dark-field (HAADF) STEM images obtained from the pristine MgF$_2$ anode. In the HAADF STEM image, the contrast is approximately proportional to the square of the atomic number (Z) of elements\(^{36}\). The intensity of Fe should be higher than that of MgF$_2$. We can see that the fine Fe particles with the sizes from tens to several nanometers are encapsulated in the pristine MgF$_2$. The selected area of electron diffraction pattern obtained from the pristine MgF$_2$ anode shown in Fig. 2c exhibits rutile-type MgF$_2$ with a space group of \(P4_2/mnm\) \((a = b = 0.4621\, \text{nm}, c = 0.3052\, \text{nm})^{37}\). This result indicates that the pristine MgF$_2$ is not amorphous but crystalline.

After defluorination, it can be confirmed that a lot of voids are formed in MgF$_2$ anode as shown in Figs 2d and 2e. These voids are thought to result from volume shrinkage associated with defluorination from MgF$_2$ to Mg. On the other hand, the electron diffraction pattern of the defluorinated MgF$_2$ (Fig. 2f) indicates the similar pattern to the pristine MgF$_2$ (Fig. 2c) although each reflection was slightly broader. Then, it is difficult to confirm the reflection from Mg metal in the electron diffraction pattern of Fig. 2f. Most of MgF$_2$ was not defluorinated and the partially formed Mg metal particles are supposed to be very small and/or unevenly distributed in the anode.

**Visualisation of Mg metal distribution in MgF$_2$ anodes.** EELS analysis was carried out to visualise the distribution of Mg metal formed after defluorination in the anode. It should be noted that MgF$_2$ is prone to release fluorine when triggered by electron beam radiations\(^{38}\). Therefore, it is necessary to minimise the exposure time and incident beam intensity during recording EEL spectra to avoid the formation of Mg...
caused by electron beam. In order to overcome this problem, we examined the low energy loss regions below 100 eV, i.e. low-loss EEL spectra with plasmon excitation. Recording of low-loss EEL spectra can be achieved faster than that of core-loss EEL spectra up to 300 eV. This analysis method allows us to reduce beam damage during data recording while recording a better signal-to-noise ratio\textsuperscript{39,40}.

Figure 3a shows the low-loss EEL spectra including Mg $L_{2,3}$ edges obtained from reference materials, i.e. Mg metal sheet and MgF$_2$ powders, and MgF$_2$ anodes after/before defluorination. The low-loss EEL spectrum of Fe is obtained from a Fe particle in the pristine MgF$_2$ anode. We confirmed that the EEL spectra of Fe particles in MgF$_2$ anode before/after electrochemical defluorination showed no obvious change. This result means that Fe did not contribute to the charge capacity. These reference spectra can be used for fingerprinting methods to understand the structural change of MgF$_2$ anode caused by electrochemical reduction processes.

The shapes of plasmon peaks of MgF$_2$ powder, pristine MgF$_2$ anode, and defluorinated MgF$_2$ anode (region A) are almost the same. This result indicates that most of the active MgF$_2$ materials are not defluorinated. This is consistent with the results of electron diffraction analysis (Figs. 2c and 2f). On the other hand, a change in the plasmon peak, indicated by the red arrow in Fig. 3a, that was detected at region B or a specific region, is deliberately extracted from low-loss EEL map data. A similar sharp peak located at an energy loss of 10.5 eV is also obtained from the Mg metal sheet as a reference. The metals with free electrons such as Li, Na, Mg, and Al are well known to show a sharp plasmon peak\textsuperscript{41}. This is because there is no significant influence of attenuation of plasma oscillations, which produce a broader plasmon peak caused by interband transitions of the valance electrons in semiconductors and insulators. The sharp peak denoted by the red arrow is assumed to have originated from Mg metal formation after defluorination.

Considering the feature of plasmon peaks, it is possible to visualise Mg metal location by extracting sharp plasmon peaks originating from Mg metal. First, the integration intensity $I_{\alpha}$ with an energy window of 0.7 eV from 10.2 to 10.9 eV as a standard spectrum intensity was calculated from a region without Mg formation in defluorinated MgF$_2$ anode as shown in Fig. 3b. Next, the integration intensity $I_{\beta}$ with an energy window of 0.7 eV from 10.2 to 10.9 eV was calculated as the intensity of a target signal (Fig. 3c). Finally, a relative plasmon intensity $I_{rp}$ was defined as $I_{rp} = \frac{I_{\beta}}{I_{\alpha}}$ for the plasmon maps. The relative plasmon intensity $I_{rp}$ is larger than 1 in the region with Mg metal as shown in Fig. 3c, and $I_{rp}$ is approximately 1 in the region without Mg metal or only MgF$_2$. Therefore, this simple method can be used for qualitative visualisation of the location of Mg metal in MgF$_2$ anode.

Figures 4a and 4b shows the HAADF STEM images of the MgF$_2$ anodes before and after electrochemical defluorination, respectively. To visualise the distribution of Mg metal in the anodes, we carried out the qualitative EEL map analysis for the area as mentioned in the previous section. In the $I_{rp}$ map from pristine MgF$_2$ anode as shown in Fig. 4c, there is no apparent region containing Mg metals. On the other hand, the $I_{rp}$ map of Fig. 4d clearly shows the distribution of Mg metal. Tens of nanometer-sized Mg
metals were found to be partially formed in the two types of areas. One is the area near conductive Fe particles where electron conductivity was secured. The other are the areas that are originally interfaces between the liquid electrolyte and the anode where F ions are easily exchanged. In the selected area where electron diffraction patterns were obtained from a formed Mg metal, the Mg metal exists as a crystalline phase rather than an amorphous phase as shown in Supplementary Note 3 and Fig. S4.

Figures 5a and 5b show magnified view of HAADF STEM image and \(I_{rp}\) map of Fig. 4d. Figure 5c show the low-loss EEL spectra extracted from rectangles 1–5 of Figs. 5a and 5b. The plasmon peak of MgF\(_2\) overlaps with that of Mg metal in all rectangle regions where Mg metal is detected. It is difficult to detect only the signal of the Mg metal partially formed in MgF\(_2\) using EDS because of overlapping of the information of MgF\(_2\) and Mg in depth directions (see Fig. S5). Therefore, the present method based on the low-loss EEL spectra is very effective for extracting of the information of Mg metal in the defluorinated MgF\(_2\) anode. In fact, the low-loss EEL spectrum obtained from the region 4 clearly shows appearance of a slight peak derived from the plasmon loss of Mg metals as shown in Fig. 5d. The average \(I_{rp}\) of each rectangle region 1, 2, 3, 4, and 5 were 25.6, 10.2, 3.6, 2.4, and 1.1, respectively. The analysis results indicate that nanosized Mg metal below 10 nm size are formed by reduction processes even in poor electronic conductivity region, indicated by the white arrows in Fig. 5a and 5b.

The \(I_{rp}\) map shows information regarding interphases on the surface of a defluorinated MgF\(_2\) anode. The surface of the MgF\(_2\) anode can be determined from the deep navy color (\(I_{rp} \approx 1\)) region, indicated by a dotted line in Fig. 5b. Further, in the HAADF STEM image (Fig. 5a), there exist contrasts, indicating the formation of different compounds on the surface of MgF\(_2\) anode; these are identified by the dashed lines in Figs. 5a and 5b. Therefore, the surface of the defluorinated MgF\(_2\) anode consists of some compounds that are different from MgF\(_2\) and Mg metal. To identify the compounds by using the fingerprint method, low-loss EEL spectra are obtained from reference materials, i.e., Mg metal, Mg(OH)\(_2\), MgO, MgF\(_2\), and LiF.

Figure 5e shows low-loss EEL spectra of reference materials and spectrum extracted from the rectangle region \(\alpha\). The shape of the plasmon peak and peak top, indicated by the dotted-lines, obtained from the region \(\alpha\), are similar to that of MgF\(_2\). However, the energy loss positions where the spectra start to rise, which is indicated by the dashed lines, are different, although the shape of the spectra obtained from the region \(\alpha\) is broader due to the existence of various unknown compounds. It should be noted that the band gap can be calculated from an energy position where a valence EEL spectrum rises\(^{42}\). The band gaps of MgF\(_2\) and LiF calculated from each valence EEL spectrum were 11.2 eV and 12.4 eV, and are in relatively good agreement with previous reports\(^{20,43}\).

Figure 5f shows Mg \(L_{2,3}\) and Li \(K\) edges obtained from reference materials. Compered to these EEL spectra of the reference materials and previous reports of lithium compounds\(^{44}\), one of the compounds in region \(\alpha\) and on the surface of the defluorinated MgF\(_2\) anode is considered to be LiF. STEM EDS analysis confirmed that a certain kind of oxide was also formed on the surface as shown in Supplementary Note 4 and Fig. S5. LiF and the oxide are considered to be formed by the decomposition reaction of the liquid
electrolyte during the reduction process. Such production is well known as solid electrolyte interphase (SEI) in the field of lithium-ion batteries\textsuperscript{28}. SEI formed on the anode materials acts as a passive agent that prevents continuous degradation of a liquid electrolyte. On the other side, SEI may also cause deterioration of battery performance, i.e. fading (dis)charge capacities, rate, and cycling performances. LiF is one of the typical SEI compounds in lithium-ion batteries\textsuperscript{45}. LiF formation as a SEI on the anode materials may lead to a serious problem for fluoride-shuttle batteries using a liquid electrolyte comprising of Li salts as LiF has poor electronic and fluoride ion conductivity.

**Discussion**

To further understand the defluorination reaction in the MgF\textsubscript{2} anode, the ratio of the Mg metal formation region was estimated by counting the number of pixels with \(I_{rp} > 1.5\) as Mg metal regions from Fig. 4d. As a result, the ratio of the formation region of Mg metal was approximately 31\%. This result is an overestimated value because the population of MgF\textsubscript{2} overlapped with Mg metals in the depth direction are neglected. Considering charge capacity of Fig. 1, Mg metal region can be expected to be about 57 \% in the anode after defluorination. The result of \(I_{rp}\) mapping is not quantitatively coincident with those of electrochemical measurements.

There are several possible reasons for the difference between STEM EELS analyses and electrochemical measurements. One of the possible factors is the limitation of our STEM observation area within several square micrometers. One can suppose that more Mg metal may have been formed in parts other than the observed areas of the anode. However, in the results of STEM observation as shown in Figs. 2d and Fig. 4b, voids caused by the volume shrinkage from MgF\textsubscript{2} to Mg metal are observed everywhere in the defluorinated MgF\textsubscript{2} anode. Since the liquid electrolyte is used for electrochemical defluorination in the present study, the defluorination is considered to proceed uniformly. Therefore, we assume that the dependence of the observation area should be low.

The main possible reasons for the formation of the lower amount of formed Mg metal are considered to be the following factors; the observed (dis)charge capacity may have increased owing to side reactions such as electrolyte decomposition. Additionally, SEI has been confirmed to form on surfaces of the MgF\textsubscript{2} anode. The detail influence of side reductions on the (dis)charge capacity is not yet clarified in the present results. Further, the Mg metal may have been fluorinated by F ion in the electrolyte after defluorination, i.e. self-discharge of anode. This is because the formation enthalpy of MgF\textsubscript{2} is lower than that of Mg metal, indicating that MgF\textsubscript{2} may be easily formed in an F ion liquid electrolyte\textsuperscript{25}. The other factor is formation of Mg metal particles with sizes below 1 nm and/or formation of non-stoichiometric MgF\textsubscript{2-\delta} with a fluoride ion deficiency. Especially, F-deficient MgF\textsubscript{2-\delta} may exist under specific environments such as particle surfaces or interfaces between Mg metal and MgF\textsubscript{2} although the formation enthalpy of MgF\textsubscript{2} suggests that the defluorination of MgF\textsubscript{2} basically occurs by a two-phase reaction\textsuperscript{25}. The information of Mg metal with a size less than 1 nm and F deficient MgF\textsubscript{2-\delta} cannot be detected in the
present method. Because the plasmon peak signal of Mg metal with smaller size is too weak to be buried in the large signal of MgF₂. Then, the plasmon peak of MgF₂,δ is expected to be similar that of MgF₂, indicating that it is difficult to extract the information from the present method. Here, we do not have any direct evidence showing nucleation of sub-nanometer sized Mg and/or MgF₂,δ. However, we do speculate that uniform generation of voids after defluorination of the anode may be originating from the volume shrinkage associated with the formation of sub-nanometer-sized Mg metals. To confirm our assumption, it is necessary to further develop the imaging and analysis techniques to avoid electron beam damages. Although the defluorination state in MgF₂ anode has not yet been fully elucidated and still faces the remaining challenges, this study gives the first result for visualisation of Mg metal distributions and is appropriate for demonstrating the existence of SEI on the surface.

Conclusions

We demonstrated the Mg metal distributions and SEI formation on the surface in MgF₂ anode before and after electrochemical defluorination using an advanced STEM EELS technique. Although HAADF STEM imaging techniques do not visualise Mg metal formation, the analysis from low-loss EEL spectra succeeded in visualising that Mg metals in tens of nanometre sizes were partially formed near the additive Fe and surfaces of MgF₂ where electronic or fluoride ion conductivities were sufficiently maintained. These results indicate that creating electrodes capable of sufficient electronic and fluoride-ionic conductions is important for improving the utilisation rate. On the other hand, several nanometre-sized Mg particles were nucleated even in the regions where electronic conductivity was poor. This implies that efficient defluorination process can be achieved by designing the electrode configuration and/or elemental composition even without a large amount of conductive material.

Furthermore, the SEI composed of LiF and some oxides was formed on the interface between electrolyte and anode after defluorination. At present, the SEI on an anode may be related to degradation of first (dis)charge capacity and cycle performance. The impact of SEI is considered to be small compared to the anode material utilisation issues. However, as research and development progress in the future, the control of the SEI composition and its properties must become an important challenge in fluoride-shuttle batteries to improve battery performances. The findings in this study do not only offer first insights into the formation state of Mg metal and SEI in defluorinated MgF₂ anode, but also have implications for the development of anode materials.

Experimental Section

Sample preparation

All sample preparations were carried out in an argon filled glovebox under low oxygen concentration below 0.3 ppm. To optimise the poor electron conductivity of MgF₂, a composite electrode of MgF₂ and Fe was prepared. The oxidation and reduction of Fe can be ignored under present charge/discharge
process of potential, and Fe can be considered to be as a conductive agent. MgF$_2$ and Fe powder were mixed at a weight ratio of 1:10 by mechanical milling at 600 rpm for 3 h. As a result of the mechanical milling, the particles of MgF$_2$ reduce to several nanometers in size. A working electrode or anode was prepared by cast film process with a polyimide binder. A composite electrode of acetylene black (AB) and polytetrafluoroethylene (PTFE) was used as a counter electrode for electrochemical measurements.

Lithium bis(fluorosulfonyl)imide (Li-FSA, Kishida Chemical Co., Ltd.) and cesium fluoride (CsF, Kanto Chemical Co., Inc.) were mixed at 4.5 mol/L and 0.45 mol/L in [2-(2-methoxyethoxy)ethyl]ether (tetruglyme: G4, Kishida Chemical Co., Ltd.), respectively. Then, the mixture was stirred at 60 °C for 70 h to obtain a liquid electrolyte for measurement. F ion conductivity of the prepared electrolyte is over 10$^{-3}$ S cm$^{-1}$ at room temperature.

The charge/discharge measurement was performed by the constant current method using a multipotentiostat (Biologic VMP–300) at room temperature. The cut-off voltages were set to –2.85 V and –1.8 V. The current density of charge and discharge were –34.4 mAg$^{-1}$ (0.04 C rate) and 17.2 mAg$^{-1}$ (0.02 C rate), respectively. The specific capacity was calculated by a weight of MgF$_2$.

**Structural analysis of MgF$_2$ anode**

Cross-sectional STEM samples were prepared using a dual-beam focused ion beam scanning microscope (NB5000, Hitachi High-Technologies Co.) equipped with a Ga ion source. The thinning processes below 2 μm thickness by FIB were performed using a cold stage at –90 °C to reduce the Ga ion beam damages and to avoid the oxidation of the sample caused by ice (H$_2$O). Ice adheres to the sample surface due to the degree of vacuum of our FIB instrument when the temperature is lower than –100 °C. Samples were transferred from the argon (Ar) filled glovebox to the FIB using a non-exposure transfer system. Reference samples were a cut sheet of Mg metal and powder samples of Mg(OH)$_2$, MgO, MgF$_2$, and LiF supported on holey carbon films prepared in an Ar-filled glove box.

The structure of the MgF$_2$ anodes before and after electrochemical defluorination was investigated by STEM using an aberration-corrected (CEOS GmbH) scanning transmission electron microscope (JEM–2400FCS, JEOL Ltd.). STEM observations were performed at accelerating voltages of 60 kV. The probe-forming aperture semiangle used was 22 mrad, and HAADF STEM images were recorded with 68–280 mrad detectors.

EEL spectra were obtained using an EEL spectrometer (Tridiem ERS, Gatan, Inc.) attached to a Wien filter monochromated aberration corrected STEM (JEM–2400FCS, JEOL Ltd.) operated at 60 kV. An energy resolution was 300 meV (full-width at half-maximum of zero-loss peak) using 0.1 eV per channel. The convergence and collection semi-angle were 33 and 43 mrad, respectively. EEL spectra were recorded within a rectangular area (about 15 × 15 nm$^2$) to reduce the electron beam damages in STEM mode. To
obtain plasmon maps, a pixel size and recording time for a spectrum were about 7 nm and 0.2 sec, respectively.

Declarations

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Author Contributions

S.K. carried out STEM observations and analysis and wrote the paper. H. N carried out the sample preparation and electrochemical measurements. D. Y carried out SEM observations. A. K, T. A. and Y.I. directed the experiments. All authors contributed to discussion of the results and have read and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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References

1 Gschwind, F. et al. Fluoride ion batteries: Theoretical performance, safety, toxicity, and a combinatorial screening of new electrodes. J. Fluorine Chem. 182, 76-90, (2016).

2 Anji Reddy, M. & Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem. 21, 17059, (2011).

3 Kennedy, J. H. Thin-film galvanic cell Pb/PbF₂/PbF₂, CuF₂/Cu. J. Electrochem. Soc. 123, 10, (1976).

4 Schoonman, J. A Solid-state galvanic cell with fluoride-conducting electrolytes. J. Electrochem. Soc. 123, 1772, (1976).

5 Nowroozi, M. A., Wissel, K., Rohrer, J., Munnangi, A. R. & Clemens, O. LaSrMnO₄: reversible electrochemical intercalation of fluoride ions in the context of fluoride ion batteries. Chem. Mater. 29,
6 Konishi, H., Minato, T., Abe, T. & Ogumi, Z. Electrochemical performance of a bismuth fluoride electrode in a reserve-type fluoride shuttle battery. *J. Electrochem. Soc.* **164**, A3702-A3708, (2017).

7 Mohammad, I., Witter, R., Fichtner, M. & Anji Reddy, M. Room-temperature, rechargeable solid-state fluoride-ion batteries. *ACS Appl. Energy Mater.* **1**, 4766-4775, (2018).

8 Yamamoto, T., Matsumoto, K., Hagiwara, R. & Nohira, T. Room-temperature fluoride shuttle batteries based on a fluorohydrogenate ionic liquid electrolyte. *ACS Applied Energy Materials* **2**, 6153-6157, (2019).

9 Yamanaka, T., Okazaki, K.-i., Ogumi, Z. & Abe, T. Reactivity and mechanisms in fluoride shuttle battery reactions: difference between orthorhombic and cubic BiF$_3$ single microparticles. *ACS Appl. Energy Mater.* **2**, 8801-8808, (2019).

10 Celik Kucuk, A., Minato, T., Yamanaka, T. & Abe, T. Effects of LiBOB on salt solubility and BiF$_3$ electrode electrochemical properties in fluoride shuttle batteries. *J. Mater. Chem. A* **7**, 8559-8567, (2019).

11 Yamanaka, T., Nakamoto, H., Abe, T., Nishio, K. & Ogumi, Z. Formation and propagation of fluorine-deficient phases in large LaF$_3$ single crystals during electrochemical defluorination. *ACS Appl. Energy Mater.* **2**, 3092-3097, (2019).

12 Mori, K. *et al.* Experimental visualization of interstitialcy diffusion pathways in fast-fluoride-ion-conducting solid electrolyte Ba$_{0.6}$La$_{0.4}$F$_{2.4}$. *ACS Appl. Energy Mater.*, (2020).

13 Thieu, D. T. *et al.* CuF$_2$ as reversible cathode for fluoride ion batteries. *Adv. Funct. Mater.* **27**, 1701051, (2017).

14 Zhang, L., Reddy, M. A. & Fichtner, M. Electrochemical performance of all solid-state fluoride-ion batteries based on thin-film electrolyte using alternative conductive additives and anodes. *J. Solid State Electrochem.* **22**, 997-1006, (2017).

15 Mohammad, I. & Witter, R. Testing Mg as an anode against BiF$_3$ and SnF$_2$ cathodes for room temperature rechargeable fluoride ion batteries. *Mater. Lett.* **244**, 159-162, (2019).

16 DuMont, J. W. & George, S. M. Competition between Al$_2$O$_3$ atomic layer etching and AlF$_3$ atomic layer deposition using sequential exposures of trimethylaluminum and hydrogen fluoride. *J. Chem. Phys.* **146**, 052819, (2017).

17 Rubloff, G. W. Far-ultraviolet reflectance spectra and the electronic structure of ionic crystals. *Phys. Rev. B* **5**, 662-684, (1972).
18 Shirley, E. L. Many-body effects on bandwidths in ionic, noble gas, and molecular solids. *Phys. Rev. B* **58**, 9579-9583, (1998).

19 Krupa, J. C. & Queffelec, M. UV and VUV optical excitations in wide band gap materials doped with rare earth ions: 4f–5d transitions. *J. Alloys Compd.* **250**, 287-292, (1997).

20 Williams, M. W., MacRae, R. A. & Arakawa, E. T. Optical properties of magnesium fluoride in the vacuum ultraviolet. *J. Appl. Phys.* **38**, 1701-1705, (1967).

21 Zheng, Y. *et al.* First-principles studies on the structural and electronic properties of Li-ion battery cathode material CuF₂. *Solid State Commun.* **152**, 1703-1706, (2012).

22 Olalde-Velasco, P., Jiménez-Mier, J., Denlinger, J. D., Hussain, Z. & Yang, W. L. Direct probe of Mott-Hubbard to charge-transfer insulator transition and electronic structure evolution in transition-metal systems. *Phys. Rev. B* **83**, 241102 (2011).

23 Feng, C. *et al.* A newly discovered BiF₃ photocatalyst with a high positive valence band. *J. Mol. Catal. A: Chem.* **401**, 35-40, (2015).

24 Kan, Y., Teng, F., Yang, Y., Xu, J. & Yang, L. Direct conversion mechanism from BiOCl nanosheets to BiOF, Bi₇F₁₁O₅ and BiF₃ in the presence of a fluorine resource. *RSC Advances* **6**, 63347-63357, (2016).

25 Haruyama, J. *et al.* Two-phase reaction mechanism for fluorination and defluorination in fluoride-shuttle batteries: A First-Principles Study. *ACS Appl. Mater. Interfaces* **12**, 428-435, (2020).

26 Rongeat, C., Anji Reddy, M., Diemant, T., Behm, R. J. & Fichtner, M. Development of new anode composite materials for fluoride ion batteries. *J. Mater. Chem. A* **2**, 20861-20872, (2014).

27 Zhang, L. *et al.* Study of all solid-state rechargeable fluoride ion batteries based on thin-film electrolyte. *J. Solid State Electrochem.* **21**, 1243-1251, (2016).

28 Verma, P., Maire, P. & Novák, P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochim. Acta* **55**, 6332-6341, (2010).

29 Gschwind, F., Zao-Karger, Z. & Fichtner, M. A fluoride-doped PEG matrix as an electrolyte for anion transportation in a room-temperature fluoride ion battery. *J. Mater. Chem. A* **2**, 1214-1218, (2014).

30 Gschwind, F. & Bastien, J. Parametric investigation of room-temperature fluoride-ion batteries: assessment of electrolytes, Mg-based anodes, and BiF₃-cathodes. *J. Mater. Chem. A* **3**, 5628-5634, (2015).

31 Darolles, I., Weiss, C. M., Alam, M. M., Tiruvannamalai, A. & Jones, S. C. Fluoride Ion Battery Compositions. U.S. Patent US20120164541 A1, June 28, 2012.
32 Weiss, C. M. et al. Fluoride Ion Battery Electrolyte Compositions. U.S. Patent US20160181665 A1, June 23, 2016.

33 Okazaki, K.-i., Uchimoto, Y., Abe, T. & Ogumi, Z. Charge–Discharge Behavior of Bismuth in a Liquid Electrolyte for Rechargeable Batteries Based on a Fluoride Shuttle. *ACS Energy Lett.* **2**, 1460-1464, (2017).

34 Davis, V. K. et al. Room-temperature cycling of metal fluoride electrodes: Liquid electrolytes for high-energy fluoride ion cells. *Science* **362**, 1144-1148, (2018).

35 Konishi, H., Minato, T., Abe, T. & Ogumi, Z. Triphenylboroxine and Triphenylborane as Anion Acceptors for Electrolyte in Fluoride Shuttle Batteries. *Chem. Lett.* **47**, 1346-1349, (2018).

36 Pennycook, S. J. & Jesson, D. E. High-resolution Z-contrast imaging of crystals. *Ultramicroscopy* **37**, 14-38, (1991).

37 Baur, W. Rutile-type compounds. V. Refinement of MnO<sub>2</sub> and MgF<sub>2</sub>. *Acta Crystallographica Section B* **32**, 2200-2204, (1976).

38 Zenser, L.-P., Gruehn, R. & Liebscher, B. H. Decomposition of MgF<sub>2</sub> in the Transmission Electron Microscope. *J. Solid State Chem.* **157**, 30-39, (2001).

39 Kobayashi, S., Fisher, C. A. J., Kuwabara, A., Ukyo, Y. & Ikuhara, Y. Quantitative analysis of Li distributions in battery material Li<sub>1-x</sub>FePO<sub>4</sub> using Fe M<sub>2,3</sub>-edge and valence electron energy loss spectra. *Microscopy* **66**, 254-260, (2017).

40 Kobayashi, S., Kuwabara, A., Fisher, C. A. J., Ukyo, Y. & Ikuhara, Y. Microscopic mechanism of biphasic interface relaxation in lithium iron phosphate after delithiation. *Nat. Commun.* **9**, 2863 (2018).

41 Williams, D. B. & Carter, C. B. *Transmission electron microscopy : a textbook for materials science.* (Plenum Press, 1996).

42 Egerton, R. *Electron Energy-Loss Spectroscopy in the Electron Microscope.* (Springer, 1996).

43 Shirley, E. L., Terminello, L. J., Klepeis, J. E. & Himpsel, F. J. Detailed theoretical photoelectron angular distributions for LiF(100). *Phys. Rev. B* **53**, 10296-10309, (1996).

44 Wang, F. et al. Chemical distribution and bonding of lithium in intercalated graphite: identification with optimized electron energy loss spectroscopy. *ACS Nano* **5**, 1190-1197, (2011).

45 Andersson, A. M. & Edström, K. Chemical composition and morphology of the elevated temperature SEI on graphite. *J. Electrochem. Soc.* **148**, A1100, (2001).

**Figures**
Figure 1

Nanosized Mg metal formation and solid electrolyte interphase. Magnified view of a HAADF STEM image and b relative plasmon intensity Irp map of Fig. 4d. Solid, dotted and dashed lines indicate the interfaces between a Fe particle and defluorinated MgF2, between defluorinated MgF2 and SEI, and between SEI and coated carbon layer, respectively. The colour scale bar shows colour changes as a function of relative plasmon intensity Irp for maps. Scale bars, 50 nm. c Low-loss EEL spectra and d magnified view of around Mg plasmon energy region of c extracted from mapping spectra from rectangles region 1-5 in b. The red arrows in d indicate the plasmon peak of Mg metal. e Low-loss EEL spectra and f magnified view around from 50 to 80 eV of e extracted from rectangle α in b. Dashed and dotted lines in e indicate the positions of intensity rise-up and peak top of plasmon, respectively. The EEL spectra of black colour in c-f are obtained from reference materials. TEM sample thickness was about 140 nm calculated by relative thickness t/λ (where t = thickness, and λ = mean free path42) using EEL spectra.
Figure 2

Visualisation of Mg metal distribution in MgF2 anode before/after defluorination. HAADF STEM image obtained from a pristine and b defluorinated MgF2 anodes. Relative plasmon intensity Irp map obtained from c pristine and d defluorinated MgF2 anodes. The colour scale bar below c and d shows colour changes as a function of relative plasmon intensity Irp for maps. White arrows in d indicate the region of Mg metal. Scale bars, 100 nm.
Low-loss EEL spectra and integration region for visualisation of Mg metal. (a) Low-loss EEL spectra of Mg metal sheet and original MgF2 powders as reference spectra, indicated by black color lines, Fe particle and MgF2 anode before/after deuorination. The EEL spectra of region A and B are obtained from defluorinated MgF2 anode. The red arrow in a indicates appearance of the plasmon peak originated from Mg metal. The integration energy region for the sharp plasmon peak of Mg metal with a width of 0.7 eV.
in the low-loss EEL spectra of b the standard spectrum (a region without Mg metal) and c the target spectrum (a region with Mg metal).

**Figure 4**

HAADF STEM images and electron diffraction patterns of MgF2 anode after/before deuorination. a low-magnification, b magnified view of HAADF STEM images and c selected area electron diffraction pattern of pristine MgF2 anode. Scale bars of a and b are 50 and 20 nm, respectively. d low-magnification, e magnified view of HAADF STEM images, and f selected area electron diffraction pattern of deuorinated MgF2 anode. Scale bars of d and e are 50 and 20 nm, respectively. White arrows in b and e indicate the Fe fine particles. Simulated electron diffraction patterns from crystal structure of MgF237 are attached in c and f.
Figure 5

Charge and discharge curves of MgF2 anode. The charge and discharge curves were obtained at room temperature in a half-cell test. The specific capacity was calculated from the weight of MgF2.

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