Characterisation of Defluorination Reaction and Solid Electrolyte Interphase in Fluoride-Shuttle Battery Anode MgF_2

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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^{1,2}. The concept of this battery was reported in 1970s^{3,4}. Reddy and Fichtner in 2011² 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^{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/L¹.

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^{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 ~ 10.8 eV¹⁶, ~ 11.8 eV^{17,18}, ~ 10.5 eV¹⁹, and ~ 11.8 eV²⁰, respectively. The band gaps of the anodes are over twice as large as typical cathode materials, for example, ~ 2 eV of CuF_2 ^{21,22} and ~ 4 eV of BiF_3 ^{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 metal²⁵, 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 electrolyte⁸ and a BiF_3 cathode using a solid electrolyte⁷ at room temperature. Meanwhile, regardless of various efforts such as improving conductivity¹⁴ and a composited 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 mAhg^{-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 anode²⁸, 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 mAhg^{-1} in the charge (defluorination) process. This capacity is 57 % of the MgF_2 theoretical specific capacity, 860 mAhg^{-1} . After charge, the discharge (fluorination) capacity is 271 mAhg^{-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 ($V = 65.18 \text{ \AA}^3$) to Mg ($V = 46.46 \text{ \AA}^3$). 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 elements³⁶. 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 $P4_2/mnm$ ($a = b = 0.4621$ nm, $c = 0.3052$ nm³⁷). 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 radiations³⁸. 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^{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 MgF₂ powders, and MgF₂ anodes after/before defluorination. The low-loss EEL spectrum of Fe is obtained from a Fe particle in the pristine MgF₂ anode. We confirmed that the EEL spectra of Fe particles in MgF₂ 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 MgF₂ anode caused by electrochemical reduction processes.

The shapes of plasmon peaks of MgF₂ powder, pristine MgF₂ anode, and defluorinated MgF₂ anode (region A) are almost the same. This result indicates that most of the active MgF₂ 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 peak⁴¹. 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 valence 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_a 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 MgF₂ anode as shown in Fig. 3b. Next, the integration intensity I_β 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 $I_{rp} = I_\beta / I_a$ 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 MgF₂. Therefore, this simple method can be used for qualitative visualisation of the location of Mg metal in MgF₂ anode.

Figures 4a and 4b shows the HAADF STEM images of the MgF₂ 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 MgF₂ 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 shows 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, $\text{Mg}(\text{OH})_2$, MgO , MgF_2 , and LiF.

Figure 5e shows low-loss EEL spectra of reference materials and spectrum extracted from the rectangle region α . The shape of the plasmon peak and peak top, indicated by the dotted-lines, obtained from the region α , 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 α 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 rises⁴². 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. Compared to these EEL spectra of the reference materials and previous reports of lithium compounds⁴⁴, one of the compounds in region α 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 batteries²⁸. 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 batteries⁴⁵. 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_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_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_2 to Mg metal are observed everywhere in the defluorinated MgF_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_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_2 is lower than that of Mg metal, indicating that MgF_2 may be easily formed in an F ion liquid electrolyte²⁵. The other factor is formation of Mg metal particles with sizes below 1 nm and/or formation of non-stoichiometric $\text{MgF}_{2-\delta}$ with a fluoride ion deficiency. Especially, F-deficient $\text{MgF}_{2-\delta}$ may exist under specific environments such as particle surfaces or interfaces between Mg metal and MgF_2 although the formation enthalpy of MgF_2 suggests that the defluorination of MgF_2 basically occurs by a two-phase reaction²⁵. The information of Mg metal with a size less than 1 nm and F deficient $\text{MgF}_{2-\delta}$ 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 MgF_2 . Then, the plasmon peak of $\text{MgF}_{2-\delta}$ is expected to be similar that of MgF_2 , 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 $\text{MgF}_{2-\delta}$. 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 MgF_2 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 MgF_2 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 MgF_2 where electronic or fluoride ion conductivities were sufficiently maintained. These results indicate that creating electrodes capable of sufficient electronic and fluoride-ionic conduction 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 MgF_2 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 MgF_2 , a composite electrode of MgF_2 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 (tetraglyme: 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} Scm^{-1} at roomtemperature.

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 mA g^{-1} (0.04 C rate) and 17.2 mA g^{-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 $-90 \text{ }^\circ\text{C}$ to reduce the Ga ion beam damages and to avoid the oxidation of the sample caused by ice (H_2O). Ice adheres to the sample surface due to the degree of vacuum of our FIB instrument when the temperature is lower than $-100 \text{ }^\circ\text{C}$. 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 $\text{Mg}(\text{OH})_2$, 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 $15 \times 15 \text{ nm}^2$) 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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Figures

Figure 1

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.

a Pristine MgF_2 anode

d Defluorinated MgF_2 anode

Figure 2

HAADF STEM images and electron diffraction patterns of MgF_2 anode after/before defluorination. a low-magnification, b magnified view of HAADF STEM images and c selected area electron diffraction pattern of pristine MgF_2 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 defluorinated MgF_2 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 MgF_{237} are attached in c and f.

Figure 3

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 defluorination. 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).

a Pristine MgF_2 anode

b Defluorinated MgF_2 anode

c

1 10 20 30
Relative plasmon intensity I_{rp}

d

1 10 20 30
Relative plasmon intensity I_{rp}

Figure 4

Visualisation of Mg metal distribution in MgF_2 anode before/after defluorination. HAADF STEM image obtained from a pristine and b defluorinated MgF_2 anodes. Relative plasmon intensity I_{rp} map obtained from c pristine and d defluorinated MgF_2 anodes. The colour scale bar below c and d shows colour changes as a function of relative plasmon intensity I_{rp} for maps. White arrows in d indicate the region of Mg metal. Scale bars, 100 nm.

Figure 5

Nanosized Mg metal formation and solid electrolyte interphase. Magnified view of a HAADF STEM image and b relative plasmon intensity I_{rp} map of Fig. 4d. 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 colour scale bar shows colour changes as a function of relative plasmon intensity I_{rp} 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.

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