Discharge/charge reaction mechanisms of FeS₂ cathode material for aluminum rechargeable batteries at 55°C

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Abstract

The aluminum rechargeable battery is a desirable device for large-scale energy storage owing to the high capacity derived from the properties of the aluminum metal anode. The development of cathode materials is needed to compose battery systems. However, the design principles of the cathode materials have not been determined. We focus on the high capacity FeS_2 cathode materials and investigate the discharge/charge reaction mechanisms in chloroaluminate ionic liquids as the electrolyte at 55°C . X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements are performed for the discharged and charged samples. S $3p$ -orbitals are shown to play an important role in the redox reactions from the results of the S and Fe K -edge XANES spectra. As a result of the redox reaction, FeS_2 is transformed into low crystalline FeS and amorphous Al_2S_3 , as shown by the XRD and S, Al, and Fe K -edge XANES spectra. This reaction mechanism is different from the reaction observed with lithium ion.

1. Introduction

Aluminum rechargeable batteries are considered viable alternatives for large-scale energy storage devices, because aluminum metal anodes have a high theoretical capacity (2980 mAh g⁻¹, 8063 mAh cm⁻³), abundance, and are safe [1]. The demonstration of electrolytes that can effectively dissolve/deposit aluminum (such as AlCl₃ mixed with organic chloride salt based ionic liquids, that is, chloroaluminate ionic liquids) [2, 3] has led to a surge in interest in the search for electrode materials that can reversibly use aluminum ions when coupled with such electrolytes.

For the cathode materials of aluminum batteries, V₂O₅ [4, 5], VO₂ [6], and fluorinated graphite [7] have been reported as an insertion host for aluminum ions. However, these cathode materials show a relatively low redox voltage, and evidence of the insertion of the aluminum ions has not been obtained. Owing to the high charge density of trivalent aluminum ions, it appears difficult to develop cathode materials using the intercalation reaction.

Therefore, we have focused on the conversion electrodes [8, 9], such as transition metal sulfides, oxides, and fluorides. Aluminum oxides and fluorides seem to show a lack of reversibility of the conversion reaction owing to the strong ionic bond between aluminum and O²⁻/F⁻. However, aluminum sulfides are expected to be excellent candidates for cathode materials for the conversion reaction in aluminum batteries because of the relatively weak ionic bond between aluminum and S²⁻. Among these compounds, iron-based pyrite (FeS₂) is an interesting material, because it exhibits a high theoretical capacity (894 mAh g⁻¹, 4470 mAh cm⁻³) and is naturally abundant.

The application of FeS₂ as a cathode material for aluminum rechargeable batteries has recently been reported [10]. Koura *et al.* were the first to demonstrate the feasibility of using FeS₂ as a cathode material for aluminum rechargeable battery systems operating at elevated

temperatures of approximately 240°C and also investigated the charge-discharge reaction mechanism [11]. For the practical application of aluminum rechargeable batteries, the charge-discharge reaction should be observed at **relatively low** temperatures. While the use of FeS₂ as aluminum rechargeable battery cathodes at **25°C** has also been reported by Koura *et al.* [12], their mechanisms are still not well understood. It is important to understand the reaction mechanisms for the aluminum rechargeable battery cathode because such knowledge is useful for the design principles of the high capacity cathode materials.

FeS₂ can be used as a cathode material for the lithium and sodium ion battery cathodes [13, 14]. In these cases, under ambient temperature conditions, the first discharge reactions have been proposed as the following equations [13, 15-17],

In the case of the lithium ion battery, Li₂FeS₂ has a layered structure assigned to the *P3m1* space group [18]. This phase transition from FeS₂ to Li₂FeS₂ is related to the rate of lithium diffusion through the bulk (for example, there were two step reactions above 37°C, at C/20 rate) [13]. Li₂FeS₂ phase is transformed to the Fe and Li₂S phases after further lithiation. At the high rate or low-temperature conditions, FeS₂ is directly converted to Fe and Li₂S through a 4 electrons reaction [13, 17]. Moreover, the charge compensation of FeS₂ during discharge is dominant at sulfur atoms [15, 19]. Compared with lithium and sodium ions, it is difficult for trivalent aluminum ions to diffuse inside solid electrode materials, which seems to vary the reaction mechanism.

In this study, the capacity of FeS₂ for use as aluminum rechargeable battery cathodes at 55°C was drastically improved by controlling the particle size of FeS₂. Moreover, the reaction mechanisms of the FeS₂ as an aluminum battery cathode are investigated. Nanoparticles were prepared by ball milling to improve the material usage of the FeS₂ cathode material for an aluminum battery. The reaction mechanism, including the crystal structure and the electronic structure changes, were investigated by X-ray diffraction and X-ray absorption spectroscopy (XAS). We report the reaction mechanism of FeS₂ aluminum battery cathodes operating at 55°C. This information is very important for the further development of aluminum battery cathode materials.

2. Experimental

FeS₂ powders (99.9%, Alfa Aesar) were put into a ball mill pot under an argon atmosphere, and the milling was carried out using a planetary ball milling machine (Pulverisette 5, Fritsch) at 500 rotations per minute for 12, 24, and 48 hours with a ball-to-powder weight ratio of 10:1. The prepared samples were characterized by X-ray diffraction (XRD) measurements conducted by Rint UltimaIII (Rigaku), scanning electron microscope (SEM; JEOL, JM-890) observations, and energy dispersive X-ray spectrometry (EDX; EDAX, Genesis APEX2).

Galvanostatic charge and discharge measurements were conducted with a two-electrode cell. The current density was 8.94 mA g⁻¹ (C/50), and the measuring temperature was 55°C. The working electrode was comprised of a composite mixture of the active material, vapor-grown carbon fiber (VGCF), and PTFE binder (70:25:5 weight ratio) pressed on a Mo foil. An aluminum wire was used as the counter electrode. An ionic liquid consisting of AlCl₃ in 1-ethyl-3-methyl imidazolium chloride (EMIC) (2:1 molar ratio) was used as the electrolyte. This liquid was prepared and purified as follows. All subsequent protocols were

conducted in an argon-filled glove box. EMIC was dissolved into acetonitrile (super dehydrated) and then precipitated from the solution by the addition of ethyl acetate (super dehydrated) and filtered in a vacuum [20]. The obtained EMIC was mixed with AlCl_3 at a molar ratio of 1:2. Aluminum foil was soaked in the prepared electrolyte for at least 24 hours to purify it. FeS_2 nanoparticles are easy to dissolve in this electrolyte. The electrolyte with FeS_2 already dissolved was used for galvanostatic measurements, and the concentration of FeS_2 in the electrolyte was 3.6 mol m^{-3} by inductively coupled plasma (ICP) measurements.

XRD and XAS measurements were carried out for each charged and discharged electrode sample. All the samples are washed with super-dehydrated ethanol and dried in vacuum conditions. XRD measurements were performed by Rint UltimaIII (Rigaku). The samples are sealed using Kapton film in an Ar-filled glovebox. S and Al *K*-edge XAS measurements were conducted at BL-10 of the Synchrotron Radiation Center (Ritsumeikan University). The partial fluorescence yield mode (PFY mode) was used for XAS measurements, and the incident X-ray beam was monochromated by a Ge 111 crystal at the S *K*-edge and by a KTP (KTiOPO_4) 111 crystal at the Al *K*-edge. In addition, the absolute photon energies were calibrated under the assumptions that the strong resonance of K_2SO_4 (S $1s \rightarrow t_2$) appears at 2487.1 eV at the S *K*-edge [21], and peaks of the Al foil appears at 1559.0 eV at Al *K*-edge. All samples were sealed in an argon-filled transfer vessel and transferred to the chamber for S and Al *K*-edge XAS measurements [22]. Fe *K*-edge XAS measurements were carried out at the BL14B2 beam line of SPring-8 (JASRI) in transmission mode. The energy scale was calibrated by the Fe foil. The first inflexion point of the Fe foil was 7112 eV. All samples were sealed in a laminated aluminum pocket under argon atmosphere.

3. Results & Discussion

Preparation of the FeS₂ nanoparticles

Figure 1 shows the particle morphology of FeS₂ after high-energy ball milling. Ball milling of FeS₂ powders decreased their particle size. The crystallite size was calculated using the Bragg diffraction peaks from the XRD pattern based on the Scherrer equation. The obtained values of the crystallite sizes were 127 (pristine), 89 (12 hours milling), 41 (24 hours milling), and 72 nm (48 hours milling). The crystallite size is smallest after 24 hours of ball milling, and there are no impurity phases, as apparent from Fig. 2. Ball milling for 12 hours yields trace amounts of the FeS phase arising from thermal decomposition of FeS₂ [23]. This FeS phase clearly reacts again to form the FeS₂ phase upon ball milling for 24 hours. The crystallite sizes depend on the milling time. However, after 48 hours of milling, the crystallite sizes of FeS₂ are increased. After longer milling time, the surface of the particle is more activated and particles are recombined. The secondary particle size distributions of milling samples are provided in Fig. S1 in the supporting information, which also show the smallest particle size of the 24 hour milled sample. The chemical composition of ball-milled FeS₂ powders does not depend on ball-milling time from the results of the EDX measurements (Table S1).

Figure 3 shows the effect of the crystallite size on the discharge capacity of FeS₂. The discharge profile is shown in Fig. S2 of the ESI. A strong correlation exists between the attainable discharge capacity and the crystallite size of FeS₂. The nanoparticles prepared by mechanical milling for 24 hours exhibit a capacity of approximately 600 mAh g⁻¹. A milling time of 24 hours of the FeS₂ nanoparticles showed the best performance among the prepared samples. We then used these particles for the analysis of the discharge/charge mechanisms for FeS₂ as cathode material in an aluminum rechargeable battery.

Discharge/charge reaction mechanisms of FeS₂ in chloroaluminate ionic liquids

We conducted XRD and XAS measurements to elucidate the reaction mechanism of FeS₂ in an aluminum ion cell. Charge-discharge curves are shown in Fig. 4, in which measurement points for XRD and XAS are also indicated as A-I. Figure 5 shows the *ex situ* XRD patterns of the charging and discharging electrodes. After discharging, the initial FeS₂ phase was maintained, and a low-crystallinity FeS phase was also formed. When the discharge reaction:

is proceeded, the theoretical capacity is 447 mAh g⁻¹. The weight of FeS₂ in the electrode was 2.8 mg and that in the electrolyte was 1.6 mg. The total amount of FeS₂ in the electrochemical cell was 4.4 mg. Therefore, in our electrochemical cell, the total capacity is 2.0 mAh if the all FeS₂ in the electrode and electrolyte is contributed. The observed capacity of the first discharge reaction was 1.7 mAh which corresponds to 85% of the theoretical capacity. Because there is the unreacted FeS₂ in the electrochemical cell even in the end of discharge, the diffraction peaks of FeS₂ are observed. The generated FeS phase converted to the initial FeS₂ phase during the charging process. Although we also performed TEM experiments, we were unable to confirm the obtained phases because the phases were affected by the electron beam.

The absorption edges of the S *K*-edge XANES spectra taken in the PFY mode for various charged/discharged samples are shown in Fig. 6. The spectra measured in the PFY mode indicates the bulk characteristics of the particles. There is a strong peak at 2472 eV. FeS₂ has dumbbell-shaped S₂²⁻ in its crystal structure [24], whose molecular orbital leads to a higher antibonding π^* state. The strong peak at 2472 eV shows a transition from the S 1*s* to the antibonding S 3*p* band [25]. After discharging, the peak maximum is decreased, and the

absorption edges are shifted to lower energies. These changes are reversible upon charging. During discharge, the sulfur is reduced and the S₂ dimer bond in the FeS₂ structure is broken. In this structure, the antibonding π^* state of the sulfur dimer has an energy corresponding to the Fermi level [25].

The absorption edges of the Fe *K*-edge XANES spectra were also analyzed to confirm the oxidation state of the iron atoms, as shown in Fig. 7. No peak shifts are observed at 7115 eV during discharging and charging. Therefore, the Fe 3*d* orbital hardly takes part in the redox reaction, which is in contrast with the results of the S *K*-edge XANES, while the Fe *K*-edge XANES spectra show an isosbestic point at ~7130 eV. The existence of the isosbestic point in the spectra indicates that two Fe compounds co-exist in the electrodes. In the conversion reaction, metallic iron is expected to be a product of the discharge reaction. If metallic iron are generated during discharging, the absorption edges of the Fe *K*-edge XANES at 7110 eV is change to resemble those of iron foil. However, there is no tendency for the pre-edge peaks at 7110 eV during discharging/charging, which indicates no iron phases in our experiment.

We discuss the discharge/charge reaction mechanisms of the FeS₂ in chloroaluminate ionic liquids. From the results of Fe and S *K*-edge XANES, S *K*-edge XANES spectra show a decrease in the peak intensity and lower energy shift, and Fe *K*-edge XANES spectra show no energy shift. These results indicate that the sulfur atoms play a significant role in the redox reaction. This is the same redox mechanism of the monovalent ion systems (such as Li and Na ion batteries) [15, 19]. From the results of the XRD, low crystalline FeS is confirmed after discharging. The appearance of two Fe species in the electrodes are also confirmed by the isosbestic points in Fe *K*-edge XANES spectra. Moreover, this low crystalline nature is also explained by the Fe *K*-edge EXAFS (Fig. S5). Then, the reaction (3) is expected during discharging.

Therefore, the absorption edges of the S *K*-edge XANES peaks are fitted with the linear combination of the standard FeS₂, FeS, and Al₂S₃. Fitting results of the linear combination for the S *K*-edge XANES spectra of the certain state D in Fig. 4 are shown in Fig. S3. The FeS and Al₂S₃ are confirmed by S *K*-edge XANES. It has been reported that the Al₂S₃ are easily dissolved into the chloroaluminate ionic liquids [26]. The aluminum reacting with the FeS₂ phase is also checked by the difference of the quantities of the aluminum after discharging (E in Fig. 4.) and charging (I in Fig. 4.) from the results of the Al *K*-edge XANES (Fig. S4). The existence of the amorphous Al₂S₃ phase are indicated by the S *K*- and Al *K*-edge XANES. These obtained phases are reversed to the original FeS₂ phase from the results of the XRD and S and Fe *K*-edge XAS measurements.

Finally, we propose schematic reaction models in Fig. 8. The FeS₂ pyrite structure contains dumbbell-shaped disulfide ions, which tend to react with aluminum ions. This reaction dominantly occurs in the vicinity of the surface through the reduction of sulfur (that is, $\text{S}_2^{2-} \rightleftharpoons 2\text{S}^{2-}$). This redox mechanism is the same phenomenon as the case of the monovalent ion carrier [15, 19]. As sulfur is reduced, the original FeS₂ phase transforms into FeS, in conjunction with the formation of amorphous Al₂S₃ phases. FeS and Al₂S₃ phases revert to FeS₂ after charging, which indicates that the reaction is reversible. At 55°C, the dissolving nature of the sulfide is the main problem to improve their performance as a cathode material for an aluminum rechargeable battery.

In the monovalent ion battery system, initially, the FeS₂ phase is transformed to M₂FeS₂ (M = Li or Na) through reaction Equation (1). Although this layered phase can be obtained at low rate conditions in the lithium ion battery case, no layered phase is observed in the aluminum battery case. Transformations for the layered phase need diffusion of the guest ion into the bulk FeS₂ [13]. The aluminum ion exhibits a high charge density and strong electronic

interactions in the host structure. These properties do not only effect the slow diffusivity of the ions into the bulk structure, but also the instability of the layered phase inserted by the aluminum ion. As a result of the reaction with the aluminum ion, FeS₂ transforms to the FeS phase and Al₂S₃ phase, as in a conversion reaction.

4. Conclusions

We investigated the discharge/charge reaction mechanisms of the FeS₂ as a cathode material for aluminum rechargeable battery systems incorporating ionic liquids. XRD and XAS measurements were conducted to determine the reaction mechanism of the FeS₂ pyrite phase reacting with aluminum ion. XRD and S, Fe, and Al *K*-edge XANES spectra show that the pristine FeS₂ transforms into low crystalline FeS and amorphous Al₂S₃, and the S 3*p* orbitals dominantly contribute to the charge compensation process during discharging/charging. Transformed phases are reversed to FeS₂ during the charging process. The products of the reaction are different from the monovalent ion battery case.

For practical application of Al/FeS₂ battery, this battery was suffer from the low cell voltage, and the poor cycle stability due to the dissolution of sulfides. The voltage differences between Al/FeS₂ and Li/FeS₂ batteries are corresponded with the difference of the potentials of anode metals. The theoretical energy density of Al/FeS₂ battery (462.7 Wh kg⁻¹, and 1939.0 Wh L⁻¹) was smaller than Li/FeS₂ battery (1337.0 Wh kg⁻¹, and 2602.7Wh L⁻¹) [27]. However, we believe that Al/FeS₂ battery has the merit for the low cost, and safety because of abundance, and high melting points of aluminum anode. The poor cycle stability in FeS₂ cathodes is caused by the dissolution of sulfides, which also becomes a problem in a lithium sulfur battery. In order to overcome the problem of sulfur compounds, several methods have been proposed [28-36]. For examples, the complex with carbon material is one of the

interesting methods for the practical application of sulfide compounds cathode materials [29, 31, 33]. Therefore, we believe the improvement of the cycle stability of Al/FeS₂ battery can be possible.

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Appendix A. Supplementary data

Electronic Supplementary Information (ESI) available: The secondary particle distributions of milling powders (Fig. S1), Chemical composition of FeS₂ powder for the charge-discharge measurements (Table S1), Discharge curves of the various ball milled sample (Fig.S2), , linear combination fit results of the S *K*-edge XANES spectra (Fig.S3), Al *K*-edge XANES spectra of the discharging and charging (Fig.S4), Fe *K*-edge EXAFS spectra of discharged/charged samples. (Fig.S5)

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Figure caption

Fig. 1. SEM images of FeS₂ particles: pristine, ball milled for 12 hours, ball milled for 24 hours, and ball milled for 48 hours.

Fig. 2. XRD patterns for FeS₂ powders: pristine, ball milled for 12 hours, ball milled for 24 hours, and ball milled for 48 hours. The inset diameters are the crystallite sizes calculated from the Scheerer equation from the results of the XRD.

Fig. 3. Dependence of the initial discharge capacity on crystallite size. Galvanostatic measurements were performed at 55°C and 8.94 mA g⁻¹.

Fig. 4. Discharge-charge curves of the FeS₂ milled for 24 hours. Galvanostatic measurements were performed at 55°C and 8.94 mA g⁻¹. The circles show the measurement points for the XRD and XAS measurements.

Fig. 5. *ex situ* XRD patterns of the ball-milled FeS₂ powder (A) and the electrodes charged to 350 mAh g⁻¹ (I) and discharged to 600 mAh g⁻¹ (E).

Fig. 6. S *K*-edge XANES spectra measured in the PFY mode for (a) discharged FeS₂ electrodes and (b) charged FeS₂ electrodes. The measurement points are indicated in Fig. 4.

Fig. 7. Fe *K*-edge XANES spectra of (a) discharged FeS₂ electrodes, and (b) charged FeS₂ electrodes. The measurement points are indicated in Fig. 4.

Fig. 8. Charge-discharge reaction model of FeS₂ with aluminum ions in an AlCl₃–EMIC ionic liquid at 55°C.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8