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FePS₃ electrodes in all-solid-state lithium secondary batteries using sulfide-based solid electrolytes

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Abstract

In bulk-type all-solid-state lithium batteries with sulfide-based solid electrolytes, composite electrodes, in which an active material, a solid electrolyte, and a conductive additive are mixed, have been used to enhance lithium ion diffusion and electronic conductivity. However, the addition of electrolytes and electron-conductive additives to the composite electrodes decreases the amount of active materials in the batteries. In the present study, FePS₃ is employed as the electrode in an all-solid-state lithium secondary battery, without mixing the solid electrolytes and conductive additives. The all-solid-state cell using the FePS₃ electrode exhibits reversible charge-discharge behavior for more than 30 cycles under a constant current density of 0.13 mA cm⁻² at room temperature. The discharge capacity of the cell is 107 mAh g⁻¹ at the 30th cycle. This behavior is comparable to that of a cell with an electrode including a solid electrolyte and/or a conductive additive, indicating that the FePS₃ electrode has sufficient paths of lithium ions and of electron conduction. These results suggest that FePS₃ is an attractive iron-based electrode for an all-solid-state battery using a sulfide-based solid electrolyte.

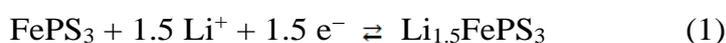
1. Introduction

Lithium secondary batteries that utilize organic liquid electrolytes are widely used as power sources for mobile devices and electric vehicles because of their light weight, high operating voltage, and long cycle life. However, there are safety concerns arising from the use of flammable organic liquid electrolytes in lithium secondary batteries. Consequently, all-solid-state lithium secondary batteries using non-flammable solid electrolytes have attracted much attention as next-generation power sources [1-4]. In these studies, sulfide-based solid electrolytes were investigated because they are known to exhibit high lithium ion conductivities (up to $\sim 10^{-2}$ S cm⁻¹), low grain boundary resistances, and a wide potential window [5-9].

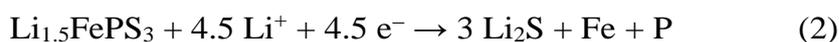
One of the key materials for all-solid-state batteries is the cathode active material. Various cathode active materials (LiCoO₂ [6,10], Li₂S [11], S [12,13], etc.) have been previously studied. However, most of the cathode active materials need to be combined with solid electrolytes and conductive additives to enhance lithium ion diffusion and electronic conductivity in the cathode. There are limited number of reports on electrodes without the added solid electrolytes and conductive additives [14]. Thus, it is imperative to develop a process for preparing composite materials that incorporate sufficient paths of lithium ions and of electron conduction. However, it is difficult to fabricate such composite materials. Moreover, the addition of solid

electrolytes and conductive additives leads to a decrease in the amount of the active materials in the cells. Thus, active materials with high lithium ion diffusion and high electronic conductivity are desired.

Because of the abundance of iron in the earth's crust, Fe-based materials (e.g., LiFePO₄[15], FeS[16,17], FeS₂[18], and FePS₃[19]) have been investigated as cathode active materials for lithium batteries. In this study, we focus on FePS₃, which has an electronic conductivity of $\sim 10^{-5}$ S cm⁻¹ [20], and a layered structure that is advantageous for high lithium ion diffusion. Indeed, the theoretical reversible capacity of FePS₃ is 220 mAh g⁻¹ in cells with an organic electrolyte, which corresponds to the insertion of 1.5 mol of Li⁺ per Fe, as shown in reaction (1):



Moreover, FePS₃ undergoes an irreversible conversion reaction with lithium in an organic electrolyte [19]. The theoretical irreversible capacity of FePS₃ is 1318 mAh g⁻¹, which corresponds to the reaction of 9.0 mol of Li⁺ per Fe, as shown in reactions (2) and (3).



Recently, we have reported NiPS₃, which is isostructural with FePS₃, as an electrode active material in an all-solid-state battery using a sulfide-based solid

electrolyte [21]. The battery using the composite electrode consisting of a NiPS₃ active material, a solid electrolyte, and a conductive additive exhibits a reversible capacity of approximately 80 mAh g⁻¹ at the 30th cycle. Both the active materials and the solid electrolytes comprise phosphorus and sulfur, and this similarity in composition may reduce degradation during the charge/discharge cycles. The higher electron conductivity of FePS₃ relative to NiPS₃ [20] and the abundance of iron motivated us to explore the potential of FePS₃ as a new active material in sulfide-based all-solid-state batteries.

In this study, all-solid-state lithium secondary batteries with an FePS₃ electrode were assembled, and the charge-discharge performance of the cells were investigated. We confirmed that these batteries show stable charge-discharge behavior even without the addition of solid electrolytes and conductive additives. This behavior is comparable to that of the cell with an electrode consisting of an added solid electrolyte and/or conductive additive.

2. Experimental

An FePS₃ chunk was synthesized from elemental iron powder (Wako Chemical, 99.9%), red phosphorus (Kanto Chemical, 98.0%), and sulfur (Kanto Chemical, 99.5%) [19]. Red phosphorus and sulfur were used in approximately 15 wt% excess of the stoichiometric amounts. The powders were mixed using an agate mortar and pestle, and the mixture was

heated in an evacuated quartz tube at 998 K for 24 h. To remove excess red phosphorus and sulfur, the obtained sample was heated at 598 K for 20 min, under vacuum. The product was ground in an agate mortar, and then, particles larger than 100 μm were removed using a 100 μm sieve. X-ray diffraction (XRD) patterns of the FePS_3 powders were recorded using an X-ray diffractometer (MiniFlex600, Rigaku) with $\text{CuK}\alpha$ radiation source. The morphologies and compositions of the obtained FePS_3 powders were investigated by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX; JSM-6510 LA, JEOL).

Laboratory-scale, all-solid-state batteries were fabricated using FePS_3 as the cathode active material, $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol%) glassy powder as the solid electrolyte, and a Li-In sheet as the anode active material [22]. $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol%) glassy powders were prepared via mechanical milling of a mixture of reagent-grade Li_2S (Mitsuwa Chemical, 99.9%) and P_2S_5 (Aldrich, 99%) powders [23] in a dry Ar atmosphere. Cathode electrodes were prepared using only FePS_3 , or mixtures of FePS_3 with $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass or vapor-grown carbon fibers (VGCF, Showa Denko), according to the composition and weight data shown in Table 1.

These electrodes and the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass (120 mg) were pressed under 360 MPa in a polycarbonate tube ($\phi=10$ mm) to obtain a bilayer pellet. The Li-In alloy foil was pressed under 120 MPa on the prepared bilayer pellet. The obtained three-layer pellet was sandwiched between two stainless-steel disks serving as the current collectors. The

electrochemical performance of the cells was investigated under a constant current density of 0.13 mA cm^{-2} and 0.64 mA cm^{-2} at room temperature, using a charge-discharge measuring device (Scribner Associates, 580 battery-type system). During all the charging processes, a constant current density of 0.13 mA cm^{-2} was used for the measurements. All the processes were performed under a dry Ar atmosphere.

3. Results and Discussion

Figure 1 shows the XRD pattern of the FePS_3 powder synthesized from elemental iron powder, red phosphorus, and sulfur. This XRD pattern is indexed to FePS_3 (ICDD#633087).

Figure 2 presents the SEM image of the prepared FePS_3 powders after grinding and passing through a $100 \mu\text{m}$ sieve. The particle size of the FePS_3 powders was approximately $10 \mu\text{m}$. The molar ratio of the elements in FePS_3 , semi-quantitatively estimated by EDX, was found to be $\text{Fe:P:S} = 1:1:3$.

Figure 3 shows the charge-discharge profiles (a) and cycle performance (b) of the all-solid state cell using the FePS_3 electrode (10 mg) without the solid electrolytes and conductive additives (Cell A). The charge-discharge performance was measured under 0.13 mA cm^{-2} at room temperature. The measured open-circuit voltage (OCV) of the cell was approximately 1.3 V (vs. Li-In). The insertion reaction ranging from 0 to 1.5 mol Li^+ per Fe has been reported to be reversible in a cell using an organic electrolyte [19]. Hence, the cell was initially discharged to a capacity of 220 mAh g^{-1} , corresponding to the insertion

of 1.5 mol Li⁺ per unit FePS₃. Subsequently, the cell was charged to 2.2 V (vs. Li-In). From the second cycle onwards, the cut-off voltage was set to 0.91 V (vs. Li-In) for discharging and 2.2 V (vs. Li-In) for charging. As is evident from Figure 3 (a), the cell showed a first charge capacity of 171 mAh g⁻¹, corresponding to the extraction of 1.2 mol Li⁺ per Fe. The cell exhibited reversible charge-discharge behavior for 30 cycles. A discharge plateau was observed at approximately 0.9 V (vs. Li-In) during the first cycle, similar to the case of an FePS₃ cell using liquid electrolytes [19]. From the second cycle onwards, the plateau disappeared and the discharge voltage increased. This behavior, analogous to that of a cell based on isostructural NiPS₃ [21], is attributed to the decrease in crystallinity [24]. Thus, this voltage change of FePS₃ may be ascribed to the decrease in the crystallinity of FePS₃ during discharging. As seen in Figure 3 (b), the cell exhibited reversible capacities of more than 107 mAh g⁻¹ for 30 cycles, corresponding to the insertion of about 0.7 mol Li⁺ per Fe. These results reveal that the cell with the FePS₃ electrode can be operated without the addition of solid electrolytes and conductive additives.

Figure 4 shows the charge-discharge curves of the all-solid-state cell using a thick FePS₃ electrode layer (30 mg), without any solid electrolytes or conductive additives (Cell B). The charge-discharge performance of Cell B was measured under 0.13 mA cm⁻² at room temperature. Cell B exhibited an initial charge capacity of 156 mAh g⁻¹, corresponding to the extraction of 1.1 mol Li⁺ per Fe. The capacity per unit volume was calculated to be

483.6 mAh cm⁻³ using the theoretical density of FePS₃ = 3.1 g cm⁻³ from ICSD #633087.

The discharge capacity subsequently decreased to 93 mAh g⁻¹ at the 10th cycle. The cell using a thick FePS₃ electrode layer also showed reversible charge-discharge behavior, indicating that the cell capacity can be increased by increasing the amount of FePS₃ used for fabricating the electrode.

The charge-discharge behavior of the FePS₃ electrode mixed with different amounts of solid electrolytes was investigated to confirm the rather high lithium ion diffusion in this electrode. Figure 5 shows the first and second charge-discharge curves of Cell A and those of the cells with 10 and 20 wt% of the solid electrolyte (Cell C and Cell D, respectively) under a constant current density of 0.13 mA cm⁻² at room temperature. Although these cells exhibited a slightly different charge behavior near 2.1 V (vs. Li-In) during the first and second charging, the charge-discharge behavior was not significantly affected by the addition of solid electrolytes. These comparable charge-discharge behaviors of Cell A, C, and D suggest that the FePS₃ electrode has adequate lithium ion conduction.

Figure 6 displays the first and second charge-discharge curves of Cell A, and the curves for the cells with 2 and 4 wt% of the conductive additives (Cell E and Cell F, respectively), under a constant current density of 0.13 mA cm⁻² at room temperature. The charge-discharge behavior did not change significantly during the first and second cycles. This suggests that the FePS₃ electrode has sufficient electron conducting paths to enable charge-discharge under the current density of 0.13 mA cm⁻².

Figure 7 shows the rate performance of Cells A, C, and E. The cells showed discharge capacities ranging from 138 mAh g⁻¹ to 152 mAh g⁻¹ at the 5th cycle under a current density of 0.13 mA cm⁻². Further, the cells exhibited discharge capacities ranging from 82 mAh g⁻¹ to 95 mAh g⁻¹ at the 10th cycle under a current density of 0.64 mA cm⁻². The discharge capacities were not significantly changed by the addition of solid electrolytes and conductive additives under the current density of 0.64 mA cm⁻², suggesting that the FePS₃ electrodes show sufficient lithium ion and electron conducting paths even in the absence of solid electrolytes and conductive additives.

4. Conclusion

All-solid-state lithium secondary batteries using an FePS₃ electrode as the cathode layer and a sulfide-based solid electrolyte as the solid electrolyte layer were assembled. The batteries using the FePS₃ electrode (10 mg) without any solid electrolytes and conductive additives showed reversible charge-discharge behavior and a discharge capacity of 107 mAh g⁻¹ at the 30th cycle. This behavior is comparable to that of a cell with an electrode containing a solid electrolyte and/or conductive additive. These results suggest that FePS₃ electrodes without any solid electrolytes and conductive additives have adequate paths of lithium ions and electron conduction to show discharge behavior at 0.64 mA cm⁻². In addition, the battery using a thick FePS₃ electrode (30 mg) also exhibited the charge-discharge behavior, suggesting that the cell capacity can be increased by increasing

the amount of FePS₃ electrodes in all-solid-state cells. Therefore, FePS₃ is a promising candidate as an iron-based electrode without the need to use solid electrolytes and conductive additives in all-solid-state batteries using sulfide-based solid electrolytes.

Acknowledgements

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Figure and Table captions

Figure 1. XRD pattern of FePS₃ powders synthesized from elemental iron powders, red phosphorus, and sulfur.

Figure 2. SEM image of FePS₃ powders used for all-solid-state batteries.

Figure 3. (a) Charge-discharge curves and (b) cycle performance of the all-solid state cell using FePS₃ electrode (10 mg) without solid electrolytes and conductive additives (Cell A).

Figure 4. Charge-discharge curves of the all-solid state cell using FePS₃ electrode (30 mg)

without solid electrolytes and conductive additives (Cell B).

Figure 5. First and second charge-discharge curves of the all-solid state cells using FePS₃ electrodes mixing 0 wt% (Cell A : red solid line), 10 wt% (Cell C : blue dashed line) and 20 wt% (Cell D : green dashed-dotted line) of solid electrolytes.

Figure 6. First and second charge-discharge curves of the all-solid state cells using FePS₃ electrodes with mixing 0 wt% (Cell A : red solid line), 2 wt% (Cell E : dark blue dashed line) and 4 wt% (Cell F : purple dashed-dotted line) of conductive additives.

Figure 7. Rate performance of all-solid-state cells using the all-solid state cells using FePS₃ electrodes without solid electrolytes and conductive additives (Cell A : red circles ●), with 10 wt% of solid electrolytes (Cell C : blue diamonds ◆) and with 2 wt% of conductive additives (Cell E : dark blue squares ■) under a constant current density of 0.13 mA cm⁻² and 0.64 mA cm⁻².

Table 1. Composition and weight of the cathode

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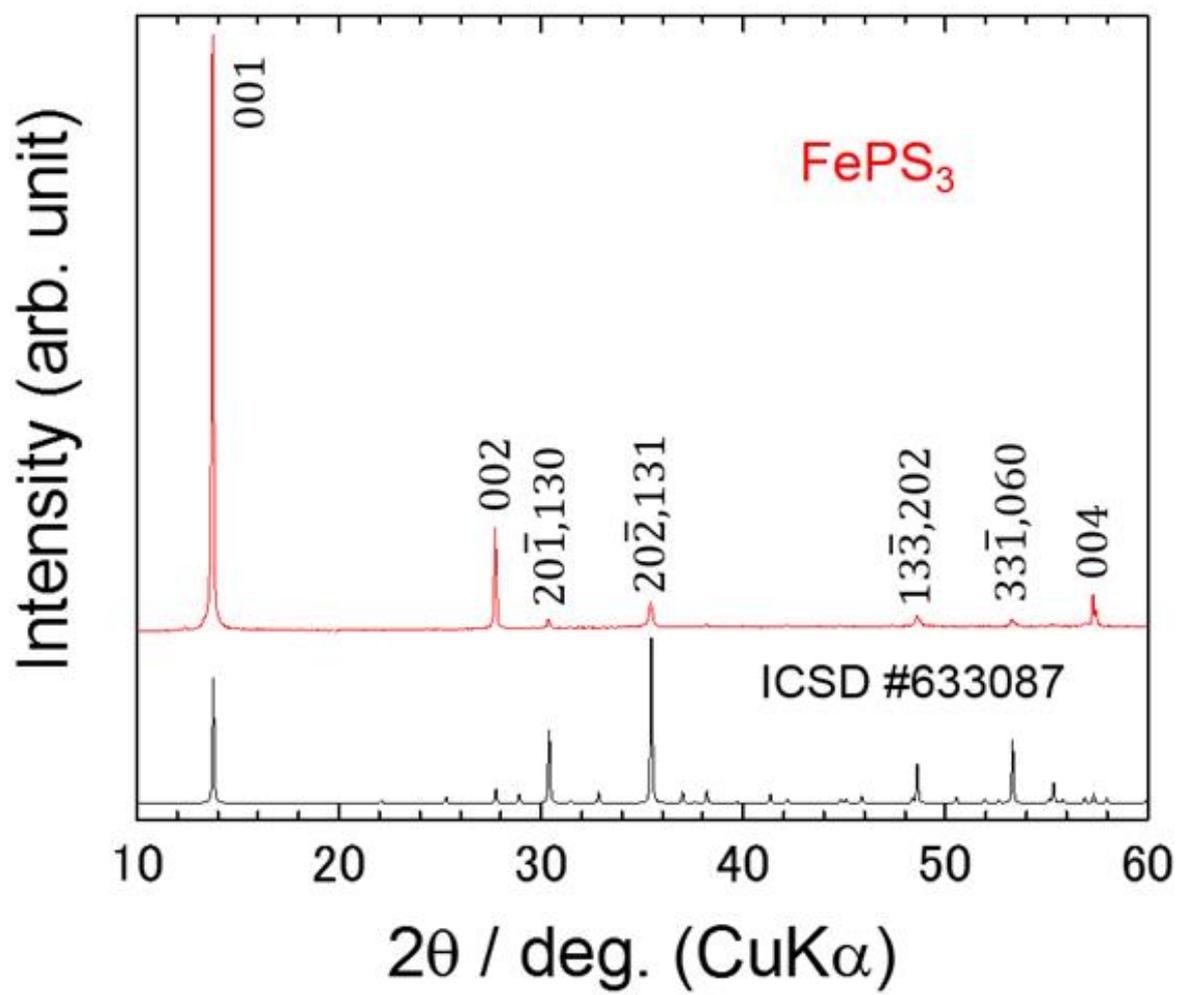


Figure 1

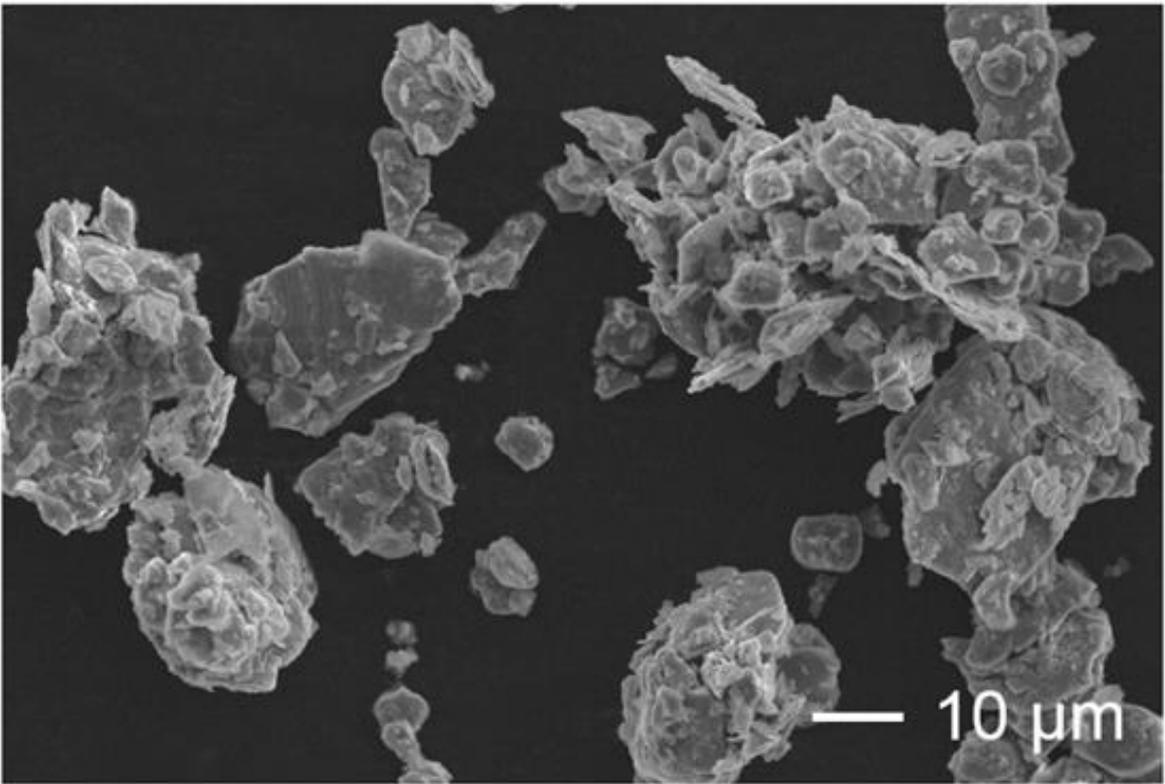


Figure 2

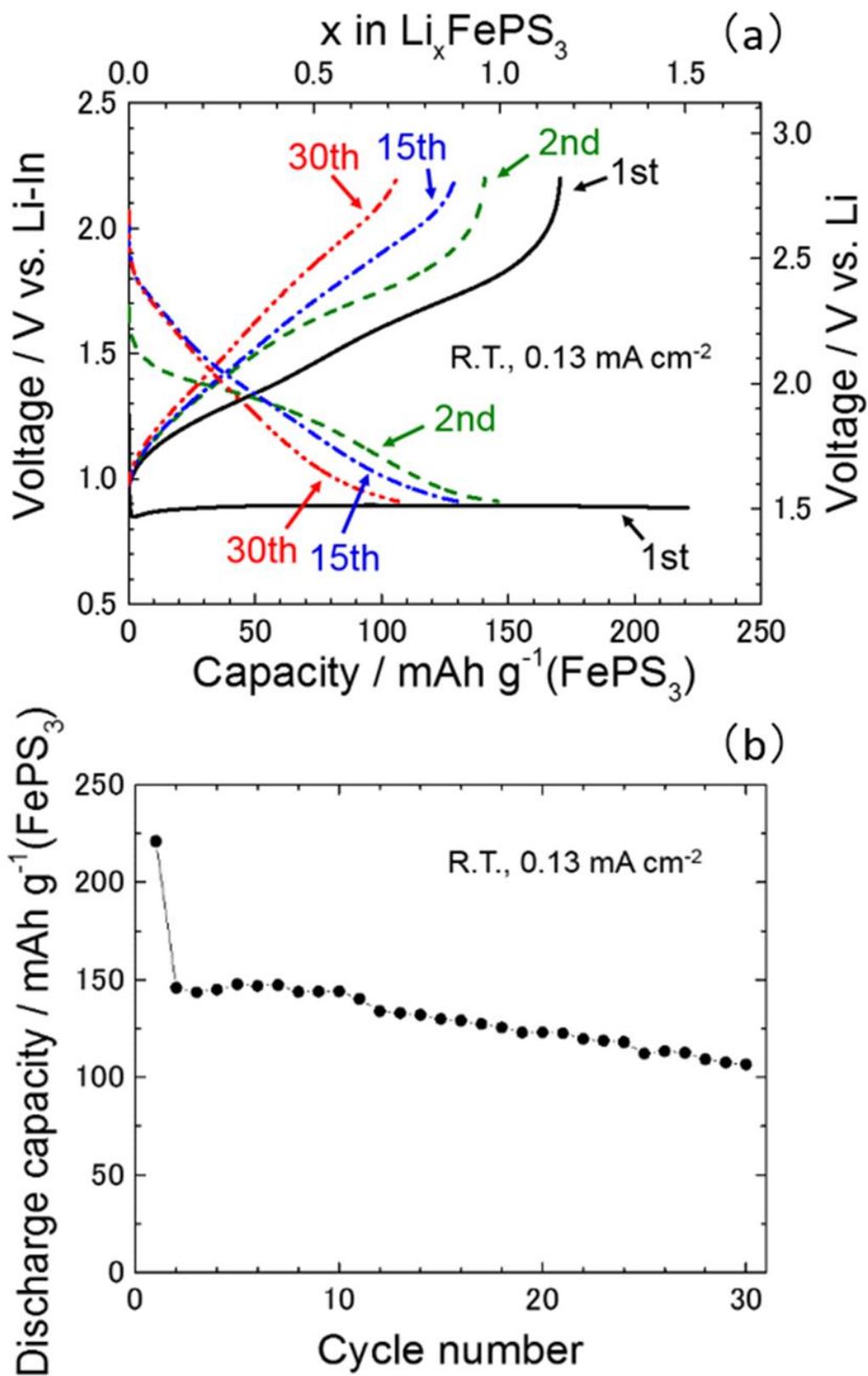


Figure 3

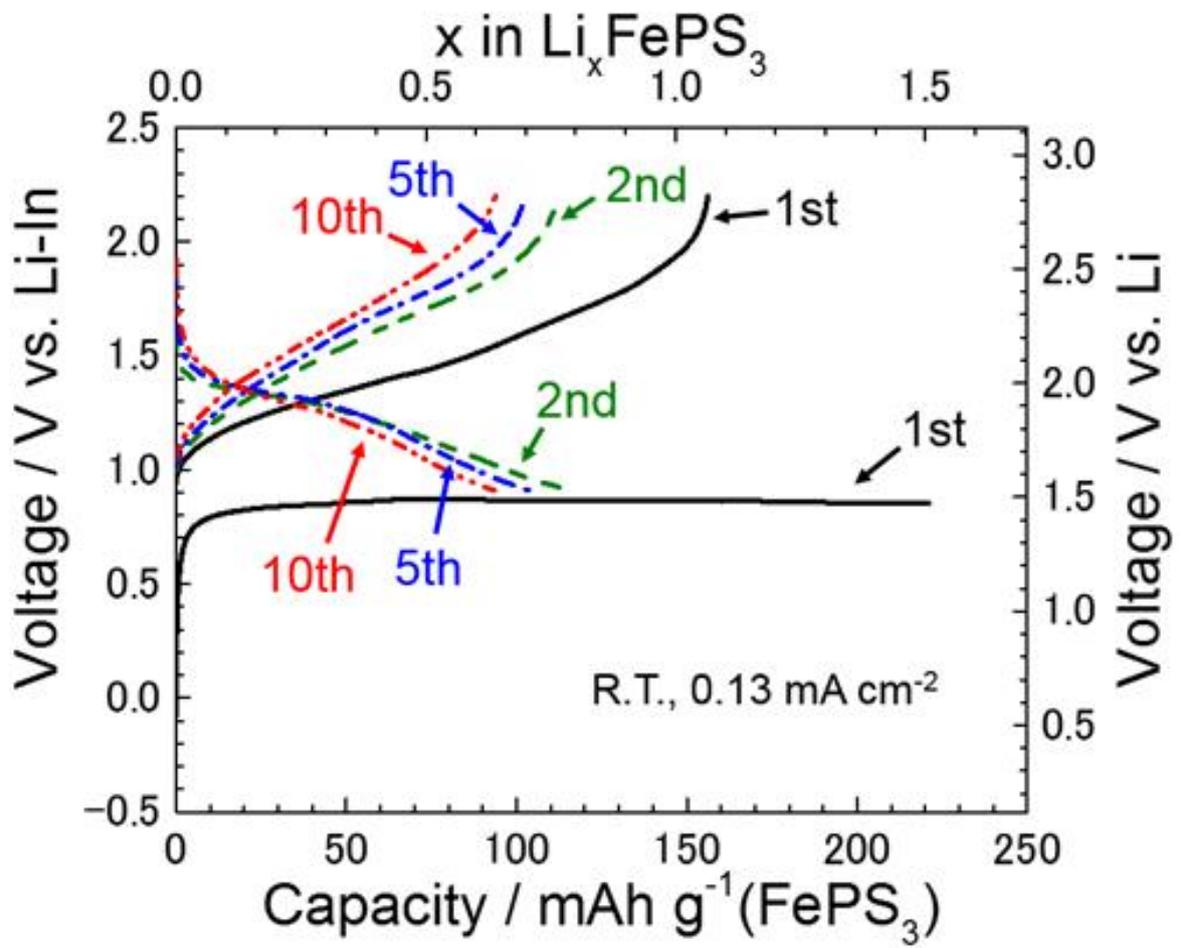


Figure 4

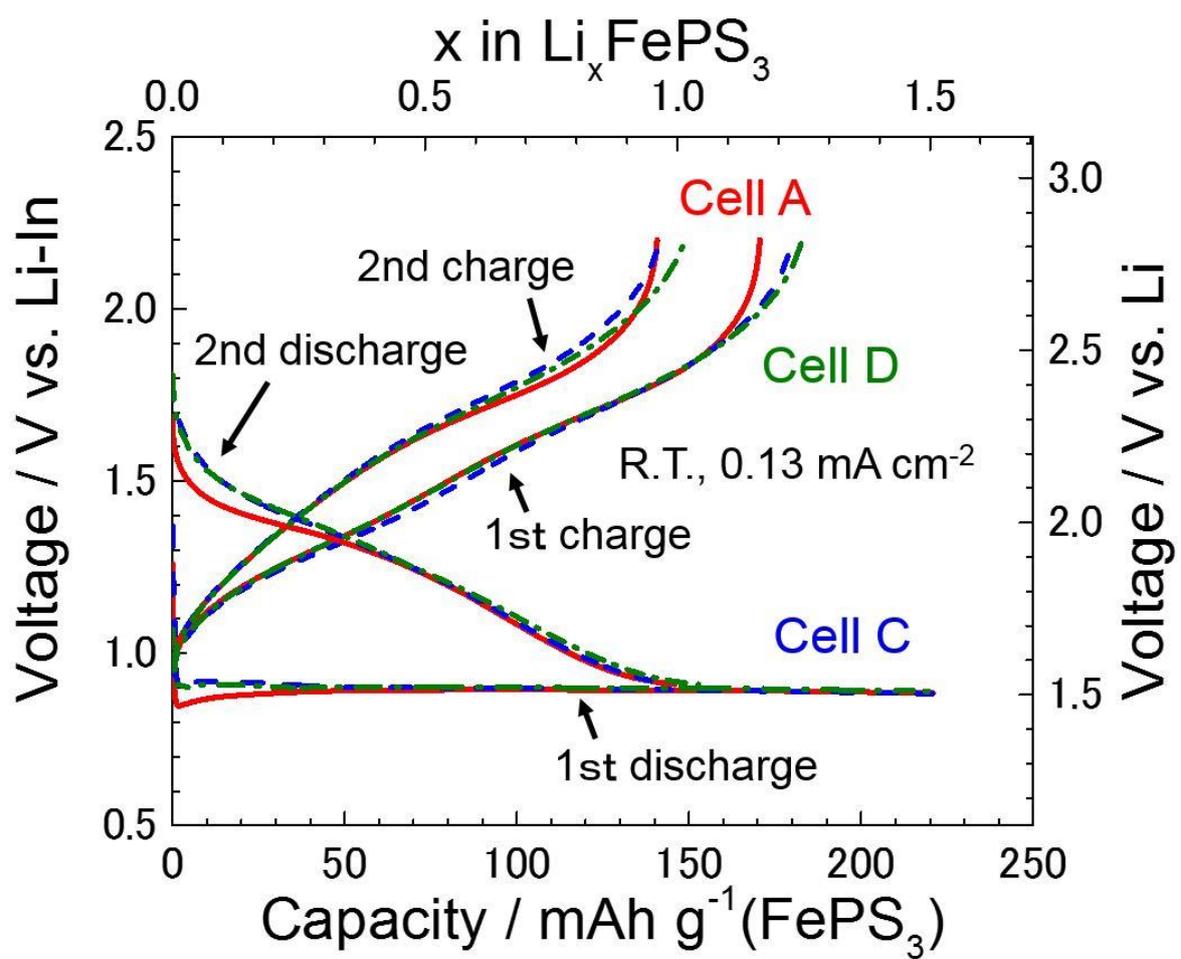


Figure 5

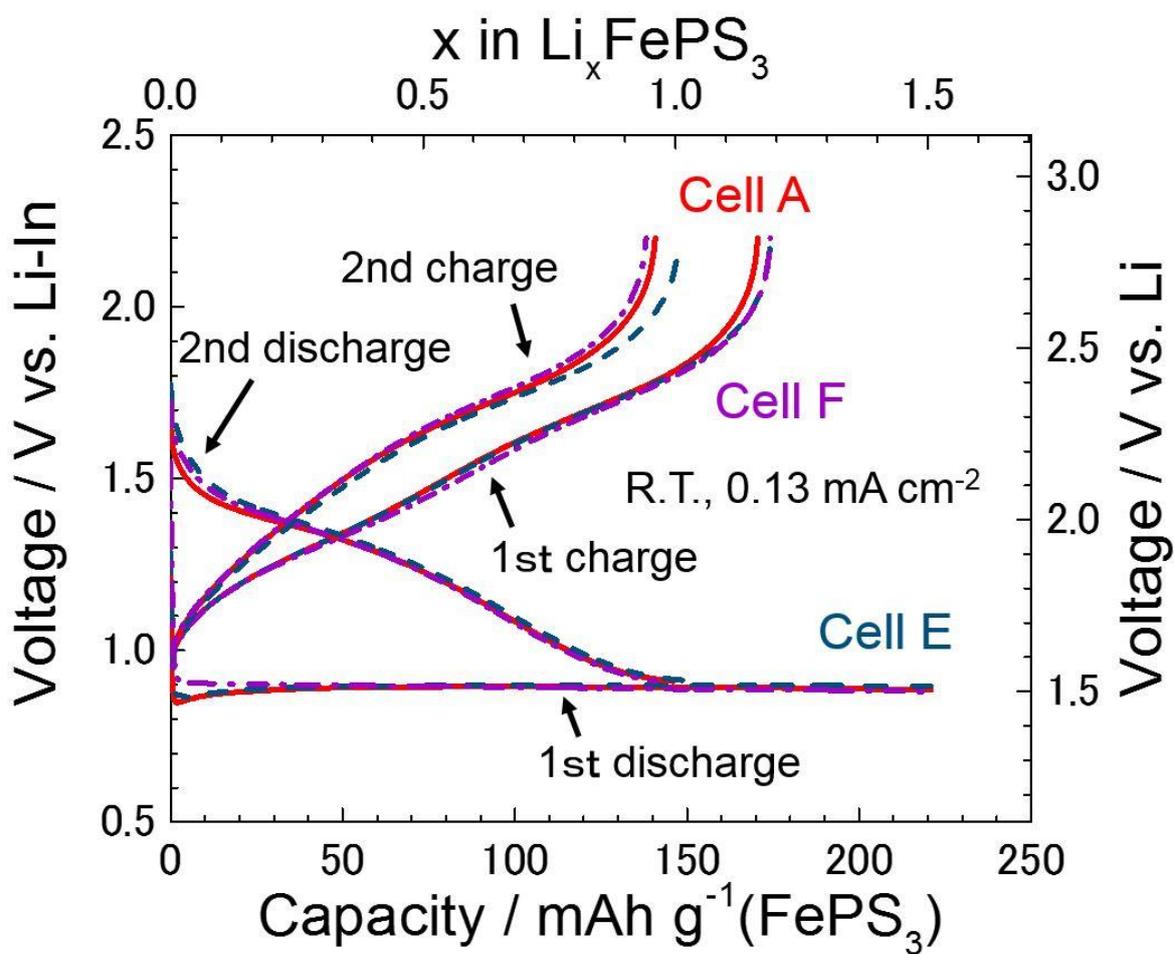


Figure 6

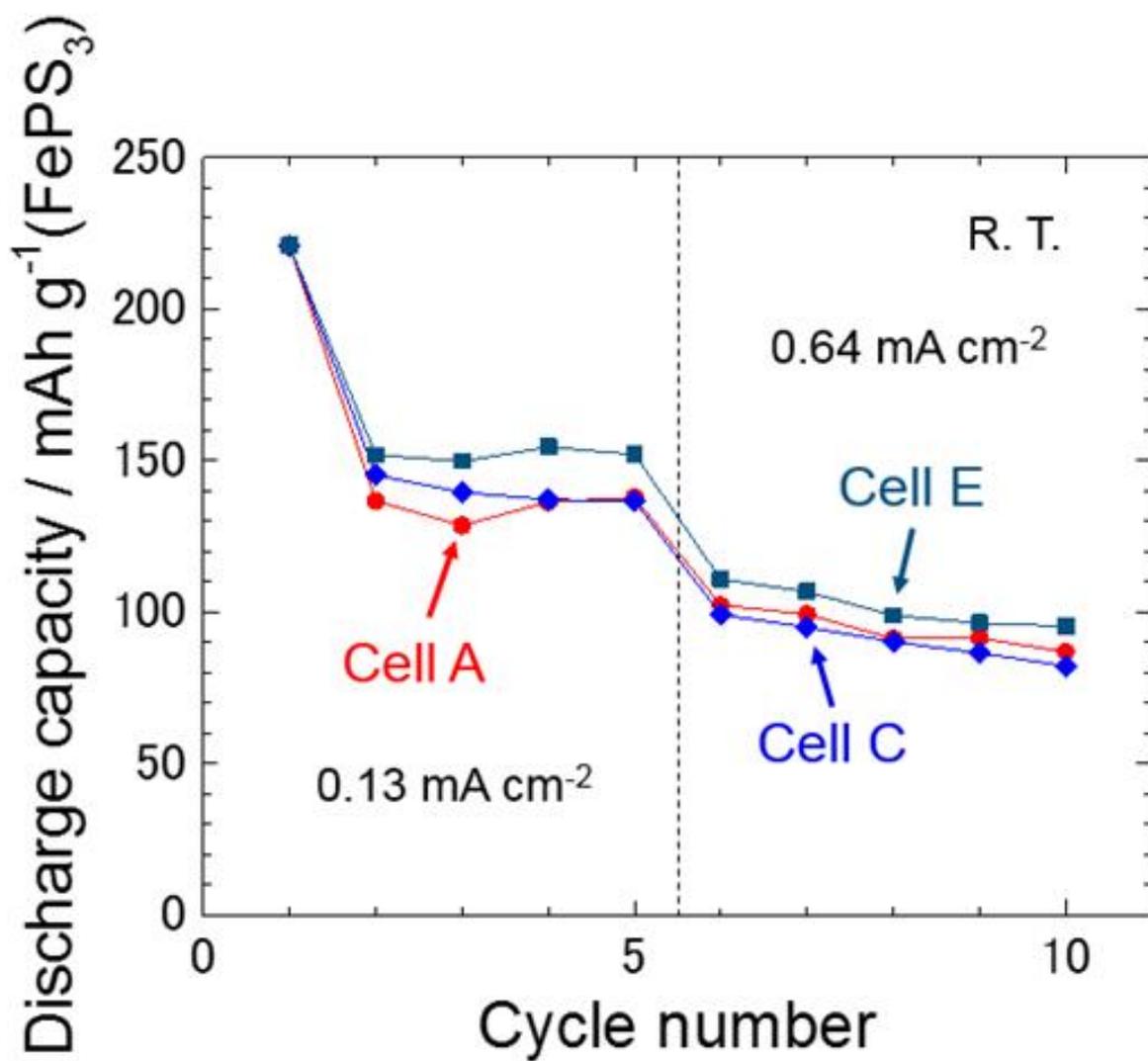


Figure 7

Table 1 Composition and weight of cathode

| | Cell composition of cathode FePS ₃ :SE:VGCF (wt. ratio) | Weight of cathode / mg |
|---|---|------------------------|
| A | 100:0:0 | 10 |
| B | 100:0:0 | 30 |
| C | 90:10:0 | 10 |
| D | 80:20:0 | 10 |
| E | 98: 0:2 | 10 |
| F | 96: 0:4 | 10 |

SE: 80Li₂S·20P₂S₅ glass slid electrolyte