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Research on highly reliable solid-state lithium batteries in NIRIM

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Abstract

Electrochemical reactions of LiVS_2 , Li_2FeS_4 , and Li_4FeS_2 were investigated by using a Li^+ ion conductive glass, $0.01\text{Li}_3\text{PO}_4\text{--}0.63\text{Li}_2\text{S--}0.36\text{SiS}_2$, as an electrolyte. The results showed remarkable differences from that in liquid electrolyte; the redox couples of both $\text{Li}_2\text{VS}_2/\text{LiVS}_2$ and $\text{LiVS}_2/\text{VS}_2$ were highly reversible, the reduction of Li_2FeS_2 led to the metastable phase Li_4FeS_2 that was completely reoxidized to the initial phase, and Li^+ ions were extracted from Li_2FeCl_4 without dissolution of the chloride itself. These improvements by using the solid electrolyte make a large choice of electrode materials. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solid-state battery; Lithium vanadium sulfide; Lithium iron sulfide; Lithium iron chloride

1. Introduction

Since “lithium ion battery” was developed early in 1990s, it has been expanding its market rapidly. In spite of a merit of its high energy, it involves a serious problem about safety because of the presence of flammable organic solvent in the electrolyte. The substitution of solid electrolyte for the organic one should be a fundamental solution to improve the reliability of conventional lithium batteries. Besides improvement of safety, a solid electrolyte may effectively suppress the side reactions that deteriorate battery performances. Liquid electrolyte in a conventional lithium battery consists of a supporting salt and a solvent; the salt dissociates into lithium ions and counter anions, and the solvent is usually a mixture of a few kinds of organic materials. The electrolyte is contacted with both highly oxidative cathode and reductive anode, namely placed in a rigorous environment, and hence it should be easy to be damaged. The battery is deteriorated even by the decomposition of one of them. Removing such species that do not directly participate in battery reaction will suppress side reactions and improve the reliability of the battery. Further, as for the solid electrolyte battery system, there are no mobile species other than Li^+ ions, which may take part in side reactions.

The suppression of side reactions is not only a key to improvement of cycle performance but also a large choice of electrode materials for lithium battery. We have investigated some compounds, which had been regarded as being inadequate for electrode materials, and found that they showed reversible electrochemical reaction by using a Li^+ ion conductive solid electrolyte, $0.01\text{Li}_3\text{PO}_4\text{--}0.63\text{Li}_2\text{S--}0.36\text{SiS}_2$ [1]. Three examples, LiVS_2 , Li_2FeS_2 , and Li_2FeCl_4 , will be presented in this paper.

2. Experimental

2.1. Synthesis of the materials

LiVS_2 was synthesized from Li_2S and V_2S_3 . A mixture of their stoichiometric amounts was pressed into a pellet and then sealed in an evacuated silica tube. The mixture was heated at 700°C for 48 h.

Li_2FeS_2 was synthesized from Li_2S and FeS . Their stoichiometric mixture was put in a vitreous carbon crucible and in vacuo sealed in a silica tube. The mixture was melted at 950°C for 5 h and then allowed to cool moderately to room temperature in a furnace.

As for Li_2FeCl_4 , LiCl and FeCl_2 were used as starting materials. The starting materials were mixed at the stoichiometric ratio. The mixture, pelletized and sealed in an evacuated pyrex tube, was heated at 450°C for 7 days.

The oxysulfide glass used as a solid electrolyte was prepared by the procedure described in [1].

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2.2. Measurements

The electrode property of LiVS_2 was examined using a working electrode that consisted of a mixture of the sulfide and the solid electrolyte in a weight ratio of 1:1. In–Li alloy was used as a counter electrode. The working electrode of 20 mg and the counter electrode, separated by a solid electrolyte layer, were pressed together in a tube made of polyethylene terephthalate.

The electrochemical cells were cycled in a voltage range of 0.8–2.3 and 0–1.2 V at a constant current of 50 μA to investigate reversibility in $\text{LiVS}_2/\text{VS}_2$ and $\text{Li}_2\text{VS}_2/\text{LiVS}_2$ reactions, respectively.

Electrochemical cells using Li_2FeS_2 instead of LiVS_2 were discharged and charged between -0.4 and 2.4 V. A cell was disassembled after reducing Li_2FeS_2 up to an electricity of $2e^-$ per Fe. The working electrode was sealed in an evacuated pyrex tube and annealed at 210°C for 30 days, and then another electrochemical cell was assembled with the annealed working electrode. The cell was charged to investigate electrochemical reaction of the annealed sample.

In the case of Li_2FeCl_4 , carbon material was added to the working electrode to make up for electronic conduction. Li_2FeCl_4 , solid electrolyte, and acetylene black were mixed in a weight ratio of 49:49:2. The cell was charged by intermittent current pulse (15 $\mu\text{A} \times 4$ h) followed by a rest period of 2 h. Quasi open circuit voltage (QOCV) of the cell was recorded at the end of the rest period.

3. Results and discussion

3.1. Lithium vanadium sulfide

Since electrochemical insertion of lithium to TiS_2 was discovered [2], transition metal dichalcogenides with layered structure have been of great interest as intercalation electrode materials for lithium batteries. LiVS_2 has a very similar structure to LiTiS_2 and has been studied as an electrode material in lithium batteries. Murphy and Carides reported that $\text{Li}_2\text{VS}_2/\text{LiVS}_2$ redox couple was reversible, but the further extraction of Li^+ ions from LiVS_2 to VS_2 rapidly led to deterioration [3]. A partial substitution of Fe for V suppressed the deterioration but made the redox between Li_2VS_2 and LiVS_2 irreversible [4].

Fig. 1 shows cycling performance of the In–Li/ LiVS_2 cell. The right vertical axis indicates the potential of Li_xVS_2 versus Li/Li^+ , and the upper horizontal axis a change of the lithium composition x in Li_xVS_2 , which is calculated from a quantity of electricity passed through the cell.

Capacity fading in the present $\text{LiVS}_2/\text{VS}_2$ and $\text{Li}_2\text{VS}_2/\text{LiVS}_2$ reactions specified as a solid electrolyte system was much smaller than that in a liquid electrolyte system given by Fig. 2 in [3] and Fig. 4 in [4]. Although the reason of poor reversibility in $\text{LiVS}_2/\text{VS}_2$ reaction was not made clear in their study, it may be the decomposition of VS_2 to a

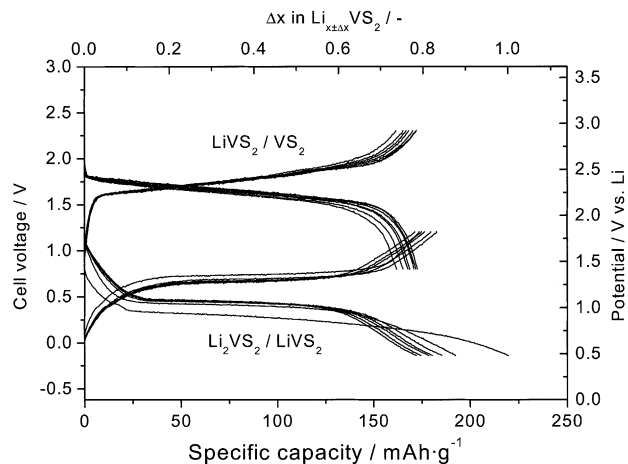


Fig. 1. Charge-discharge cycle of the cell, In–Li alloy/ LiVS_2 .

vanadium sulfide with lower valence by a proceeding reaction. This improved reversibility can be thought to have resulted from suppression of the proceeding reaction in the solid electrolyte system.

3.2. Lithium iron sulfide

FeS_2 has been studied as a cathode material in thermal cells. It showed two plateaus at 2.3 and 1.7 V versus Li/Li^+

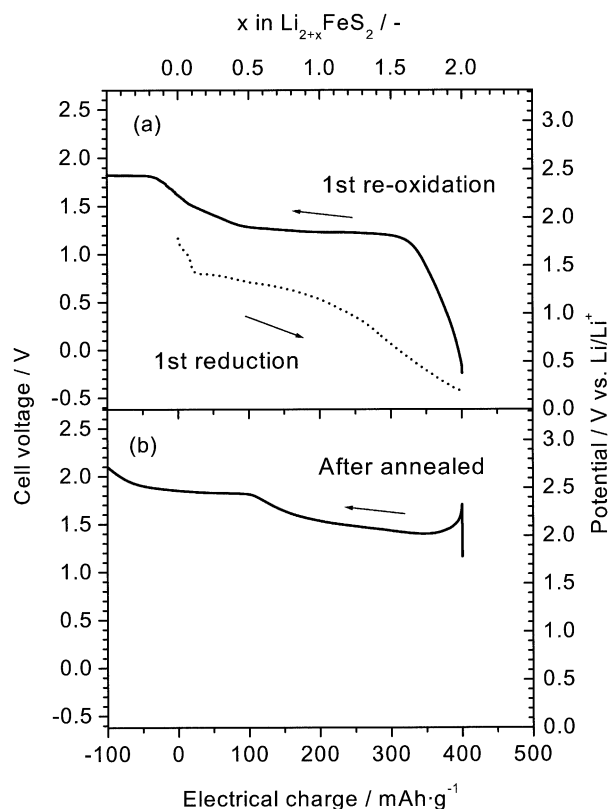


Fig. 2. Potential profile of Li_2FeS_2 : (a) Li_2FeS_2 was reduced to Li_4FeS_2 and then reoxidized after a rest period of 1 h; (b) potential profile of annealed Li_4FeS_2 .

during its reduction process [5]. It was reported that the former was based on the insertion of Li^+ ions to Li_xFeS_2 with a layer structure, and that the later led to formation of Fe metal, i.e. $\text{Li}_2\text{FeS}_2 + 2e^- + 2\text{Li}^+ \rightarrow 2\text{Li}_2\text{S} + \text{Fe}$. If Fe metal was formed, the later would be irreversible because Fe metal was thought to be electrochemically inactive in our experience. On the contrary, the actual reaction at the 1.7 V plateau was reversible [6]. It was considered that the electrochemical reduction of Li_2FeS_2 in the oxysulfide electrolyte resulted in the formation of metastable phase described as Li_4FeS_2 rather than $2\text{Li}_2\text{S} + \text{Fe}$.

Fig. 2(a) displays the voltage profile of Li_2FeS_2 during reduction and reoxidation in the oxysulfide electrolyte. The reoxidation profile consisted of two plateaus at 1.7 and 2.3 V. The higher plateau is ascribed to extraction of lithium from Li_2FeS_2 . On the lower, the reaction was thought to be based on the coming and going of Li^+ ions between two phases of Li_4FeS_2 and Li_2FeS_2 . As the plateaus were connected at $x = 0$, Li_4FeS_2 was completely reoxidized to Li_2FeS_2 . The $\text{Li}_4\text{FeS}_2/\text{Li}_2\text{FeS}_2$ reaction was reversible, and Li_4FeS_2 gave no evidence of formation of Fe metal on its powder X-ray diffraction (XRD) pattern. It is suggested, therefore, that Li_2FeS_2 reduced in the solid electrolyte led to a metastable phase with the apparent chemical composition Li_4FeS_2 .

If the metastable phase can be present, some changes in electrode reaction should be observed after annealing Li_4FeS_2 . The oxidation profile of Li_4FeS_2 after annealing at 210°C , shown in Fig. 2(b), consisted of two plateaus, but they were connected at $x = 0.5$. In the XRD pattern of the annealed sample, Fe metal and Li_2S were distinctly observed, i.e. metastable Li_4FeS_2 was considered to be partially decomposed to Fe metal and Li_2S . A small shift ($\Delta x < 0.5$) of the connecting point (compare Fig. 2(a) and (b)) suggests that only one-fourth of metastable Li_4FeS_2 was decomposed even by the long duration of annealing at 210°C . It is suggested that metastable Li_4FeS_2 may be so stable as to result in the reversible reaction at room temperature.

3.3. Lithium iron chloride

Lithium transition metal chlorides with spinel structure are known as Li^+ ion conductors. The chlorides have high ionic conductivities [7] and contain transition metal elements that contribute to redox reactions, and hence they are expected to be available for electrode materials in lithium batteries. However, their ionicities are so high that they are easily dissolved in a liquid electrolyte and cannot be used as electrode materials. Solid electrolytes are effective to suppress such dissolution of the chlorides and open up the possibility of chloride-electrodes. In this aspect, we investigated the electrochemical reaction of Li_2FeCl_4 in a solid electrolyte.

Fig. 3 indicates a potential profile of Li_2FeCl_4 in the oxidation process in the solid electrolyte. It showed a

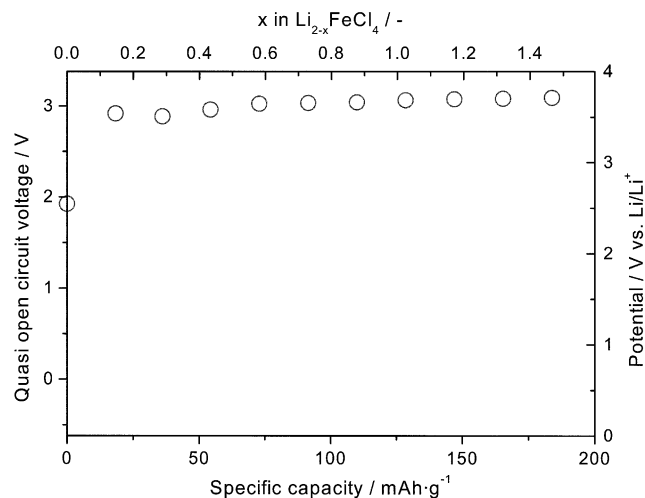


Fig. 3. Potential profile (QOCV) of Li_2FeCl_4 during the oxidation in the Li^+ ion conductive glass.

potential plateau at ca. 3.5 V versus Li/Li^+ . Our structural studies revealed that the reaction was based on the extraction of Li^+ ions from Li_2FeCl_4 , and more than 1.4 Li^+ ions were extracted from Li_2FeCl_4 . These results suggest that Li_2FeCl_4 may be available for electrode materials in lithium batteries.

4. Conclusions

We showed electrode properties of LiVS_2 , Li_2FeS_2 , and Li_2FeCl_4 in a solid electrolyte. Although they have not been regarded as reversible electrodes in lithium batteries with liquid electrolytes, they showed excellent electrode performance in the solid electrolyte system. These results are believed to be good examples demonstrating advantage of solid-state lithium batteries eloquently.

Acknowledgements

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