Potassiation and Depotassiation Properties of Sn₄P₃ Electrode in an Ionic-Liquid Electrolyte

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1. Introduction

Toward building a sustainable society, there is an increased demand for rechargeable alkali-metal-ion batteries with a high energy density, long cycle life, and adequate safety. Li-ion battery (LIB) has been commercially utilized due to the advantage of the lowest standard electrode potential among alkali metals and the lightest atomic weight. However, the abundance of lithium in the Earth’s crust is only 20 ppm, and lithium metal reserve is unevenly distributed in South America.1 Thus, Na-ion battery (NIB) attracts attention because of the second lightest atomic weight among alkali metals, abundant resources, and nontoxicity. Many researchers have considered effort on the development of active materials for NIB.2,3 We have also synthesized various active materials for negative electrodes in NIB.4,5 Among them, Sn₄P₃ electrode has exhibited superior sodiation/desodiation properties in a pyrolydinium-based ionic-liquid electrolyte.4

It was reported that a Sn₄P₃/C electrode showed a reversible capacity of 385 mA h g⁻¹ at 50 mA g⁻¹ in an organic-liquid electrolyte of 0.8 mol dm⁻³ (M) KPF₆ dissolved in ethylene carbonate (EC) + diethyl carbonate (DEC) and maintained the capacity up to 40 cycles.6 The theoretical capacity of the Sn₄P₃ electrode is 802 mA h g⁻¹ when K₃P and K₅Sn phases are formed in the charge process.7,8 Assuming that a KSn phase is formed instead of K₂Sn, the theoretical capacity is estimated to be 614 mA h g⁻¹. K-ion battery (KIB) is attractive as a next-generation rechargeable battery because the standard electrode potential of potassium is −2.94 V vs. standard hydrogen electrode (SHE) in water at 298 K, close to lithium (−3.04 V vs. SHE). Interestingly, the standard electrode potential of potassium is lower than that of lithium in some organic-liquid electrolytes including propylene carbonate and EC+DEC.9,10 In molten alkali bis(fluorosulfonyl)amide at intermediate temperature, the similar tendency is indicated.11 Therefore, KIB is worth investigating as a high energy density rechargeable battery.

Ignition risk increases with an increase in the atomic number of alkali metals; potassium intensely reacts with moisture. The improvement of KIB safety is absolutely essential for its commercialization. As a safe electrolyte, ionic liquids are potential candidates as alternatives to flammable carbonate-based organic-liquid electrolytes because of their superior physicochemical properties, such as nonflammability and wide electrochemical windows.12 We have demonstrated that the cells with Si-based electrodes for LIB delivered not only high safety but also excellent electrochemical performance in ionic-liquid electrolytes compared to that in usual organic-liquid electrolytes.13,14 This study explored the applicability of an ionic-liquid electrolyte to the Sn₄P₃ negative electrode for KIB to improve the electrochemical performance and safety of the electrode.

2. Experimental

Sn₄P₃ powder was synthesized by a mechanical alloying (MA) method. Synthesis procedure and characterization were described in our previous report.4 A Sn₄P₃ electrode was fabricated by a slurry coating method. The synthesized active material powder of Sn₄P₃ was mixed with a conductive agent of acetylene black (AB) and a binder of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR). The weight ratio of Sn₄P₃/AB/CMC/SBR was 70/15/10/5 wt.%. Deionized water was used as a dispersing agent. The prepared slurry was pasted on a Cu current collector and was dried to form active material layer (120°C). The mass loading and film thickness of active material layer were about 0.89 mg cm⁻² and 15 µm, respectively. 2032-type coin cell was assembled in an Ar-filled glove box with a dew point below −90°C and an oxygen content less than 1 ppm. The Sn₄P₃ slurry electrode, potassium metal sheet, and a glass fiber filter (Whatman GF/A) was used as the working electrode, the counter electrode, and the separator, respectively. We used an ionic-liquid electrolyte comprised of potassium bis(fluorosulfonyl)amide (KFSA) dissolved in N-methyl-
formation. At 0.2 V, the potassiation reaction of Sn₄P₃ should occur.

Concentrative potassiation/depotassiation reactions occur on the thinner parts of the electrode surface, preventing the K⁺ storage, as we have demonstrated for Si negative-electrode in LIB. Hence, local change in the volume of Sn₄P₃ occurs, which leads to disintegration of the active material layer and rapid capacity fading. By contrast, in the ionic-liquid electrolyte, a uniform and thin surface film should be formed and K⁺ is homogeneously stored on the entire electrode surface, preventing the occurrence of local stress. Thus, severe disintegration of Sn₄P₃ electrode is suppressed, which provides excellent performance of the Sn₄P₃ electrode. In addition, KFSA salt should support good cyclability for the electrode. Although the first Coulombic efficiency is only 66.7%, the second efficiency reaches 98.2%. Higher efficiency of 99.8% is also confirmed at the 20th cycle. High Coulombic efficiency after the second cycle is characteristic of the combination of Sn₄P₃ electrode and Py13-FSA ionic-liquid electrolyte.

Figure 2 shows cycling performance of the Sn₄P₃ electrode in the ionic-liquid electrolyte. The electrode exhibits initial reversible capacity of ca. 400 mAh g⁻¹, which is more than 1.5 times higher than that of a graphite-based electrode. Additionally, the Sn₄P₃ electrode maintains a discharge capacity of 365 mAh g⁻¹ over 100 cycles; no degradation of the cycling performance occurs up to the 100th cycle in the ionic-liquid electrolyte of KFSA/Py13-FSA (20/80 mol%). While the initial capacity of the Sn₄P₃ electrode in an organic-liquid electrolyte of 0.8 M KPF₆/EC+DEC was almost the same as that in the ionic-liquid electrolyte, the capacity faded at around the 40th cycle in the organic-liquid electrolyte.

The difference in cycling performance should be attributed to properties of surface film formed on the Sn₄P₃ electrode in each electrolyte. In the organic-liquid electrolyte, a surface film with uneven thicknesses forms through reductive decomposition of the electrolyte. Concentrative potassiation/depotassiation reactions occur on the thinner parts of the film because the thicker parts prevent the K⁺ storage, as we have demonstrated for Si negative-electrode in LIB. Hence, local change in the volume of Sn₄P₃ occurs, which leads to disintegration of the active material layer and rapid capacity fading. By contrast, in the ionic-liquid electrolyte, a uniform and thin surface film should be formed and K⁺ is homogeneously stored on the entire electrode surface, preventing the occurrence of local stress. Thus, severe disintegration of Sn₄P₃ electrode is suppressed, which provides excellent performance of the Sn₄P₃ electrode. In addition, KFSA salt should support good cyclability for the electrode. While the first Coulombic efficiency is only 66.7%, the second efficiency reaches 98.2%. Higher efficiency of 99.8% is also confirmed at the 20th cycle. High Coulombic efficiency after the second cycle is characteristic of the combination of Sn₄P₃ electrode and Py13-FSA ionic-liquid electrolyte.

Figure 3 gives rate capability of the Sn₄P₃ electrode in the ionic-liquid electrolyte. The electrode exhibits an initial discharge capacity of ca. 400 mAh g⁻¹ at a current density of 50 mA g⁻¹. The reversible capacity gradually decreases with an increase in the current density and the capacity of 100 mAh g⁻¹ is confirmed at 1000 mA g⁻¹ between 21st and 25th cycles, which is approximately half of the capacity in inorganic-liquid electrolyte at the same current density. However, with a prolonged rate capability test, the capacity of the Sn₄P₃ electrode reaches 200 mAh g⁻¹ at 1000 mA g⁻¹ between 46th and 50th cycles, which is comparable to the performance in the organic-liquid electrolyte. There are some possibilities of these phenomena: a surface film growth with better properties by repeated charge-discharge cycling, activation process of active material of Sn₄P₃, and so on. We are now trying to clarify these possibilities.
Additionally, the discharge capacity recovers at the initial current density of 50 mA g\(^{-1}\); thus, no electrode disintegration occurs. Consequently, the rate performance of Sn\(_4\)P\(_3\) electrode is almost the same in both ionic- and organic-liquid electrolytes.

4. Conclusions

A Sn\(_4\)P\(_3\) electrode exhibited a superior cycling performance with reversible capacity of 365 mA h g\(^{-1}\) over 100 cycles in a certain ionic-liquid electrolyte of KFSA/Py13-FSA (20/80 mol%). To commercialize KIB, the improvement of safety is very important. The electrode achieved not only high safety but also excellent cycling and rate performances for KIB in the ionic-liquid electrolyte compared to that in the organic-liquid electrolyte.

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