

Improvement of FeF₃ cathode properties by adding V₂O₅-P₂O₅ glass system for Li-ion batteries

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Conversion-type ferric electrode active materials such as FeF₃ and FeOF are promising for large-scale Li-ion batteries, because these have low cost and large specific capacities. However, FeF₃ cathode shows a large overpotential during discharge-charge cycles, such that the rechargeable capacity is almost lost after a few cycles. Therefore, the cathode properties of FeF₃ should be improved for using the large-scale Li-ion batteries as cathode. On the other hand, TiF₃ having a same symmetry as FeF₃ showed the smaller overpotential, better rate capability and cyclability than that of FeF₃ [1]. It is considered that the better cathode properties and smaller overpotential of TiF₃ is reflection of the higher conductivity (1×10^{-9} S/cm) than that of FeF₃ (1×10^{-11} S/cm). Therefore, by adding V₂O₅ glass system with high conductivity ($\sim 10^{-5}$ S/cm) to FeF₃, we tried to cover the low electric conductivity of FeF₃ and improve its cathode performances. In this presentation, we report the cathode properties and the reaction mechanism of FeF₃-V₂O₅ glass nano-composite cathode.

FeF₃-V₂O₅ glass nano-composites were prepared by dry ball-milling method. The nano-composite cathode properties were evaluated by using coin-type cell with 1 M LiPF₆ in EC:DMC = 1:1 as electrolyte, polypropylene as separator and lithium metal as anode. Here, the electrodes were prepared by mixing the obtained above products with 5 wt% poly (acrylic acid) binder in N-methylpyrrolidone. The slurry was coated on aluminium foil and dried at 100°C until the solvent had evaporated completely. All electrodes were dried again at approximately 110°C overnight under a vacuum before the cells were assembled. The coin-type cell was assembled in an Ar-filled glove box.

Figure 1 shows the initial discharge-charge profiles of FeF₃ and FeF₃-V₂O₅ glass nano-composite at a rate of 70 mA/g (FeF₃) and 63 mA/g (FeF₃-V₂O₅ glass). Although the rechargeable capacity of FeF₃-V₂O₅ glass (Fe:V=1:1 molar ratio) composite was smaller than that of pure FeF₃ cathode, its overpotential was small. In addition, the rate capability and cyclability were also improved by adding V₂O₅ glass. To compare the reaction mechanism between FeF₃ and FeF₃-V₂O₅ glass during the initial discharge-charge cycle, we performed TEM-EDS analysis after initial discharge cycle. Figure 2 shows TEM image of electrodes at 1.0 V discharged state. In the case of pure FeF₃, it is obvious that iron particles with the size of around 2~3 nm disperse evenly in the secondary particles. On the other hand, iron particles were not confirmed in the case of FeF₃-V₂O₅ glass, iron and vanadium were dispersed uniformly in all particles.

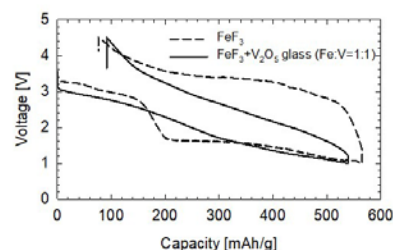


Fig. 1 Initial discharge-charge curves of FeF₃ and FeF₃-V₂O₅ glass at a rate of 70 mA/g (FeF₃) and 63 mA/g (FeF₃-V₂O₅ glass).

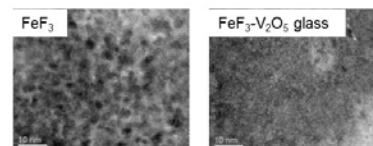


Fig. 2 TEM images of FeF₃ and FeF₃-V₂O₅ glass after discharge state down to 1.0 V.

Acknowledgement:

This work was financially supported by the RISING2 projects of NEDO.

References:

[1] A. Kitajou, I. Tanaka, Y. Tanaka, E. Kobayashi, H. Setoyama, T. Okajima, and S. Okada, *Electrochemistry*, **85**(8), 472 (2017).