

Development of Conversion-Type FeF₃ Cathode in Rechargeable Lithium Battery (1): Degradation Factors of FeF₃ Cathode

Hiroshi Senoh^a, Keitaro Matsui^a, Masahiro Shikano^a, Toyoki Okumura^a, Hikari Sakaebe^a, Hisao Kiuchi^b, Keisuke Yamanaka^c, Toshiaki Ohta^c, Toshiharu Fukunaga^b, Hironori Kobayashi^a and Eiichiro Matsubara^b

^a National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

^b Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^c Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

E-mail: h.senoh@aist.go.jp

Iron trifluoride (FeF₃) has attracted considerable attention as a cathode material due to its high energy density and low cost [1]. However, the FeF₃ cathode operating via insertion/conversion process suffers from degradation over repeated cycles [2]. To improve the reversibility of the FeF₃ cathode, in this study, we investigate the degradation factors of conversion-type FeF₃ cathode during repeated cycling. FeF₃-carbon composite was first synthesized by mixing anhydrous FeF₃ powder (Rare Metallic) and acetylene black (DENKA) in a weight ratio of 70:25 using a planetary ball mill (Fritsch, premium line P-7). Finally, FeF₃ cathode was prepared by mixing FeF₃/C composite powder and PVdF (Kureha). Galvanostatic discharge and charge measurements were conducted using the standard CR2032 coin-type cell configuration with a 1.0 mol dm⁻³ LiPF₆/EC:DMC (1:1 v/v) as an electrolyte. At the initial stage, the FeF₃ cathode exhibited a specific capacity of approximately 600 mAh g⁻¹ at a cut-off voltage between 1.0 and 4.5 V, but the attained capacity decreased drastically beyond the 10th cycles. A remarkable increase in the resistance of FeF₃ cathode beyond the 10th cycles was also observed by the electrochemical impedance spectroscopy. X-ray pair distribution function (PDF) analyses revealed that, at the charge state, FeF₃ phase is prone to disappear gradually as the cycle proceeded, while at the discharge state the formation of Fe does not occur drastically beyond the 10th cycles. The change of Fe *K*-edge XAFS spectra upon cycling indicated that the FeF₃ cathode is scarcely reduced to Fe⁰ at the discharged state. In addition, the Li *K*-edge and F *K*-edge X-ray XAFS analyses revealed that the formation of LiF is more pronounced as the cycle proceeded. From SEM observation, it was found that a film formation was observed on the surface of FeF₃ cathode at the initial stage, and eventually the surface was completely covered by a thick film beyond the 10th cycles. It is suggested that the thick film on the FeF₃ cathode prevents the progress of the conversion reaction, leading to the degradation of the FeF₃ cathode.

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References:

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