

A New Insight Derived from Two-Compartment Cell: Electrochemical Behavior of FeF₃ Positive Electrode

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Table of Contents

Experimental Details	2
Additional Results and Discussion	5
References	7
Fig. S1-S7	8

Experimental Details

Preparation of FeF₃ composite electrode: FeF₃ composite electrode was prepared following our previous literature.¹ Anhydrous FeF₃ powder (Rare Metallic Co., Ltd.) and carbon (KS-15, Timcal) were mixed in a weight ratio of 70:25. The mixture was put in zirconia pot with zirconia balls, which was sealed in an air-tight steel container in Ar-filled glove box (Miwa MFG). Then, milling was conducted for 24 h using planetary ball mill (Premium line P-7, Fritsch Japan Co., Ltd.) at 200 rpm under. The composite electrode was prepared by mixing the FeF₃/acetylene black and polyvinylidene difluoride (PVdF, Kureha) under a dry-air atmosphere (dew point < -40°C) in a weight ratio of 95:5. *N*-methyl-2-pyrrolidinone (NMP, Kishida Chemical Co., Ltd.) was added, which was cast onto a piece of carbon-coated Al-foil as a current collector with a typical loading of 1–2 mg cm⁻². The resulting FeF₃ composite electrode sheet was dried at 120 °C for at least 12 h under vacuum to eliminate NMP. The electrode sheet was punched into a circle with 1.77 and 1.31 cm² for the coin cell and two-compartment cell, respectively.

Electrochemical measurements: 1.0 mol dm⁻³ LiPF₆/ethylene carbonate (EC) : dimethyl carbonate DMC (1:1 vol%) was purchased from Mitsubishi Chemical. Lithium difluoro(oxalato)borate (LiDFOB) and DMC were purchased from Sigma-Aldrich and Kishida Chemical Co., Ltd, respectively.

CR2032 coin-type cell was assembled using Li metal as a counter electrode and polypropylene separator under a dry-air atmosphere (dew point < -40°C). The two-compartment cell (EC Frontier Co., Ltd.) was assembled using Li metal as a counter electrode and polypropylene separators and lithium-ion conducting glass-ceramics (OHARA, LICGCTM, thickness: 150 μm) in Ar-filled glove box. Galvanostatic charge and discharge cycling test was conducted at a current density of 0.1 C using a potentiostat/galvanostat (Hokuto Denko, HZ-Pro S12). Here, nC means that the current will discharge or charge to the theoretical capacity in 1/n hours. The cutoff voltages were set at 1.0 and 4.5 V for the discharge and charge process, respectively. After charge and discharge cycling test, the cell was disassembled in Ar-filled glovebox. Electrodes and separators were washed with DMC and dried prior to measurements.

Analyses: Morphology of the electrode was observed by a scanning electron microscopy (SEM) (JEOL, JSM-6510LA). Separators were analyzed by an X-ray fluorescence analyzer (XRF) (HORIBA, XGT-7200). The chemical state of the elements contained in the electrode was examined by an X-ray photoelectron spectroscopy (XPS) (SHIMADZU, KRATOS ULTORA2). The sample was transferred to SEM and XPS without exposure to the air using transfer-vessel. An electron energy-loss spectroscopy (EELS) measurement was carried out by using a scanning transmission electron

microscope (TEM) (FEI company, Titan³ G2 60-300) equipped with an EELS (Gatan, Inc., GIF-Quantum) with acceleration voltage of 300 kV. The sample powder for TEM analysis was obtained from the electrode and directly dispersed on a holey carbon film supported on a Cu mesh for TEM analysis in Ar environment. The samples were transferred to the electron microscope without exposure to the ambient atmosphere using the transfer holder.

Additional Results and Discussion

Fig. S6 exhibits the XPS spectra of the FeF_3 composite electrode before and after 18 cycles of discharge/charge cycling with or without LiDFOB in the electrolyte at the positive electrode compartment. All binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV. In the C1s spectra, after discharge/charge test, the peak attributed to the binder was not found and peaks which were corresponded to the C-O bond and carbonate became strong regardless of the use of LiDFOB. As for the chemical state of Fe, divalent and trivalent Fe was confirmed from $\text{Fe}2p_{3/2}$ after discharge/charge test. But in $\text{Fe}2p_{1/2}$, the identification of the peaks was difficult because plasmon loss peaks of F were considered overlapped.^{1,2} Inorganic species, such as LiF, Li_xPF_y , and $\text{Li}_x\text{PF}_y\text{O}_z$ which are typical decomposition products of the LiPF_6 , were found in the F1s, Li1s, and P2p spectra.³ The ratio of $\text{Li}_x\text{PF}_y\text{O}_z$ was large when LiDFOB was added into the electrolyte, suggesting that the oxygen contained in LiDFOB was reacted with LiPF_6 during discharge/charge cycling. When LiDFOB was used for the positive electrode compartment, the formation of the surface film containing B element should be considered. However, it was difficult to discuss by deconvolution of the spectrum because the B1s core level partially overlaps with P2s and various inorganic species containing P were thought to exist.⁴ As above, we could not obtain the result that directly proves the effect of LiDFOB on the cycle performance of FeF_3 electrode.

References

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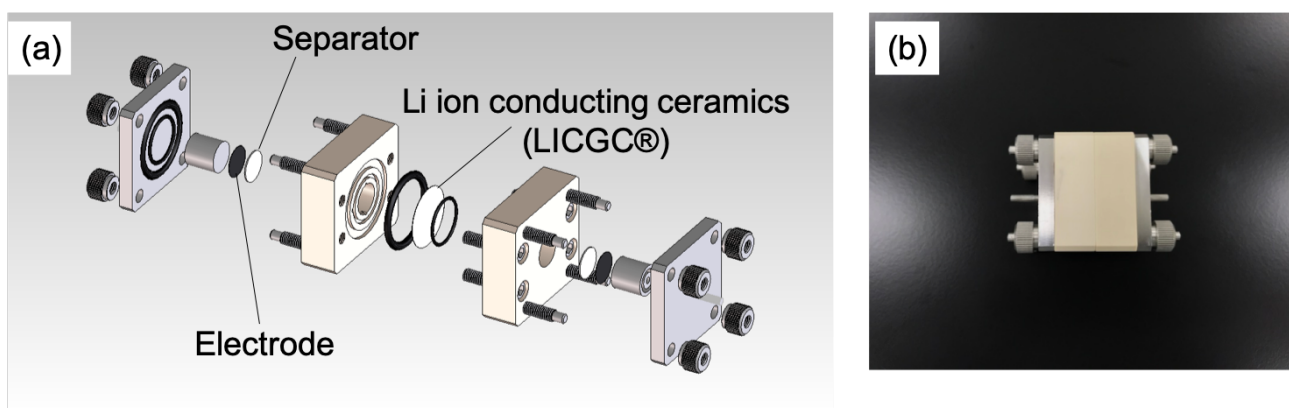


Fig. S1 (a)The developed view and (b) the picture of the two-compartment cell designed in this study.

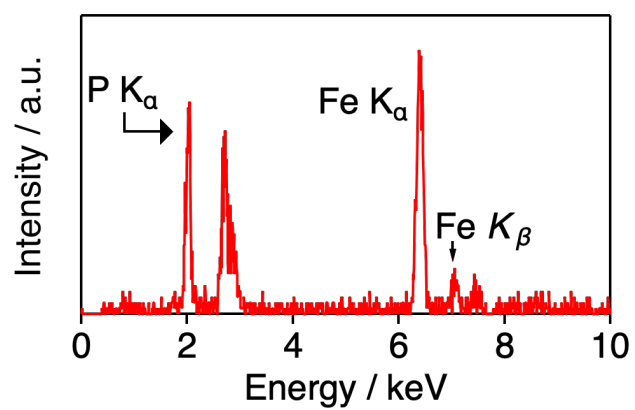


Fig. S2 XRF spectra of the separator after 30 cycles of discharge/charge cycling in the coin cell.

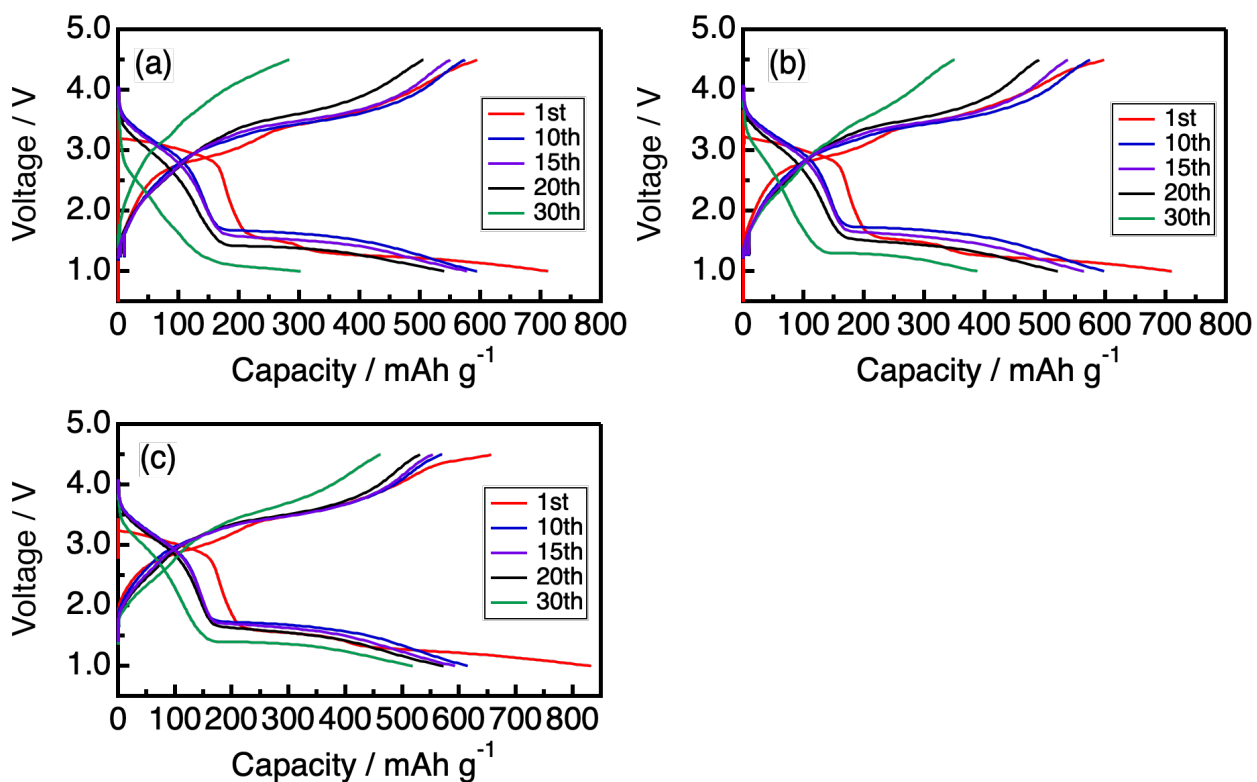


Fig. S3 Charge and discharge curves of the FeF_3 composite electrode in the two-compartment cell. The electrolyte in the negative electrode compartment was 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC}:\text{DMC}(1:1)$. The electrolyte in the positive electrode compartment was 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC}:\text{DMC}(1:1)$ with (a) 50 mM, (b) 100 mM, and (c) 200 mM of LiDFOB . The charge and discharge were performed at 0.1 C rate at 25°C .

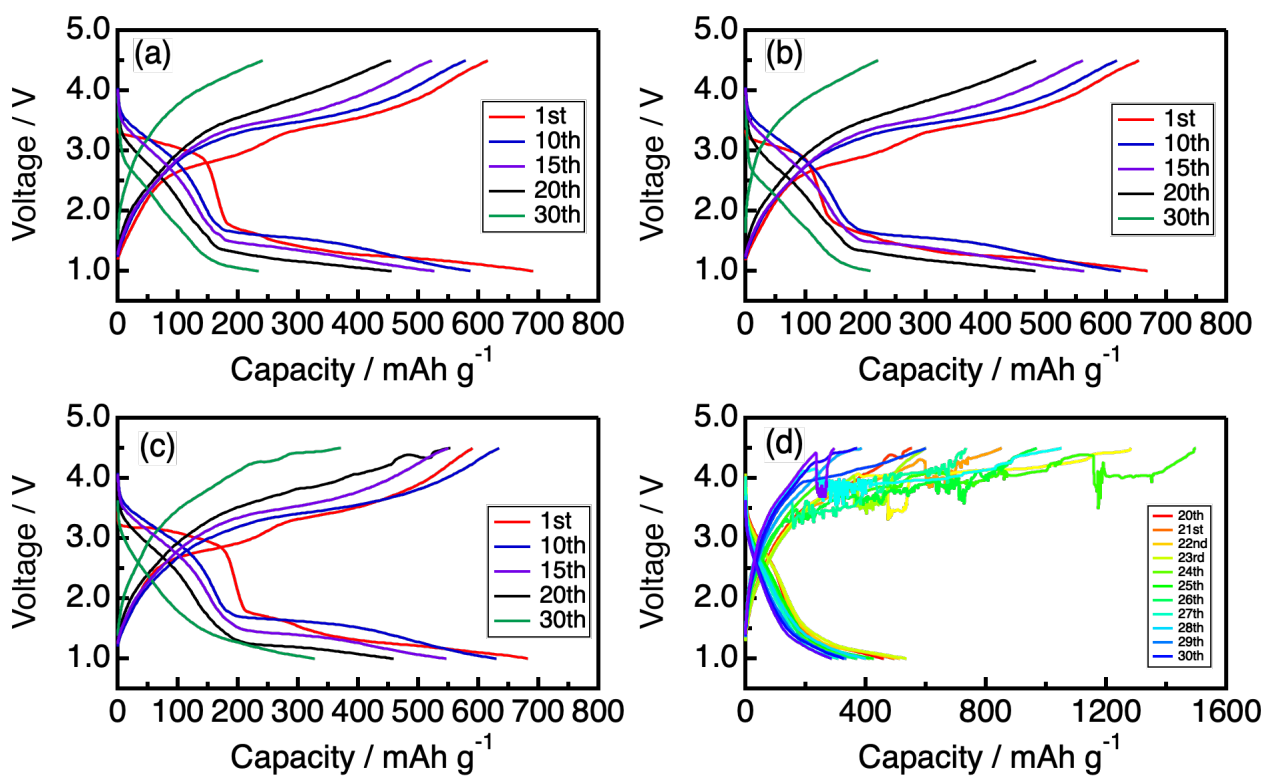


Fig. S4 Charge and discharge curves of the FeF₃ composite electrode in the coin cell. The electrolyte was 1.0 mol dm⁻³ LiPF₆/EC:DMC(1:1) with (a) 50 mM, (b) 100 mM, and (c, d) 200 mM of LiDFOB. The charge and discharge were performed at 0.1 C rate at 25°C.

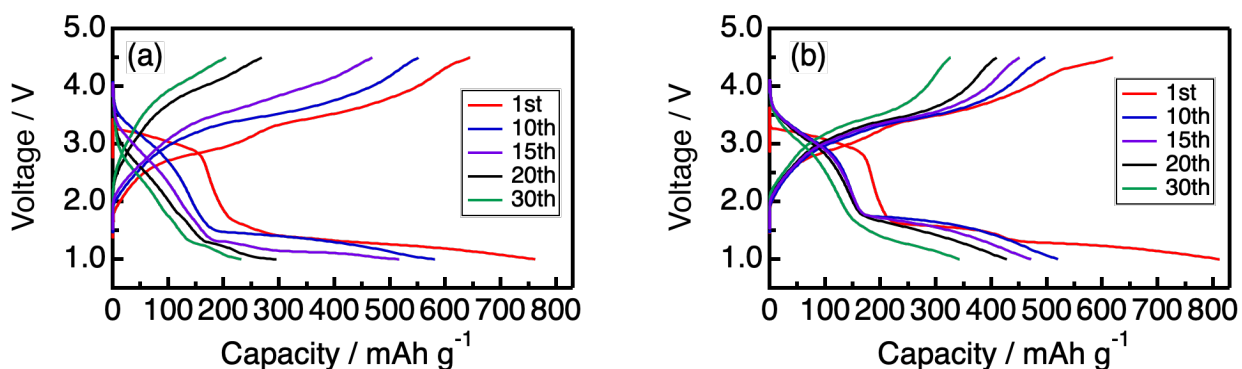


Fig. S5 Charge and discharge curves of the FeF_3 composite electrode in the two-compartment cell. (a) The electrolyte in the negative electrode compartment was 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC}:\text{DMC}(1:1)$ with 200 mM of LiDFOB and that in the positive electrode compartment was 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC}:\text{DMC}(1:1)$. (b) The electrolyte in both negative and positive electrode compartment was 1.0 mol dm^{-3} $\text{LiPF}_6/\text{EC}:\text{DMC}(1:1)$ with 200 mM of LiDFOB. The charge and discharge were performed at 0.1 C rate at 25°C .

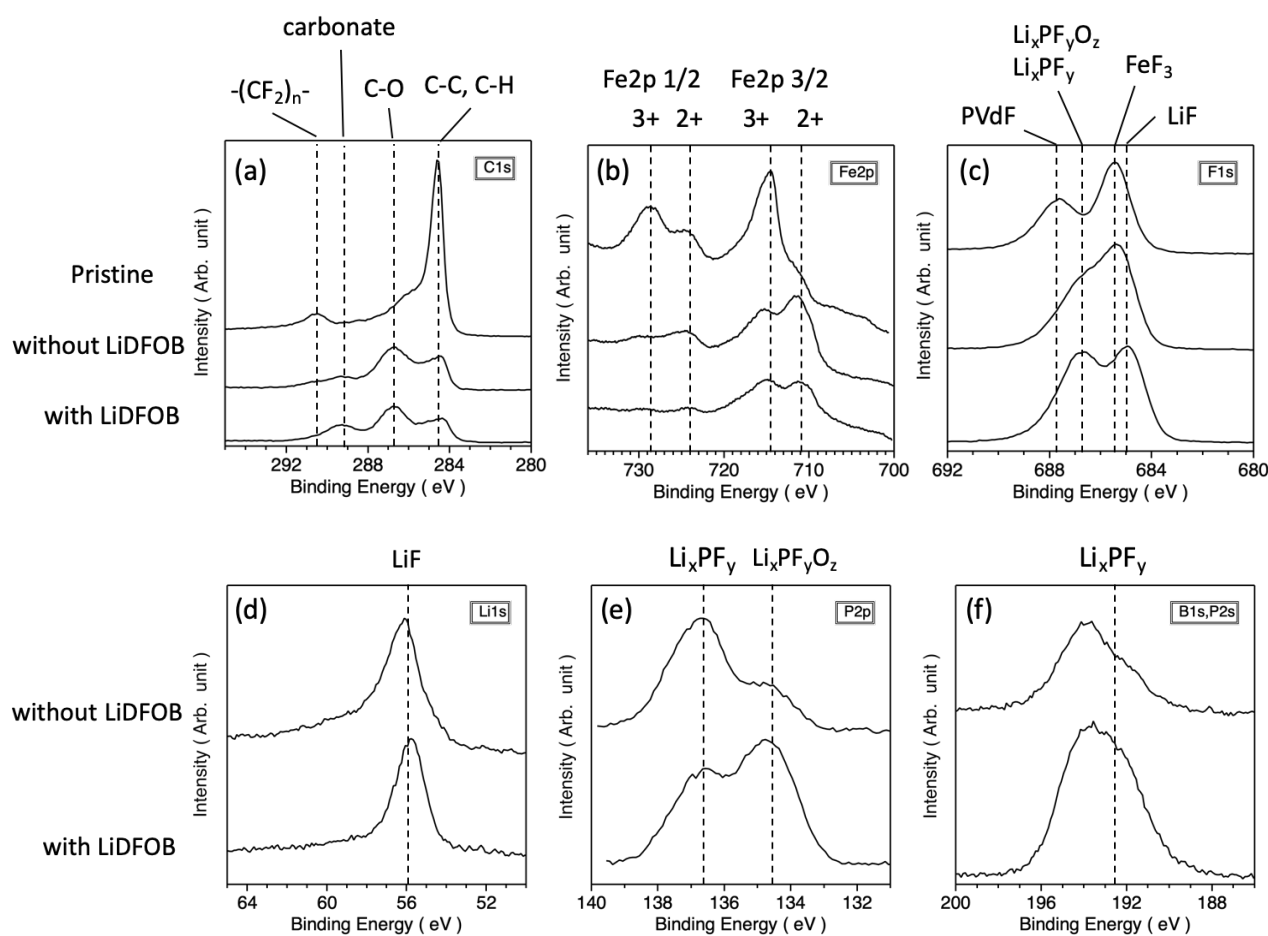


Fig. S6 XPS spectra of the FeF_3 composite electrode before and after 18 cycles of discharge/charge cycling with or without LiDFOB in the electrolyte at the positive electrode compartment. (a) C1s, (b) Fe2p, (c) F1s, (d) Li1s, (e) B1s and P2s, and (f) P2p. All binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV.

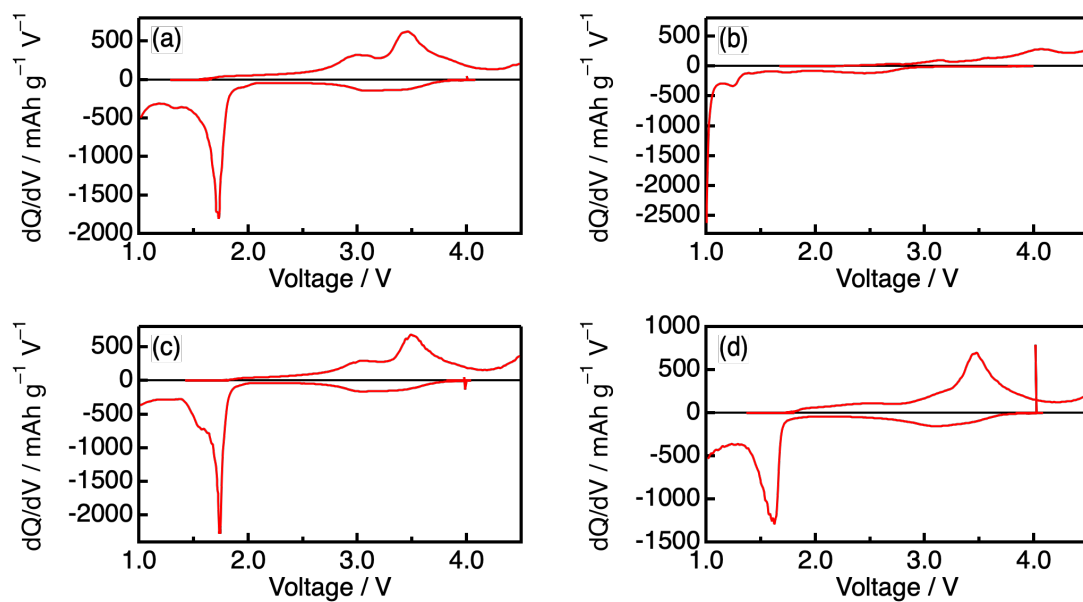


Fig. S7 The dQ/dV plots of the two-compartment cell (a,b) without or (c, d) with 200 mM of LiDFOB in the positive electrode compartment. Represented cycle was (a, c) 5th and (b, d) 20th cycle. The charge and discharge were performed at 0.1 C rate at 25°C.