

Supporting Information

Degradation Mechanism of Conversion-Type Iron Trifluoride: Toward Improvement of Cycle Performance

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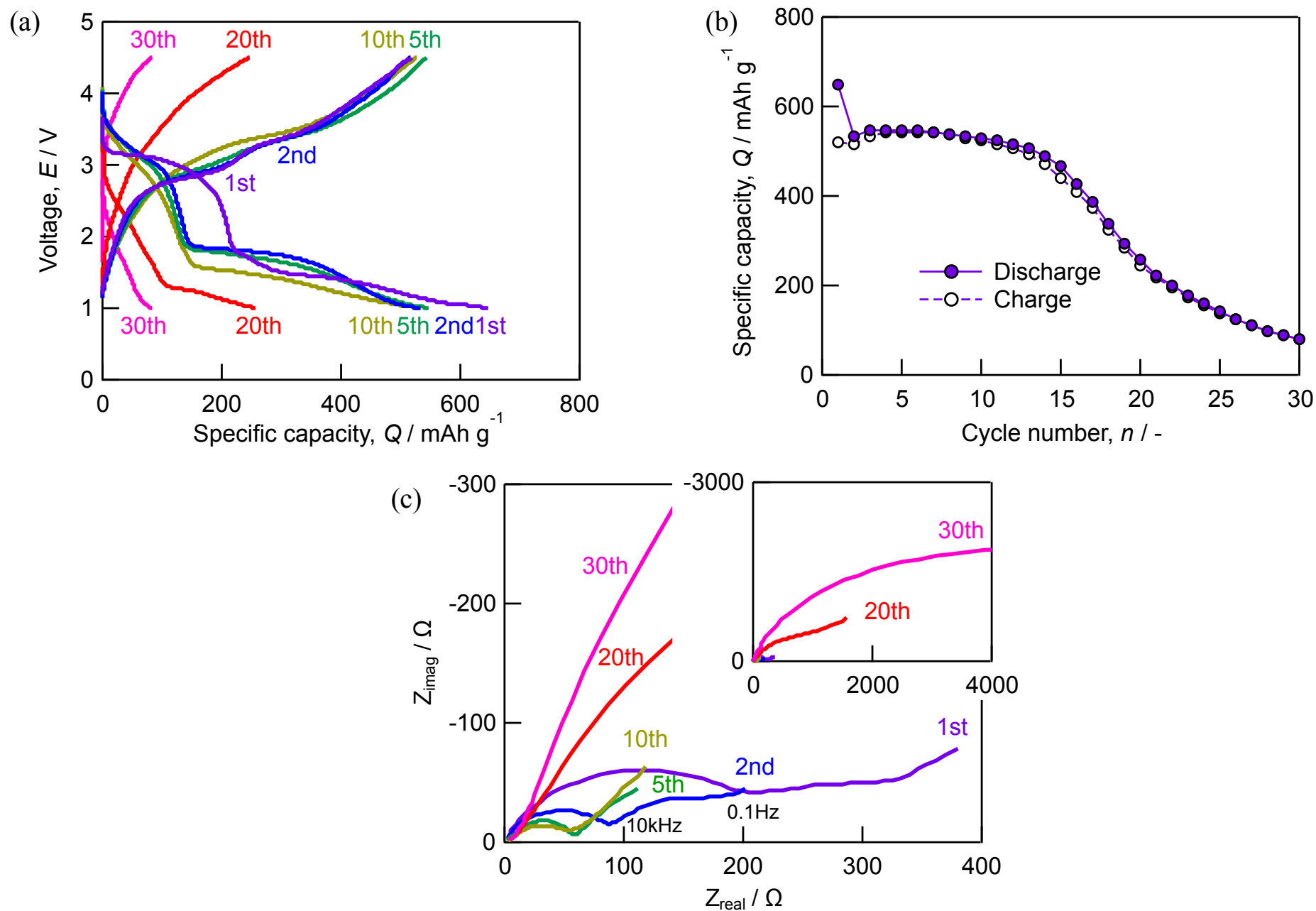


Figure S1. Electrochemical performance of FeF_3 electrode upon cycling at 0.05 C rate. (a) Voltage-capacity profiles in electrolyte consisting of 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$. (b) Discharge and charge capacity plots, showing the attainable capacity decreasing drastically after 10 cycles. (c) Electrochemical impedance data at the discharge state, indicating a remarkable increase in the resistance of FeF_3 electrode after 10 cycles.

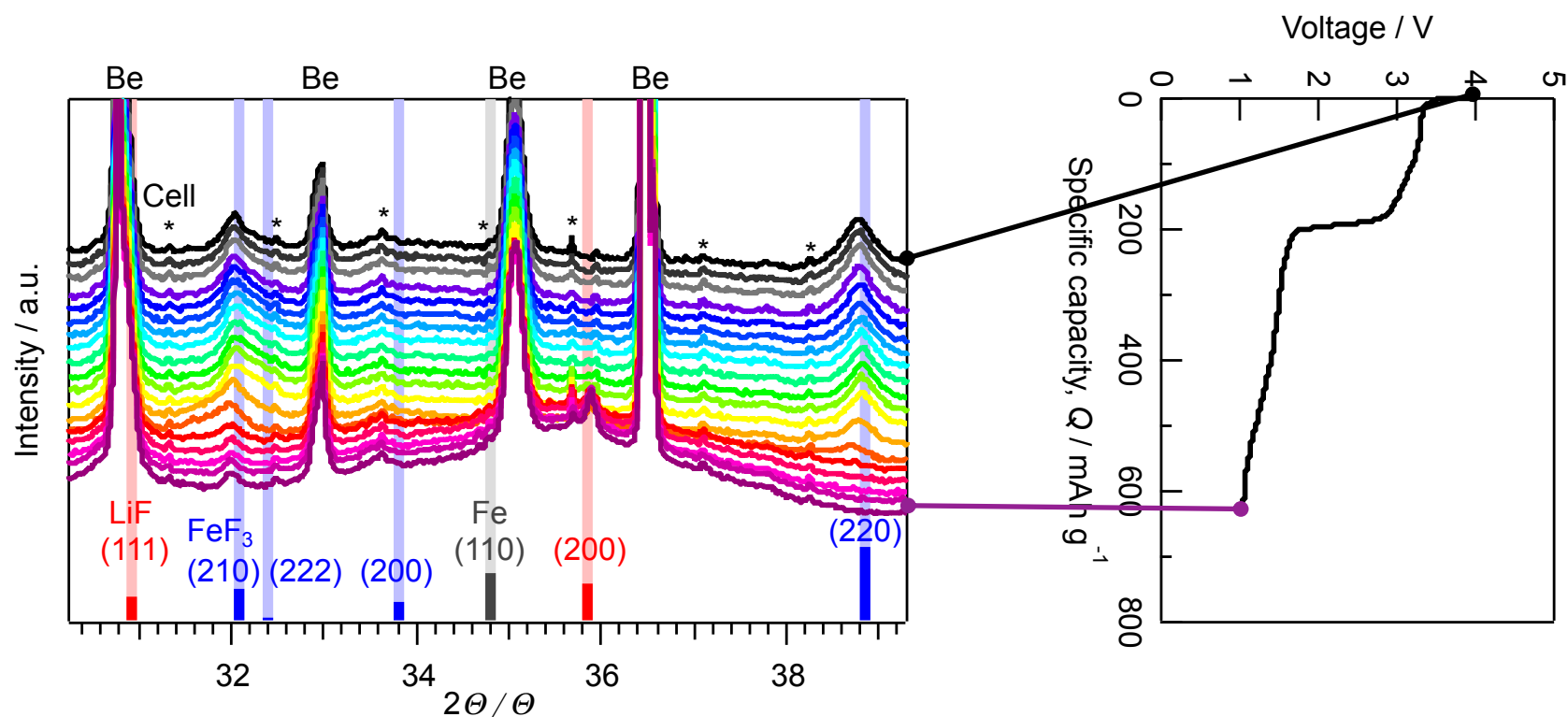


Figure S2. *Operando* XRD profiles of FeF_3 electrode at the first discharge process and room temperature (ca. 30 °C). During the conversion reaction that takes place at the first discharge process, a broad peak for Fe is observed due to the formation of Fe nanoparticles.

	Discharged state		Charged state	
	Li composition	OCV / V	Li composition	OCV / V
1st	2.7	2.00	0.5	3.64
2nd	2.8	1.57	0.6	3.71
5th	3.0	1.73	0.7	3.44
10th	3.0	1.72	0.8	3.18
20th	2.4	1.82	1.4	3.17
30th	1.8	2.13	1.5	3.12

Table S1. Nominal Li composition estimated from the discharged/charged capacities and open circuit voltages (OCVs) after discharge/charge cycles. Nominal Li composition for 1st charged state is different from that for 30th state.

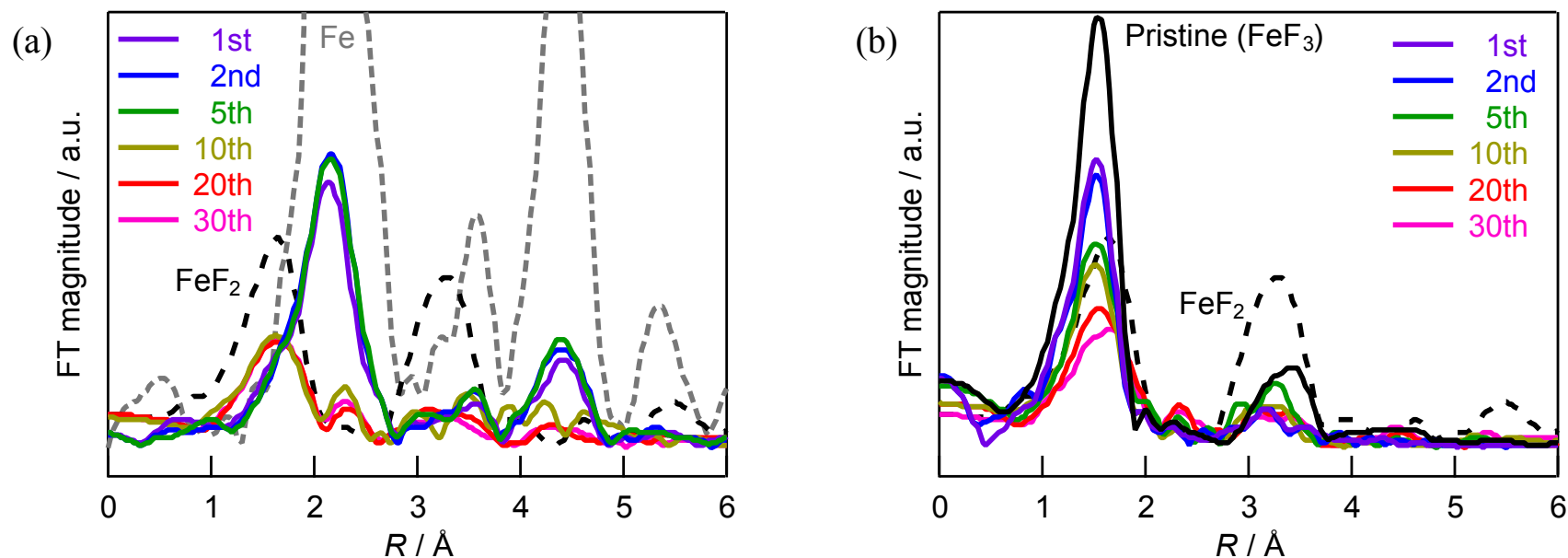


Figure S3. Fe *K*-edge EXAFS spectra of FeF₃ electrode at (a) initial and subsequent discharge process. The formation of Fe⁰ is suppressed after 10 cycles. (b) Fe *K*-edge EXAFS spectra at the charged state on subsequent cycling, showing the oxidation state at the charged state of FeF₃ electrode decreasing steadily from Fe³⁺ to Fe²⁺.

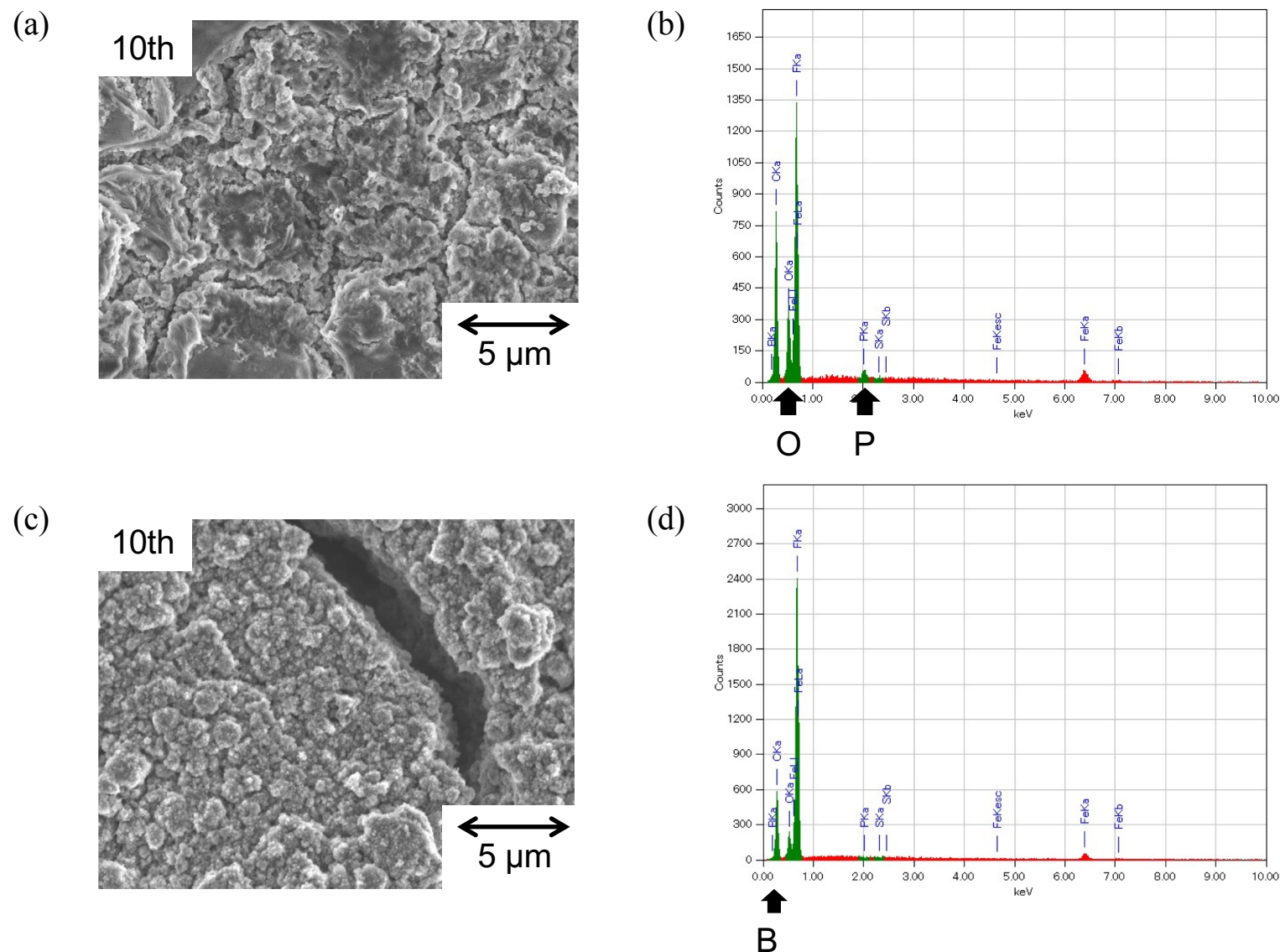


Figure S4. (a) SEM images and (b) EDX profile of FeF₃ electrode surface after 10 cycles in electrolyte containing 1 M LiPF₆/EC:DMC. A thick film containing phosphorus and oxygen can be found on the electrode surface after 10 cycles. (c) SEM images and (d) EDX profile of FeF₃ electrode surface after 10 cycles in electrolyte comprising 1 M LiBF₄/EC:DMC. Boron was scarcely observed on the electrode surface.

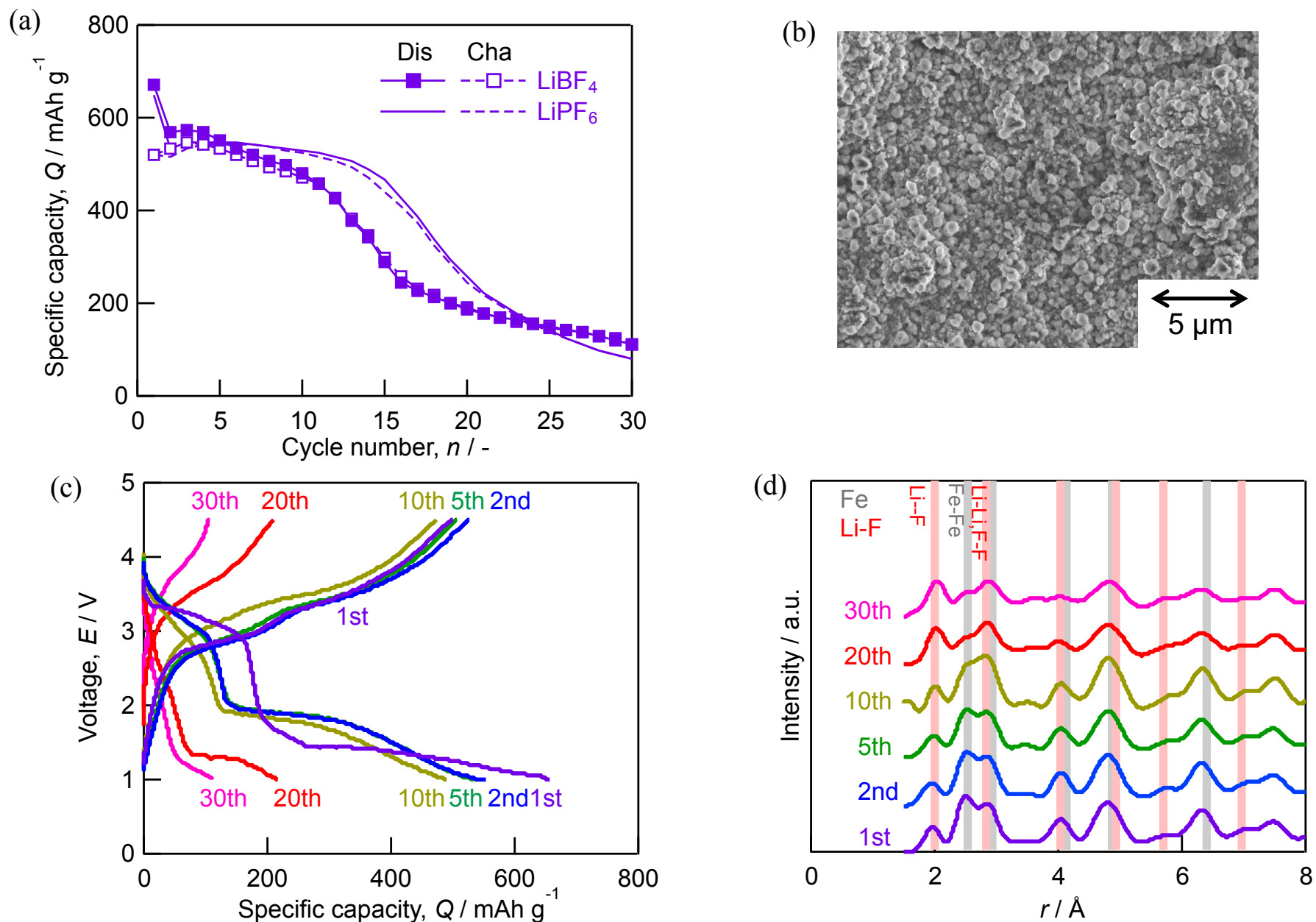
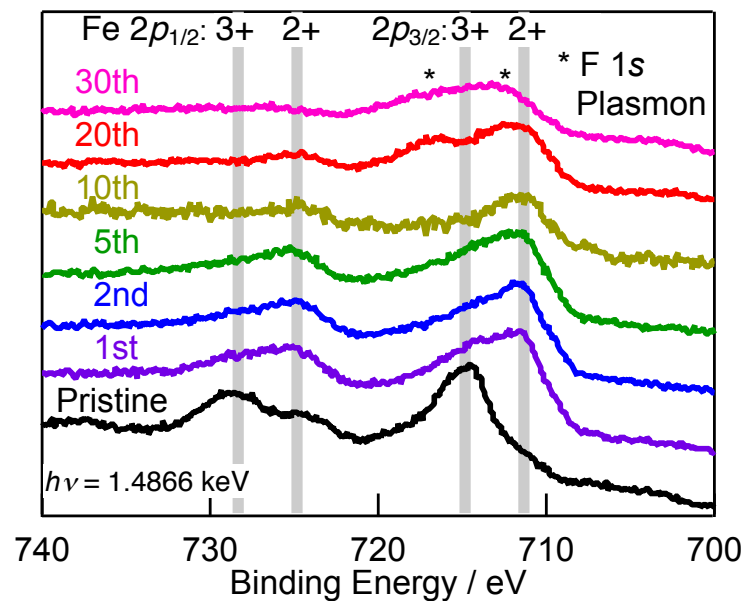


Figure S5. Electrochemical performance and surface morphological analyses of FeF_3 electrode upon cycling at 0.05 C in 1 M $\text{LiBF}_4/\text{EC}:\text{DMC}$. (a) Discharge (Dis) and charge (Cha) capacities attained on subsequent cycling. The replacement of LiPF_6 with LiBF_4 leads to higher attainable capacities beyond 25 cycles. (b) SEM image of the electrode surface after 30 cycles. FeF_3 composite particles are apparent. (c) Voltage-capacity profiles of FeF_3 . (d) PDF spectra of FeF_3 at the charged state. The peaks of Fe-Fe bonds still remain even after 10 cycles.

(a)



(b)

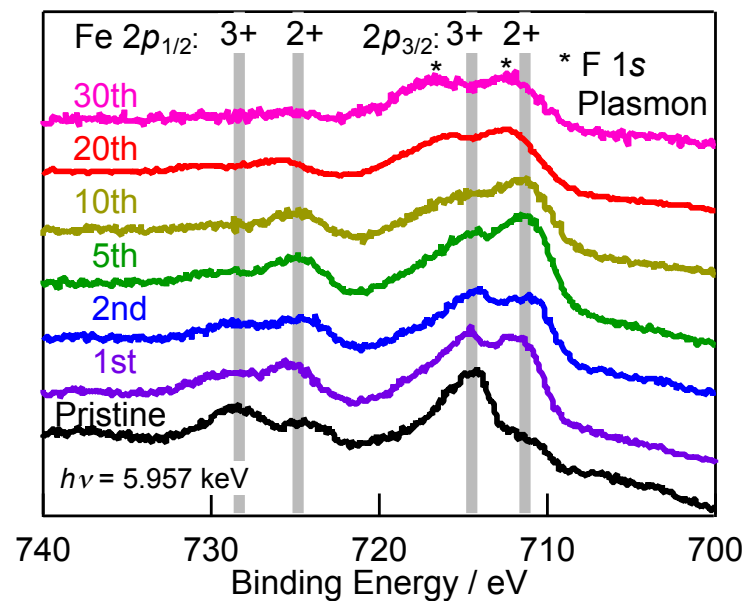


Figure S6. (a) XPS spectra and (b) HAXPES spectra of FeF_3 electrode at the charge state. FeF_3 was cycled in 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$. The $\text{Fe } 2p_{1/2}$ peaks around 725-728 eV decreased significantly as the number of cycles increases, which suggests the formation of a thick film on the electrode. The peaks around 712-716 eV after 20 and 30 cycles are mainly composed of the F 1s plasmon loss peaks.

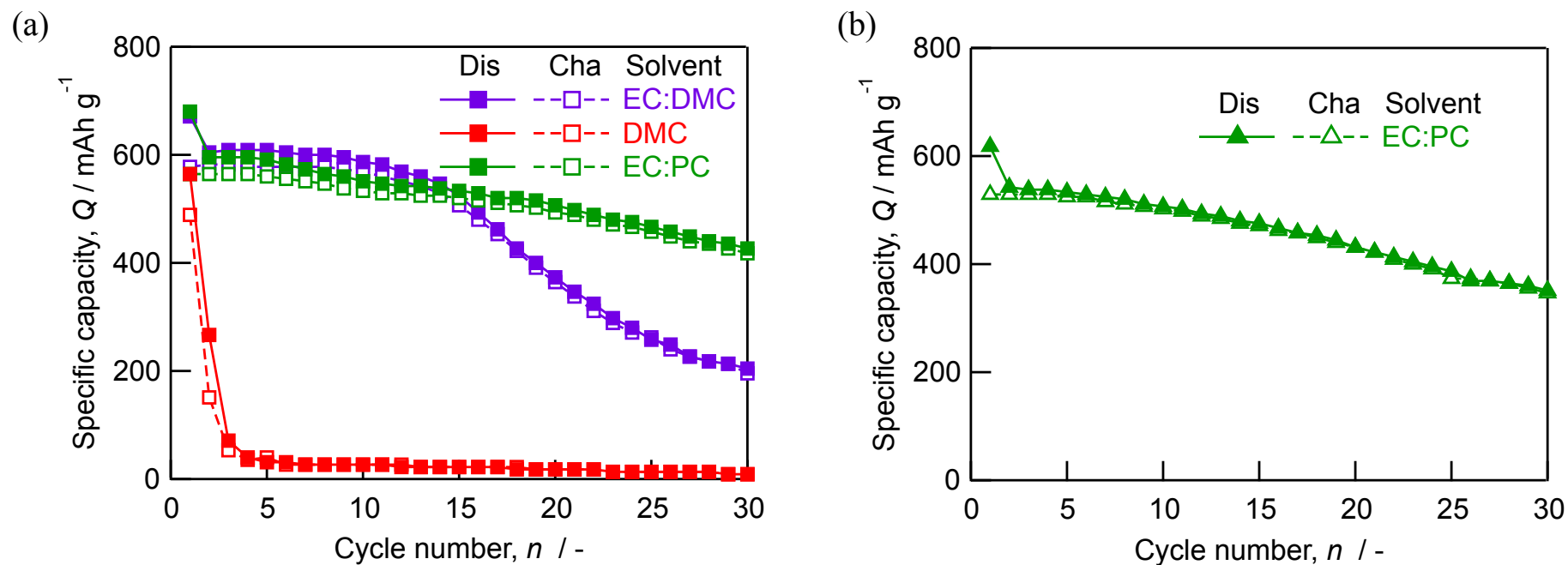


Figure S7. Attained (dis)charge capacities of FeF_3 electrode upon successive cycling at 0.1 C rate (a) in 1 M LiBF_4 with various solvents and (b) in 1 M $\text{LiClO}_4/\text{EC:PC}$. These data show that the selection of solvent, rather than solute, is crucial to improve the cycle performance of FeF_3 electrode.

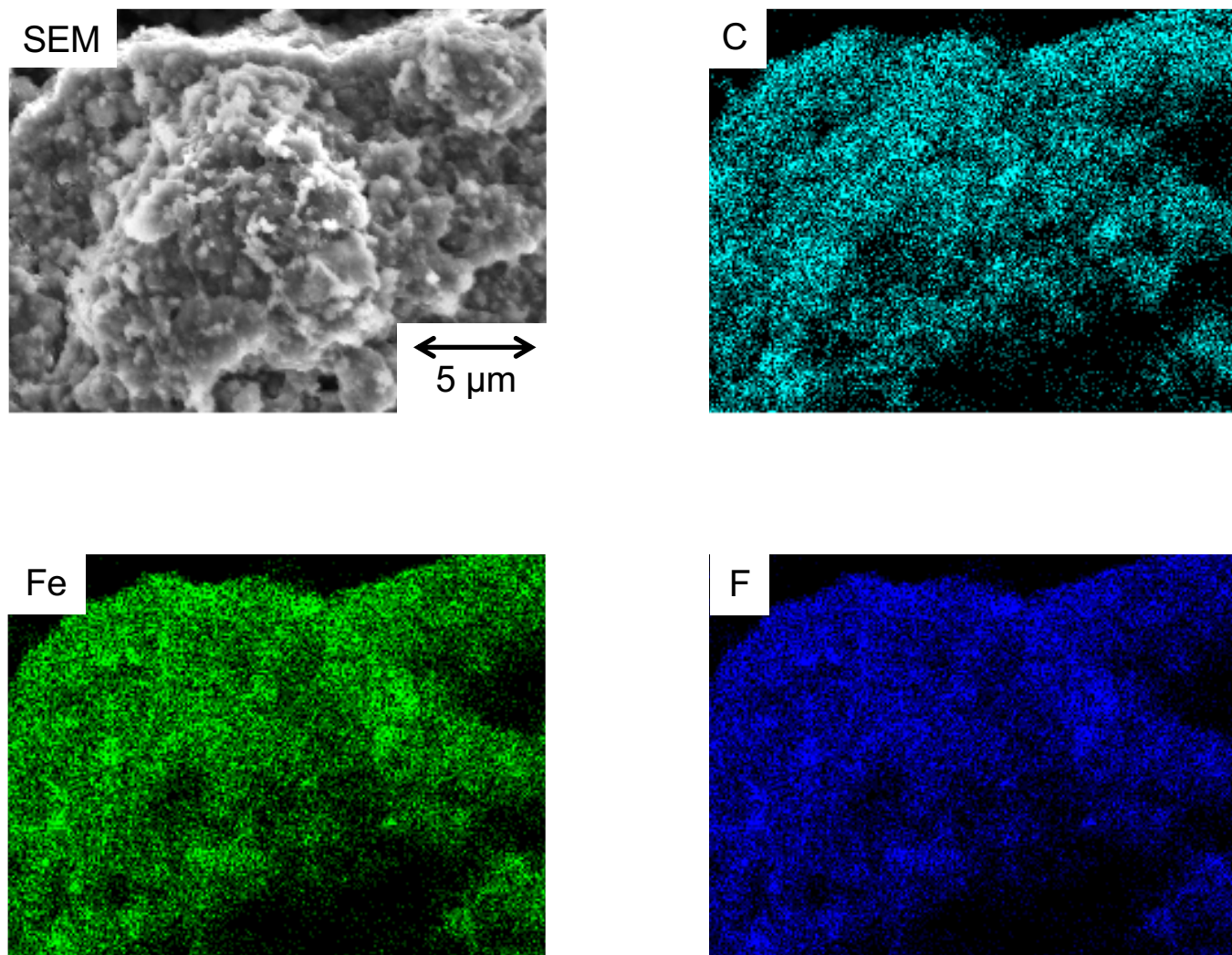


Figure S8. SEM image and EDX mappings of FeF_3 electrode after 30 cycles in 1 M $\text{LiClO}_4/\text{EC:PC}$ at 0.1 C rate. These data show that the particles of FeF_3 /carbon powder can be clearly observed after 30 cycles.