Supplementary Information

Dual-Carbon Batteries Using Fluorination and Defluorination Reactions

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Furthermore, the formation of Li-GIC stage 2 was confirmed from the XRD of the graphite negative electrode after charging (g). Since N/P = 1.6–2.3, it was confirmed that the DCBs functioned.

- Figure S7. Air-free *ex situ* XRD patterns of graphite anode of cycled graphite/1.0LiF@carbon in 4.6 M $LiBF_4$/sulfolane.

1. Experimental

1.1 Material Preparation

Graphite fluoride (CF_x) electrodes were prepared by coating a slurry of $CF_{0.52}$ or $CF_{1.0}$ (Daikin Industries Ltd., 80 wt%), acetylene black (Denka Company Co. Ltd., 10 wt%), and polyvinylidene fluoride (PVdF, Kureha Co. Ltd., 10 wt%) in N-methylpyrrolidone (NMP, Kishida Chemical Co. Ltd.) onto an Al foil (20 μm, Hosen Co. Ltd.) and drying at 353 K for 12 h. Graphite anodes for dual carbon batteries (DCBs) were prepared by coating a slurry of SNO-15 (SEC Carbon Ltd., 15 μm) and PVdF (9:1 w/w) in NMP onto a copper foil (20 μm, Hosen Co. Ltd.) and drying at 353 K for 12 h.

Composite cathodes (xLiF@carbon) were formed by discharging Li/CF_x cells (two-electrode setup, TOYO System Co. Ltd.) using Li metal (0.3 mm, Honjo Metal Co. Ltd.). All Li salts and solvents were battery-grade and obtained from Kishida Chemical Co. Ltd. Half-cell tests used 300 μL of 1 M $LiBF_4$ or 1 M $LiPF_6$ in propylene carbonate (PC) + ethyl methyl carbonate (EMC) (1:1 v/v), to assess reversibility (Figure S2).

For full-cell DCB evaluation, 300 μL of 1.0 M $LiBF_4$ in ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1 v/v), or 4.6 M $LiBF_4$ in sulfolane, were used for electrochemical defluorination of Li/CF_x cells to generate xLiF@carbon cathodes. DCBs were assembled by replacing Li metal with graphite electrodes. Filters and spacers were replaced, and 200 μL of electrolyte was added (Figure S3).

1.2 Electrochemical Measurements of DCBs

Li/CF_x cells were discharged at 20 mA g^{-1} with a cutoff voltage of 1.5 V (vs. Li^+/Li). Charge/discharge measurements of DCBs were performed in the voltage ranges of 0−5.0, 0−5.1, and 0−5.2 V, and 2−5.1 V at a current density of 200 mA (g-carbon cathode)$^{-1}$ in $LiPF_6$-based electrolyte (Figure S4). A voltage range of 2−5.1 V and a current density of 200 mA (g-carbon cathode)$^{-1}$ were used in 1 M $LiBF_4$ in EC+DMC. A voltage range of 2−5.1 V and 50 mA (g-carbon cathode)$^{-1}$ were used in 4.6 M $LiBF_4$ in sulfolane. To ensure sufficient wetting in the electrolyte, cells were rested for 12 h after Li/CF_x discharge and for 12 h after replacing Li with graphite prior to cycling. Negative/Positive (N/P) ratio ranged from 1.6 to 2.3. Charge/discharge capacities were reported based on the weight of carbon (W_c), which was calculated as follows:

$$W_c = W_{GF} \cdot \frac{Q_{GF}^{p}}{Q_{GF}^{t}} \cdot \frac{MM_c}{MM_{GF}}$$

where $^{W_{GF}}$ is a weight of pristine CF_x, $^{Q_{GF}^{p}}$ is the capacity per weight of pristine CF_x during electrochemical defluorination process in Li/CF_x cells, $^{Q_{GF}^{t}}$ is the theoretical specific capacity per weight of pristine CF_x during electrochemical defluorination process (637 mAh g^{-1} for x=0.52 and 864 mAh g^{-1} for x=1.0, x is a composition of F), ^{MM_c} is the molar mass of C (12.011 g mol^{-1}), and $^{MM_{GF}}$ is the molar mass of $CF_{0.52}$ (21.89 g mol^{-1}) or $CF_{1.0}$ (31.009 g mol^{-1}). All the cells were assembled in an Ar-filled glove box, and electrochemical measurements were performed at 298 K.

1.3 Material Characterization

Reversible LiF formation/decomposition in Li/CFx half-cells was confirmed by *ex situ* X-ray diffraction (XRD, Cu *Kα*, 40 kV, 20 mA, 5° min^{-1}). Pristine CF_x and electrochemically reacted active materials were placed in sample holders in the Ar-filled glove box; however, the samples were exposed to air when the measurements were performed. The results are shown in Figures S2 and S6.

X-ray photoelectron spectroscopy (XPS) was conducted on the DCBs using 1 M $LiPF_6$ in EC+DMC before and after cycling, with an Al *Kα* (10 kV, 20 mA) X-ray source. The results are shown in Figures S5 d−f).The electrodes were lightly washed using the DMC solvent in the Ar-filled glove box and dried in vacuum for 1 h in the side chamber of the glove box before the XPS measurements.

Air-free ex situ XRD was performed on the DCBs. The cells were disassembled in the glove box, and active materials were transferred directly to airtight holders without washing. XRD scans were conducted with Cu *Kα* (40 kV, 10 mA) at a scan speed of 2° min^{-1}. The results are shown in Figures 3, 4, and S7). Peak fitting was performed using Origin Pro 2025; intermediate and carbon peaks were fitted with Gaussian functions, and LiF peaks with Gaussian–Lorentz cross functions.

2. Supplementary Figures

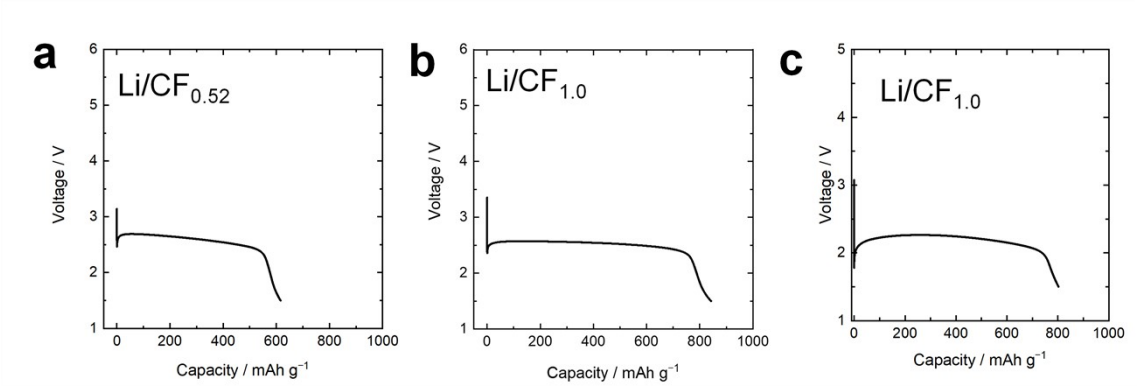
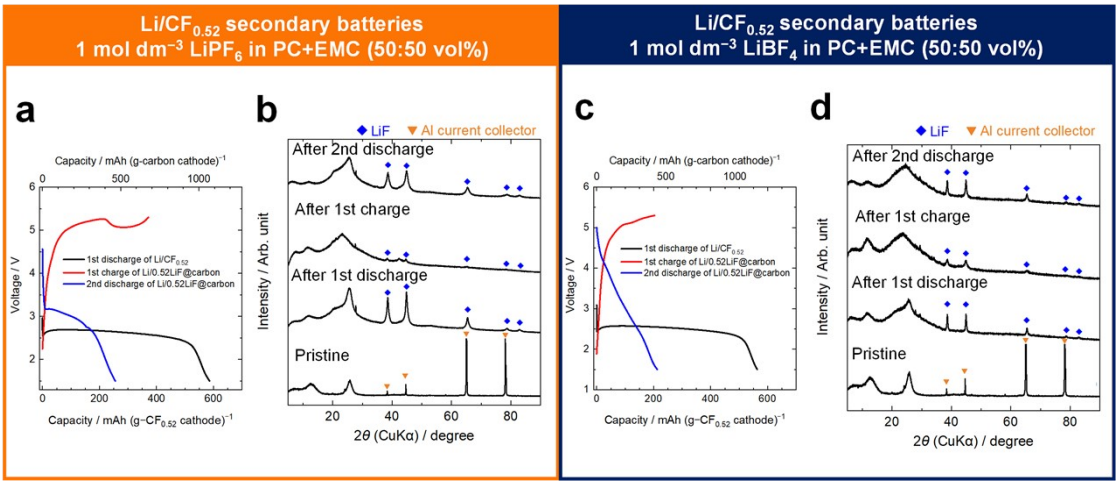


Figure S1. Discharge profiles of (a) $Li/CF_{0.52}$ and (b) $Li/CF_{1.0}$ in 1 mol dm^{-3} $LiBF_4$ / EC+DMC (1/1 vol. %), and (c) $Li/CF_{1.0}$ in 4.6 mol kg^{-1} $LiBF_4$ / sulfolane at a current density of 20 mA g^{-1}.



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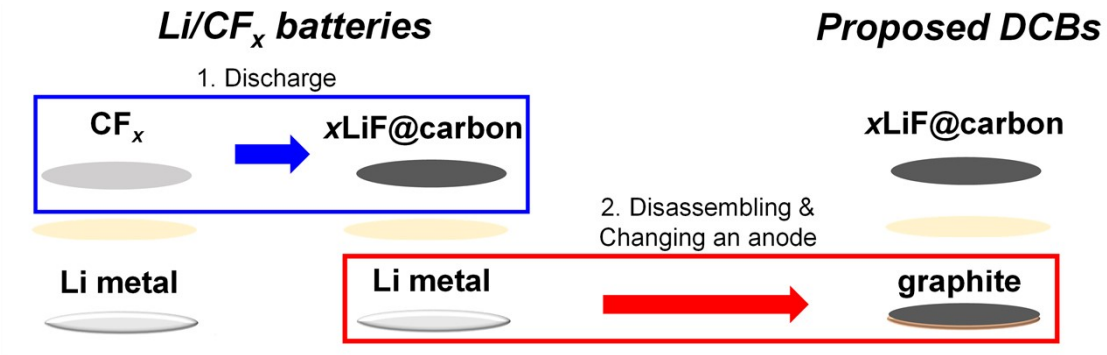
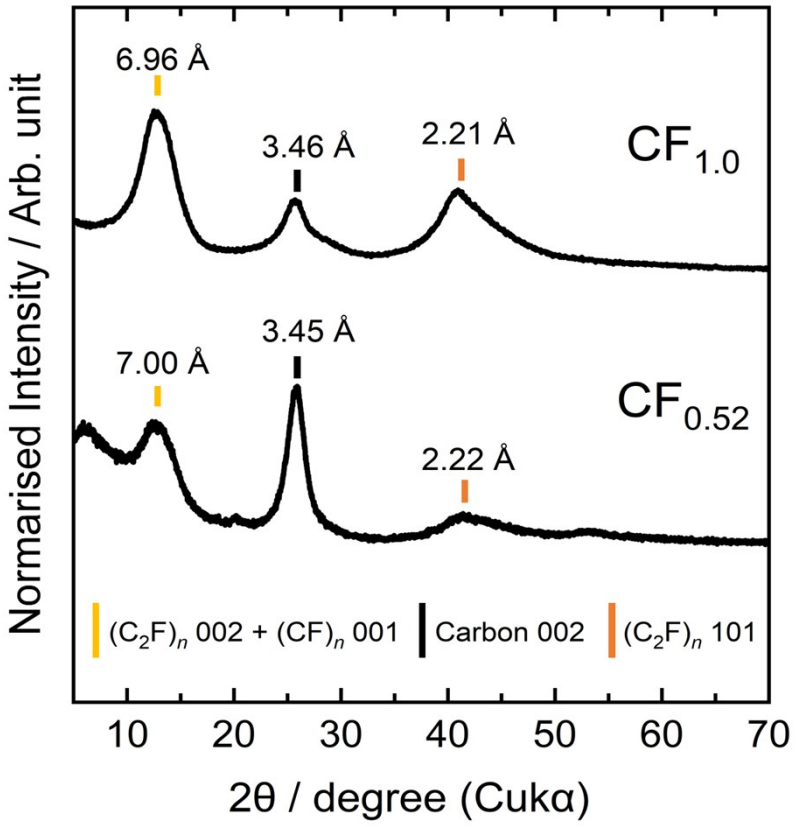


Figure S3. Schematic of the preparation procedure of the proposed DCBs.



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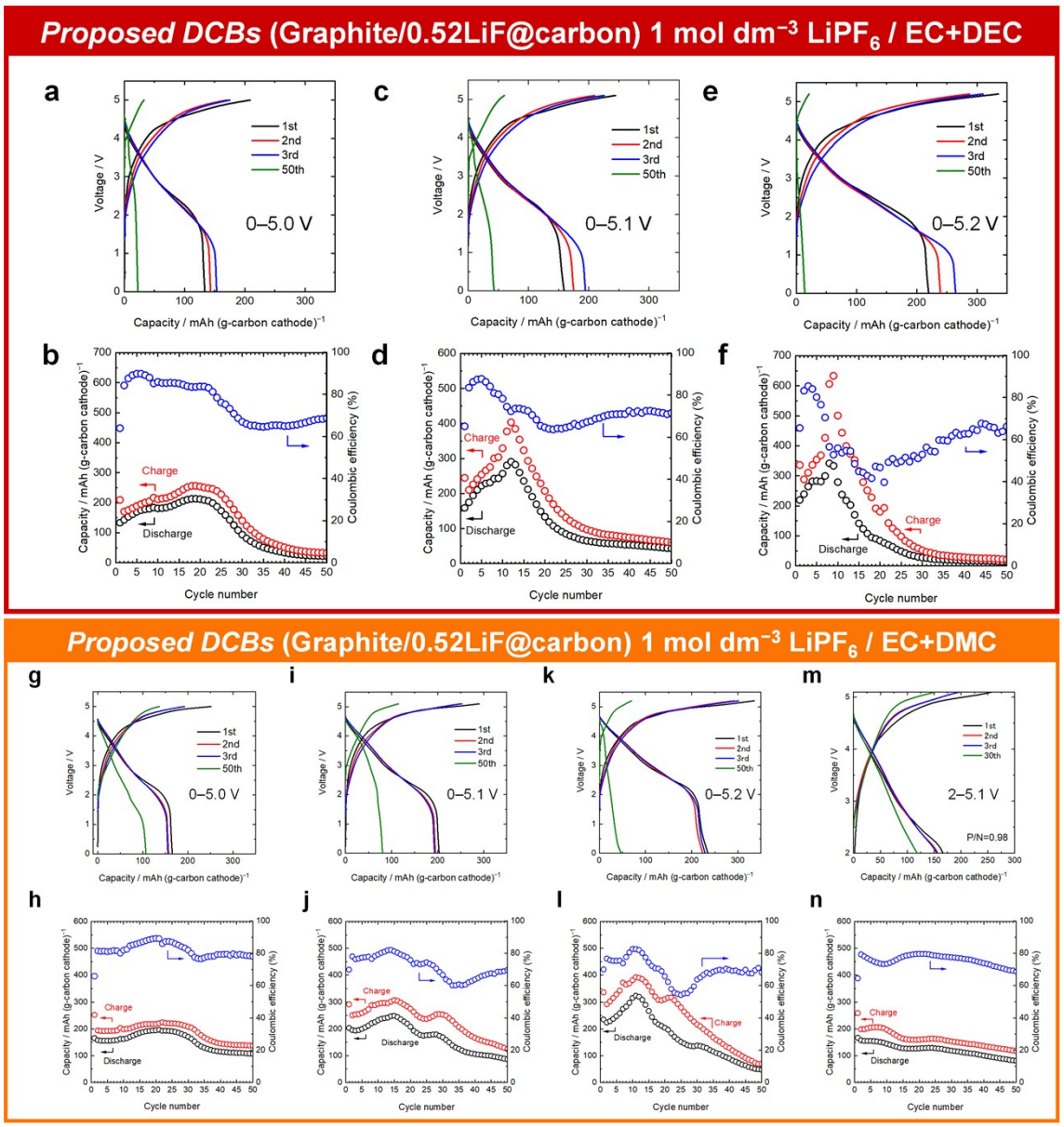

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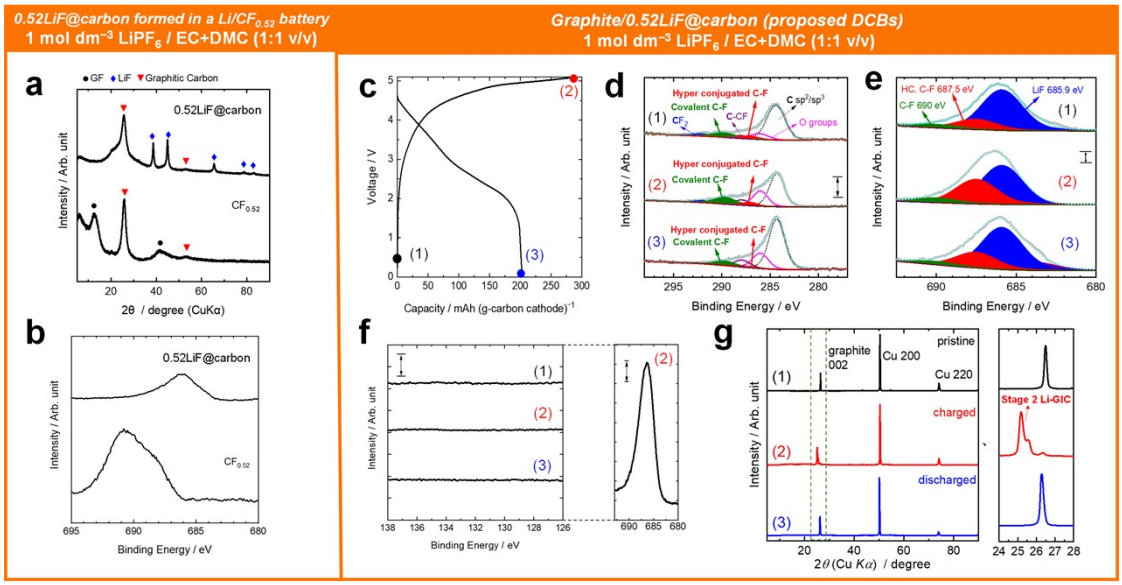

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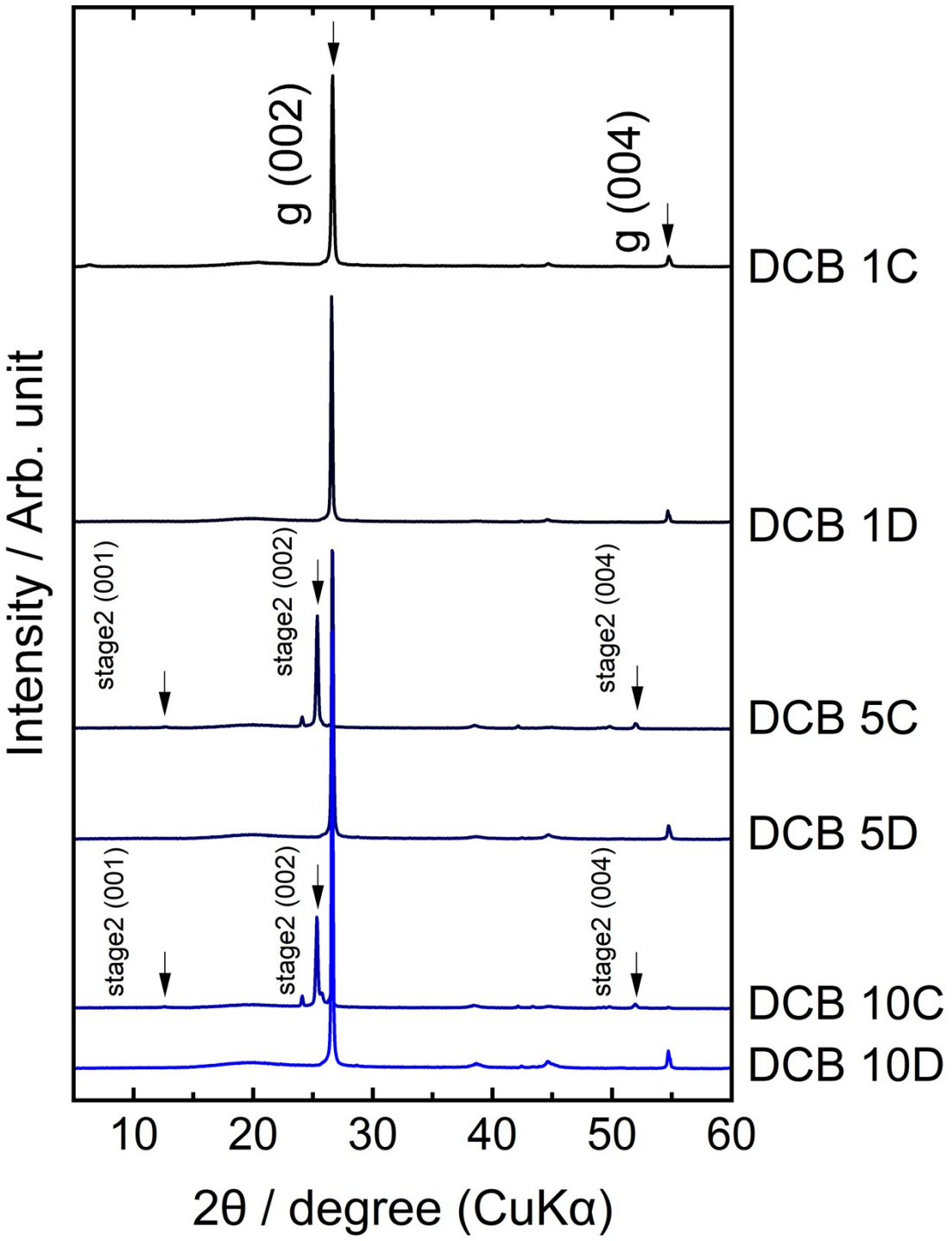

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