

## Supporting Information

### **FeCl<sub>2</sub>-graphite sandwich composite with Cl doping in graphite layers: A new anode material for high-Performance Li-Ion batteries**

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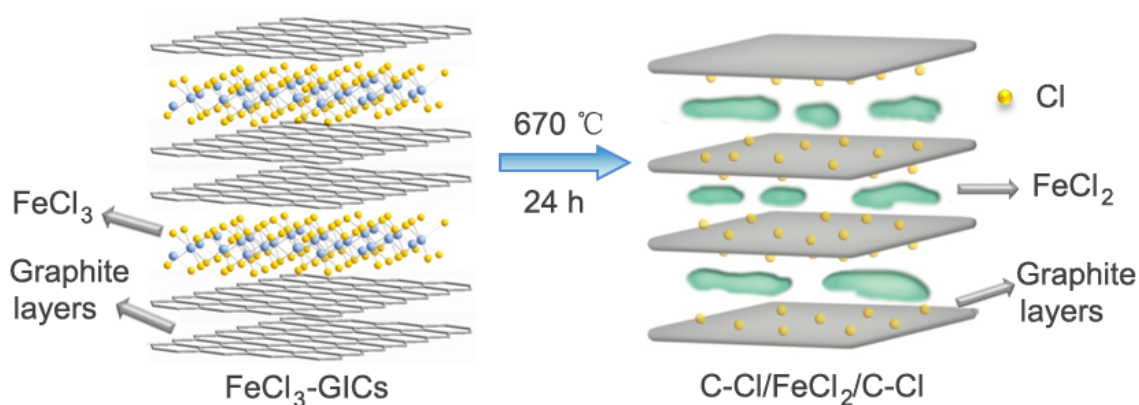
### **Experimental section**

**Sample Synthesis:** The precursor stage 2 FeCl<sub>3</sub>-GICs was prepared by annealing FeCl<sub>3</sub> with EG (molar ratio of 1:4) at 460 °C for 12 h in stainless-steel autoclave. Then annealing the precursor under N<sub>2</sub> gas atmosphere at 670 °C for 24 h to obtain the C-Cl/FeCl<sub>2</sub>/C-Cl.

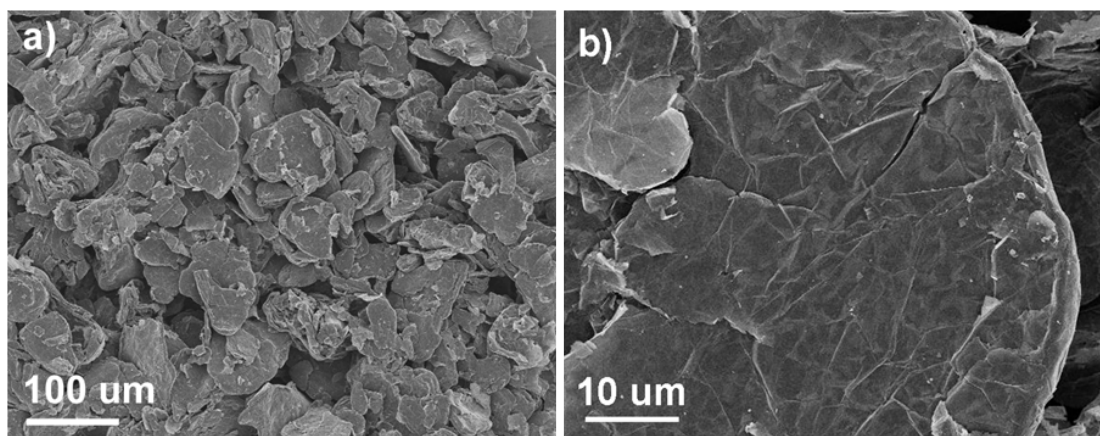
**Sample Characterization:** The product was characterized by using XRD (Philips X'pert PRO X-ray diffractometer, CuKα, λ=1.54182 Å), SEM (JEOL-JSM-6700F), TEM (Hitachi H7650), HRTEM (JEM-ARM 200F), EDX (JEM-ARM 200F), XRF (XRF-1800), XPS (ESCALAB 250 spectrometer, Perkin-Elmer) and Raman spectra (Invia Raman spectrometer with an excitation laser wavelength of 514.5 nm from an argon laser).

**Electrochemical Measurements:** The electrochemical performance versus Li was tested using coin-type 2016 cells. The working electrodes were prepared by spreading a mixture of 70 wt% active materials, 20 wt% of carbon black, and 10 wt % of polyvinylidene fluoride (PVDF) on copper foils, which was followed by drying in vacuum at 110 °C for 12 h. The mass of the active materials was controlled in the range of 1.5-2 mg. The coin cells were assembled in an argon-filled glove box

(Celgard 2400) with Li metal as an anode, and with the solution of 1.0 M LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) as the electrolyte. The galvanostatic discharge/charge tests were conducted on a battery cycler (Land-CT2001A) in the voltage range of 0.01–3.0 V (vs. Li<sup>+</sup>/Li) at room temperature. EIS were performed on CHI660D electrochemical workstation.

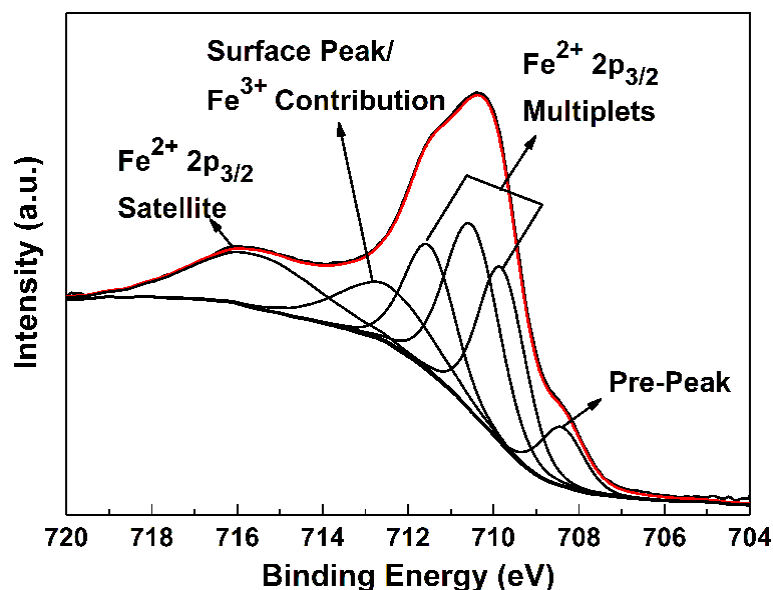


**Figure S1.** Schematic of the C-Cl/FeCl<sub>2</sub>/C-Cl formation from FeCl<sub>3</sub>-GICs.



**Figure S2.** Low-magnification (a) and high-magnification (b) SEM images of the as prepared C-Cl/FeCl<sub>2</sub>/C-Cl.

The SEM images show that the C-Cl/FeCl<sub>2</sub>/C-Cl still keeps the morphology and size of EG precursor, with two-dimensional scale of several tens of micrometers.



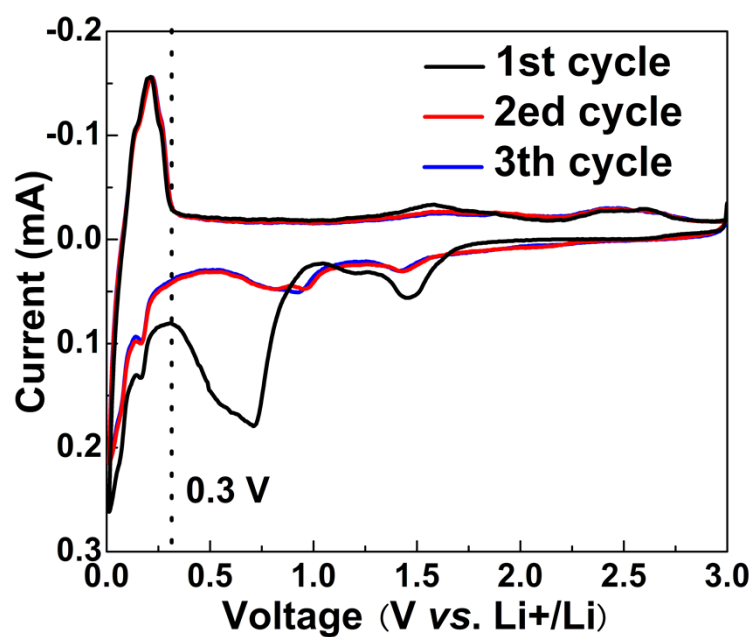
**Figure S3.** Detailed XPS information of Fe 2p<sub>3/2</sub> orbital of C-Cl/FeCl<sub>2</sub>/C-Cl.

As shown in Figure S2, the Fe 2p<sub>3/2</sub> envelope was curve-fit. The multiplet peaks at binding energies (BE) of 709.8 eV, 710.5 eV and 711.5 eV with a shake-up satellite at ~715.7 eV is observed. This is characteristic of Fe<sup>2+</sup> in FeCl<sub>2</sub> from the literature.<sup>[S1]</sup> Besides, a single low-intensity peak marked as ‘pre-Peak’ at BE of 708.4 eV, was derive from the formation of Fe ions with a lower than normal oxidation state by the production of defects in neighbouring sites.<sup>[S2]</sup> It is reported that, the defect sites for many of the compounds studied were more than likely formed during sample preparation when the surface was either cleaved in a vacuum or crushed under the cover of inert gas. The peak with a BE of 712.5 eV (identified as the surface peak in Figure S3) also has been found in FeCl<sub>2</sub> XPS spectra of the literature. One possible cause of the surface structures is the reduction in coordination of the molecules located at the surface after the surface has been cleaved in a vacuum or crushed under the cover of N<sub>2</sub> or Ar.<sup>[S3]</sup>

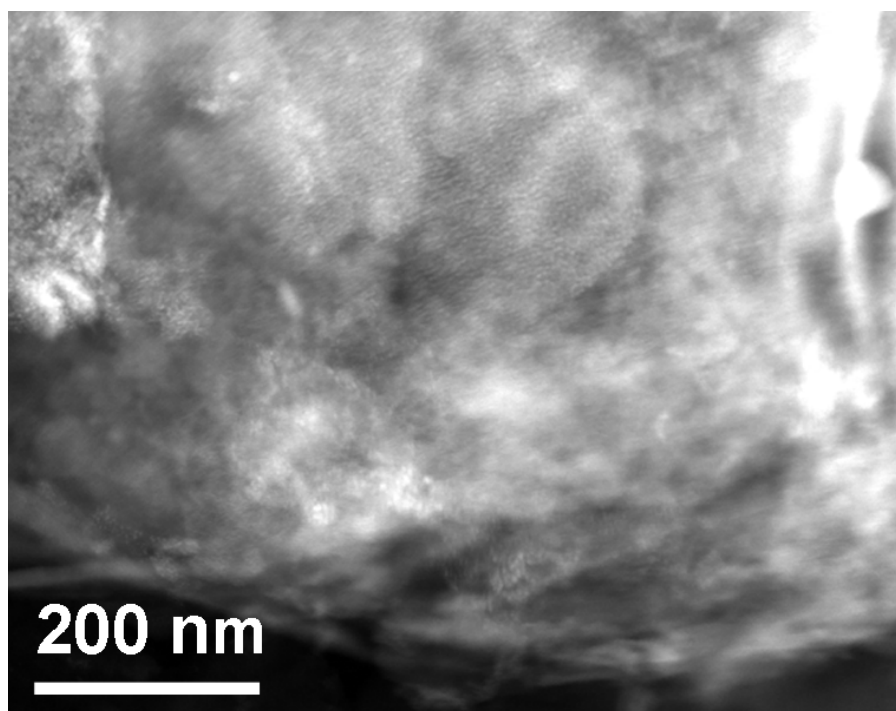
\*Ref. S1 A. P. Grosvenor, B. A. Kobe1, M. C. Biesinger and N. S. McIntyre, *Surf. Interface Anal.*, 2004, **36**, 1564.

\*Ref. S2 V. E. Heinrich, P. A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, 1994.

\*Ref. S3 M. Bronold, Y. Tomm, W. Jaegermann, *Surf. Sci.*, 1994, **314**, L931.

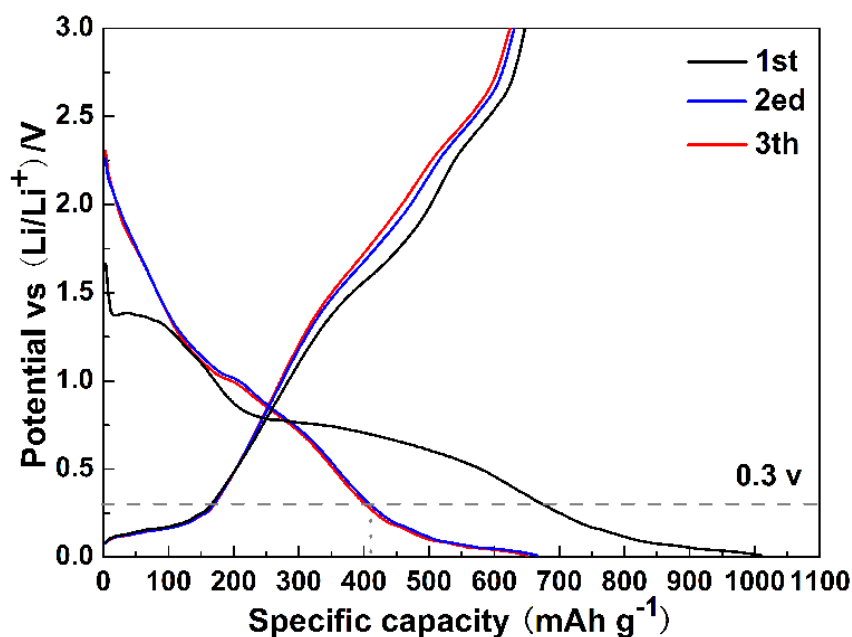


**Figure S4.** CV curves of the C-Cl/FeCl<sub>2</sub>/C-Cl at a scan rate of 0.1 mV s<sup>-1</sup>.



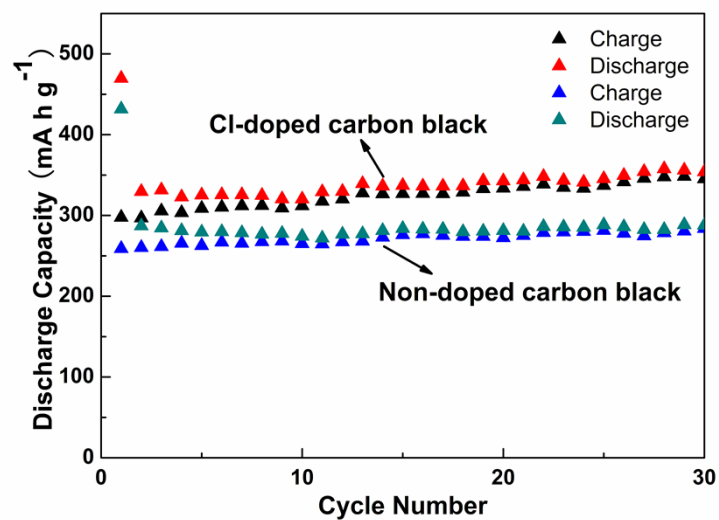
**Figure S5.** STEM of image of the C-Cl/FeCl<sub>2</sub>/C-Cl electrode after initial discharge to 0.01 V.

The STEM image of the discharged electrode shows small nanoparticles evenly dispersed in the graphite matrix. The nanoparticles (3-6 nm) can be assigned to Fe from the Ex situ HRTEM analysis.



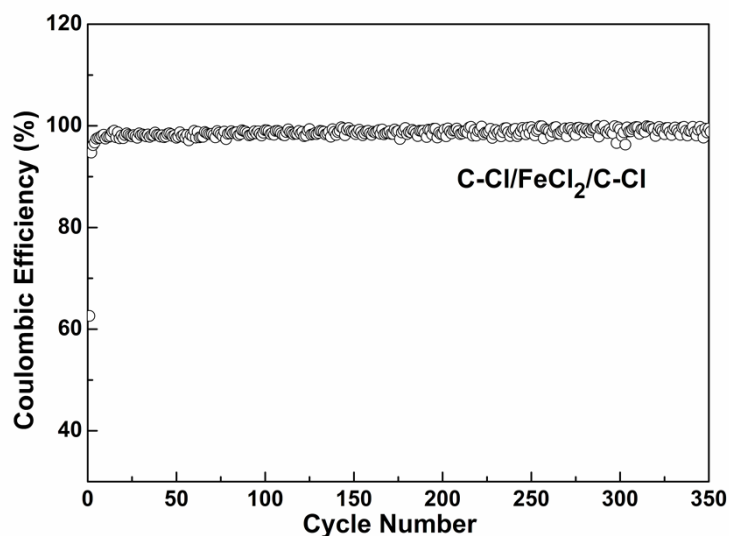
**Figure S6.** Charge and discharge profiles of the C-Cl/FeCl<sub>2</sub>/C-Cl at 0.2 A g<sup>-1</sup> for the first three cycles.

The following discharge/charge profiles of the sample shows two distinct potential regions above and below 0.3 V. The potential below 0.3 V shows a capacity of 236.7 mAh g<sup>-1</sup>, corresponding to the conventional lithium intercalation/deintercalation processes in the natural interlayer of graphite (Li-GICs). The curve shape above 0.3 V has a capacity of 411 mAh g<sup>-1</sup>. The capacity most likely derived from the formation of LiCl accompanying the reduction of Fe nanoparticles in the graphite layers. While, the capacity (411 mAh g<sup>-1</sup>) is much larger than the estimated capacity of 145 mAh g<sup>-1</sup> from the content of FeCl<sub>2</sub>. As the FeCl<sub>2</sub> content of the as-prepared sample determined by X-ray fluorescence spectroscopy (XRF) is approximately 34.3 wt%. The capacity contributed by FeCl<sub>2</sub> can be calculated by:  $422.9 \text{ mAh g}^{-1} \times 34.3\% = 145 \text{ mAh g}^{-1}$ .



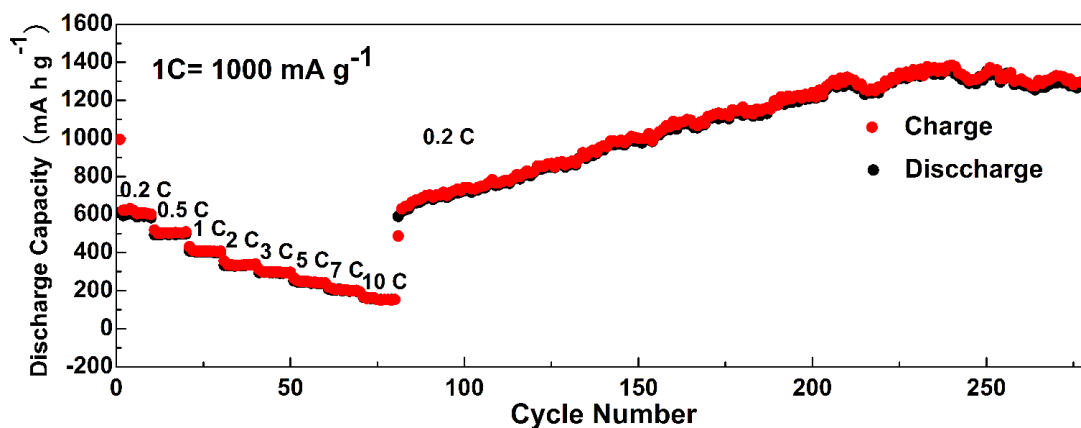
**Figure S7.** Cycle performance of Cl-doped and non-doped carbon black electrodes at a current of  $200 \text{ mA g}^{-1}$  in the voltage range of  $0.01\text{--}3 \text{ V}$ .

To further prove that Cl-doping is benefit to the reversible capacity of the electrode, we have synthesized Cl-doped carbon black with Cl content of about 0.98% (At. %). Compared with the non-doped carbon black electrode, the doped carbon black shows higher reversible capacity, as shown in the Figure S7.



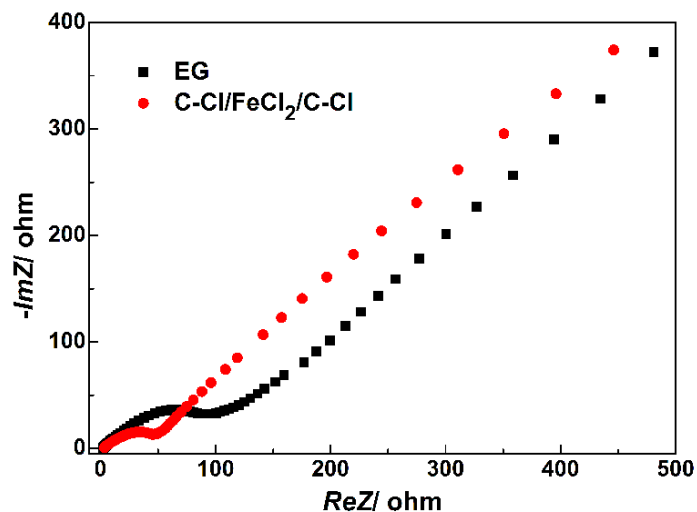
**Figure S8.** Coulombic efficiency of the C-Cl/FeCl<sub>2</sub>/C-Cl electrode at a current density of 500 mA g<sup>-1</sup>.

The coulombic efficiency of the C-Cl/FeCl<sub>2</sub>/C-Cl electrode is 63.6% in the first cycle, and about 99% in the subsequent cycles.



**Figure S9.** Rate performance of C-Cl/FeCl<sub>2</sub>/C-Cl at a current of 1000 mA g<sup>-1</sup>. The sign “C” represent a current density of 1000 mA g<sup>-1</sup>.

After a series of high rate discharge/charge cycles, the current rate turns back to 0.2 A g<sup>-1</sup>, and the capacity of the C-Cl/FeCl<sub>2</sub>/C-Cl electrode can be retained as high as 1286 mA h g<sup>-1</sup> even after 200 cycles.



**Figure S10.** AC impedance of the electrodes based on the C-Cl/FeCl<sub>2</sub>/C-Cl and EG.

The superior ionic conductivity of the C-Cl/FeCl<sub>2</sub>/C-Cl was confirmed by the electrochemical impedance spectroscopy (EIS) measurements. It shows that the semicircle diameter of composites electrode is rather small with respect to that of EG after 3 discharge/charge cycles. The high-frequency semicircle is attributed to SEI film and/or contact resistance, the semicircle in medium-frequency region is assigned to the charge-transfer impedance on electrode/electrolyte interface. Apparently, the C-Cl/FeCl<sub>2</sub>/C-Cl have the smaller surface film resistance and lithium ion charge transfer resistance than those of the EG.