

***Fe₃O₄-Modified FeCl₃/Graphite Intercalation Compound Confinement
Architecture for Unleashing High-Performance Anode Potential of
Lithium-Ion Batteries***

***Kai Zhou¹, Baiyu Guo¹, Jun Ma¹, Siyu Cui¹, Yuying Bao¹, Tao Wang^{1*},
Hailong Qiu^{1*}, Di Jin^{2*}***

1 Clean Nano Energy Center, State Key Laboratory of Metastable Materials Science and Technology, School of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, P. R. China

2 State Key Laboratory of Metastable Materials Science & Technology and Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, China

*Corresponding author: wtcnec@stumail.ysu.edu.cn (T. Wang),
jindi0124@ysu.edu.cn (D. Jin), qiuhl@ysu.edu.cn (H.L. Qiu)

Material characterization. The phase of the as-prepared samples was confirmed by X-ray diffraction (XRD) on a DMAX 2500 (40 kV, 200 mA, Cu K α radiation, $\lambda = 0.15406$ nm), and the measurement settings were 0.02° and 0.25 seconds per step. X-ray photoelectron spectra (XPS) were recorded using a Thermo ESCALAB 250Xi system with monochromatic Al K α radiation as the excitation source. All XPS spectra were calibrated with respect to the C 1s peak (284.8 eV). Scanning electron microscopy (SEM, Helios G4 CX. Thermo Fisher Scientific) and transmission electron microscopy (TEM, Titan cubed Themis Z 60-300 kV) were used to characterize the morphology and microstructure. Energy dispersive X-ray spectroscopy (EDX) elemental mapping and selected area electron diffraction (SAED) were conducted on a Titan cubed Themis Z 60-300 kV system.

Electrochemical measurement. The working electrode was consisted of 80 wt% active material, 10 wt% conductive carbon black and 10 wt% polyvinylidene fluoride (PVDF) binder. The as-prepared mixture was dispersed in NMP to obtain a uniform slurry, which was coated on copper foil and dried in a vacuum oven at 80°C for 12 h to remove NMP. The loading mass of the active material was $1\text{--}1.2$ mg cm^{-2} . The testing cells were assembled using CR2032 coin cells with lithium as the counter electrode. The electrolyte was 1.0 M LiPF $_6$ in ethylene carbonate/diethyl carbonate/dimethyl carbonate (EC/DEC, 1:1 by volume) with 5.0% fluoroethylene carbonate (FEC). Celgard 2325 was used as the separator, lithium metal as counter electrode. All coin-type cells were assembled in an argon-filled glove box ($\text{H}_2\text{O} \leq 0.1$ ppm, $\text{O}_2 \leq 0.1$ ppm).

The galvanostatic charge and discharge tests were performed on a Land CT2001A battery test system in the voltage window of 0.01–3.0 V. Cyclic voltammetry (CV) curves were recorded using PMC CH808A-200 electrochemical workstation with a scan rate of 0.1 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) measurements were carried out from 1000 kHz to 1 Hz with an amplitude of 10 mV on a PMC CH808A-1000 electrochemical workstation.

Computational methods

All calculations were performed using density functional theory (DFT) as

implemented in the CP2K package with Perdew-Burke-Ernzerhof generalized gradient approximation [1-2]. The Goedecker-Teter-Hutter (GTH) pseudopotentials and DZVP-MOLOPT-SR-GTH basis sets were utilized to describe the core region and the wave function, respectively[3-4]. An energy cutoff of 350 Ry was used for plane wave basis set. A vacuum layer of 15 Å in vertical direction to preclude interaction between the adjacent periodic images. The heterostructures were constructed by VASPKIT package with a lattice mismatch less than 3% [5]. The binding energy (ΔE_B) is defined as:

$$\Delta E_{B1} = E(\text{FeCl}_3) + E(\text{substrates}) - E(\text{FeCl}_3\text{-substrates})$$

$$\Delta E_{B2} = E(\text{LiCl}) + E(\text{substrates}) - E(\text{LiCl-substrates})$$

where $E(\text{FeCl}_3\text{-substrates})$ and $E(\text{LiCl-substrates})$ are the total energy of the heterostructures consisting of $\text{FeCl}_3(001)$ or $\text{LiCl}(001)$ with graphite layer, $\text{Fe}_3\text{O}_4(001)$ and $\text{Li}_2\text{O}(001)$, respectively. $E(\text{FeCl}_3)$, $E(\text{LiCl})$ and $E(\text{substrates})$ are the energy of FeCl_3 , LiCl and the substrates(graphite layer, Fe_3O_4 and Li_2O), respectively.

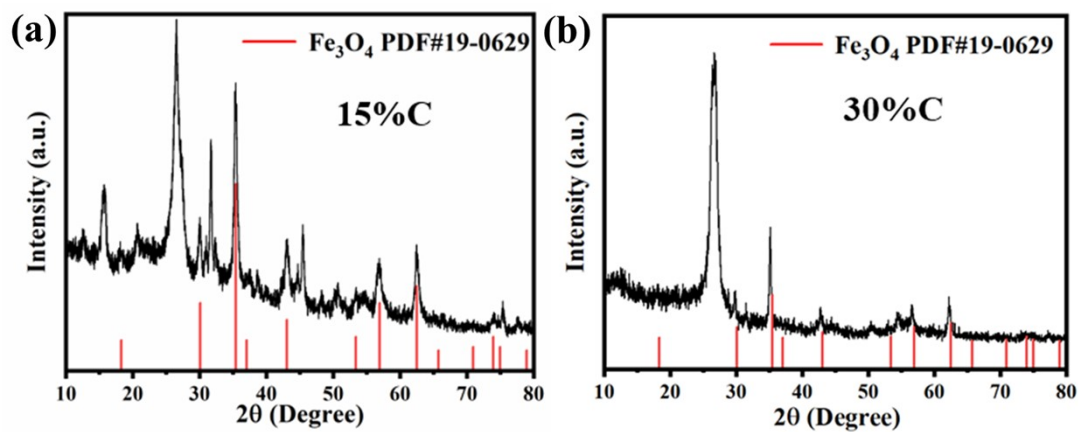


Figure S1. XRD patterns of Fe_3O_4 - FeCl_3 /GIC (a) 15%C and (b) 30%C.

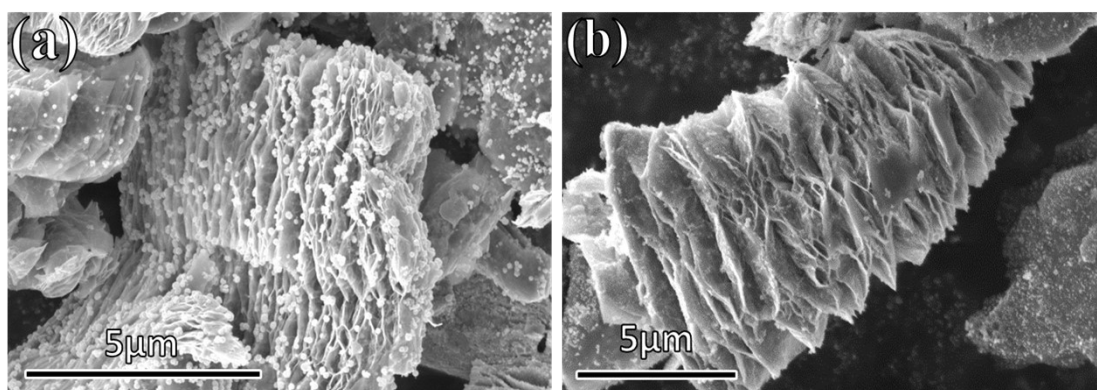


Figure S2. SEM images of (a) Fe_3O_4 - FeCl_3 /GIC 15%C, (b) Fe_3O_4 - FeCl_3 /GIC 30%C.

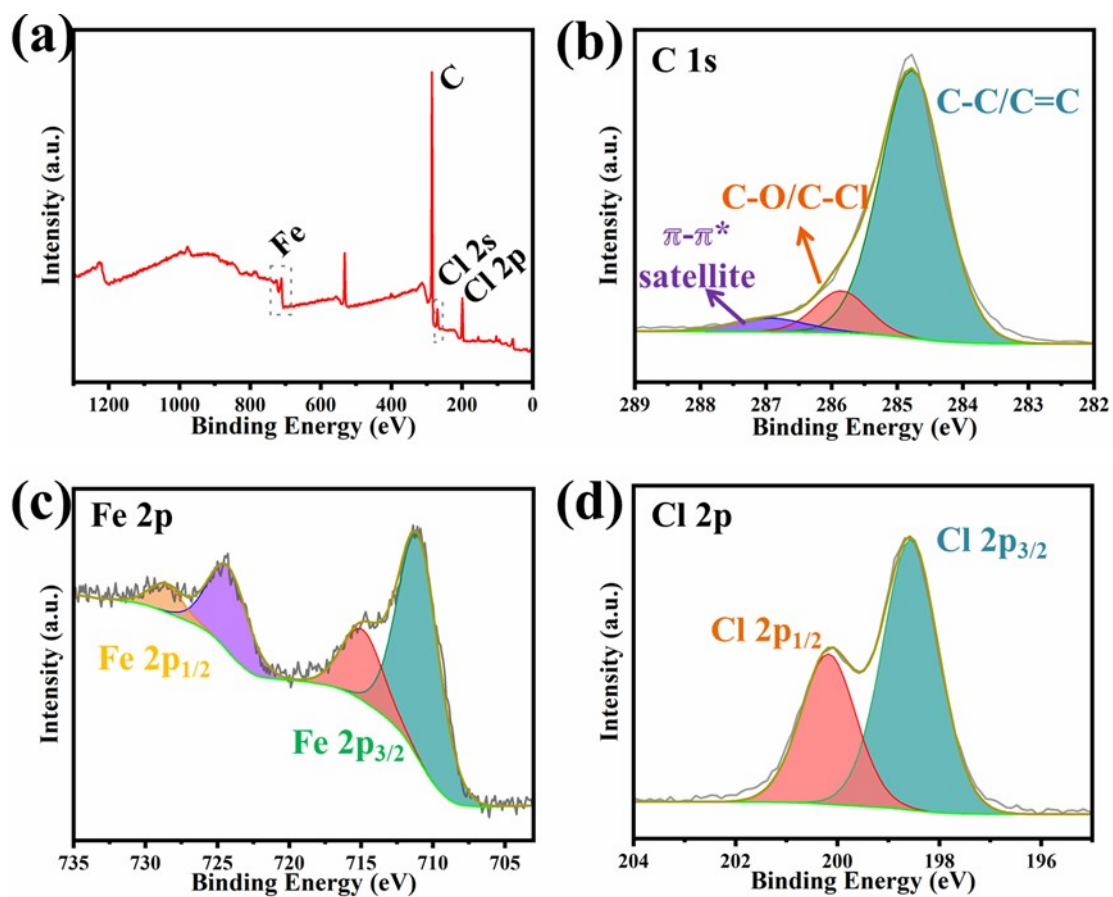


Figure S3. (a) XPS survey spectrum of FeCl₃/GIC 25%C, High-resolution XPS spectrum of (b) C 1s, (c) Fe 2p and (d) Cl 2p.

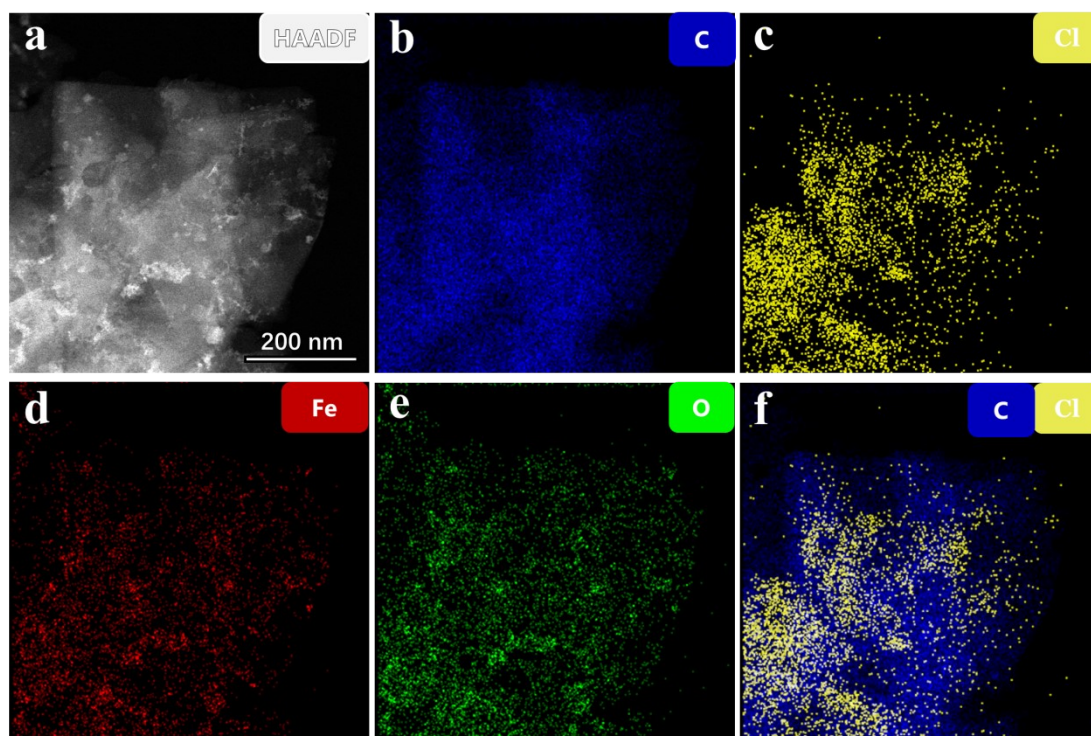


Figure S4. EDS mapping of $\text{Fe}_3\text{O}_4\text{-FeCl}_3/\text{GIC 25\%C}$ (a) HAADF, (b) C, (c) Cl, (d) Fe, (e) O and (f) C and Cl.

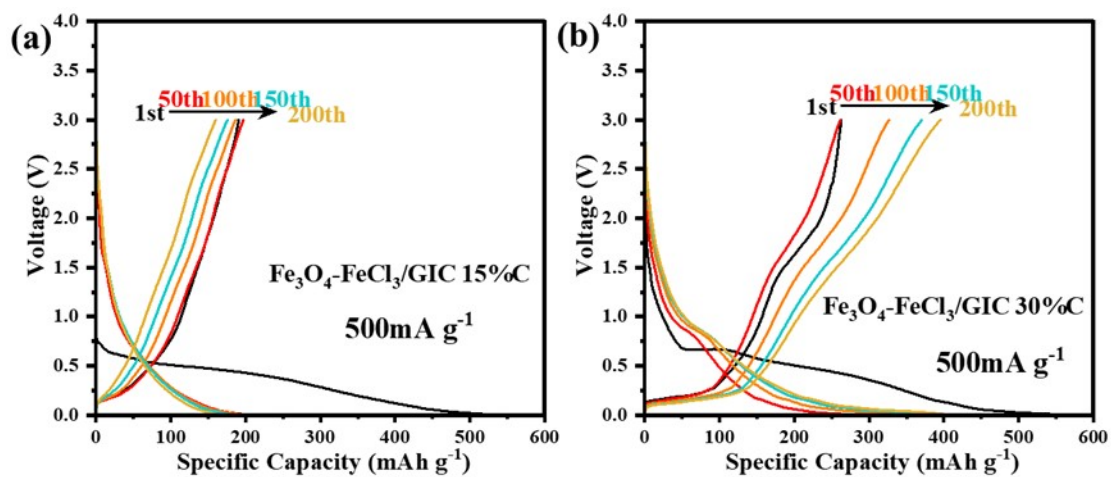


Figure S5. The charge-discharge curves of $\text{Fe}_3\text{O}_4\text{-FeCl}_3/\text{GIC 15\%C}$ and $\text{Fe}_3\text{O}_4\text{-FeCl}_3/\text{GIC 30\%C}$ at 500 mA g^{-1} .

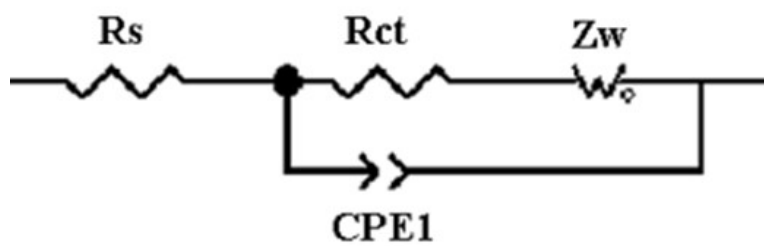


Figure S6. The fitting equivalent circuit

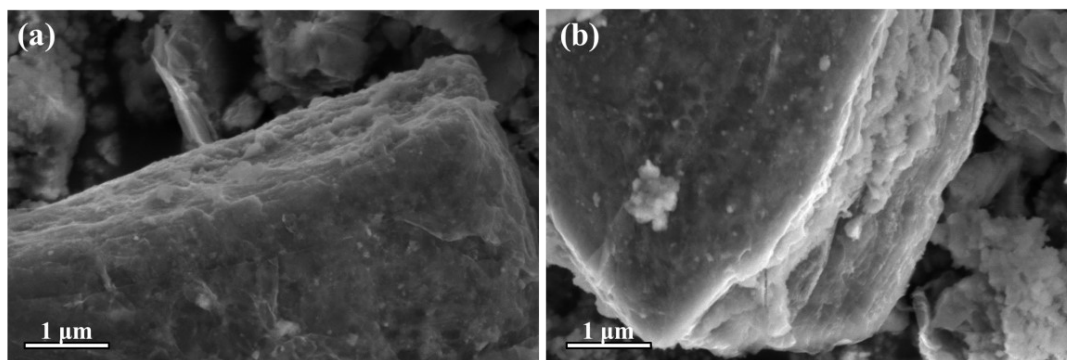


Figure S7. SEM images of (a) and (b) $Fe_3O_4-FeCl_3/GIC$ 25%C after 100 cycles at a current density of 200 mA g^{-1} .

Table S1. EIS pattern of fitted resistance values under different cycle.

	Open	1st	50cycle	100cycle
R_{ct} (Ω)	672.7	39.8	30.0	27.9

References

- [1] Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. CP2k: Atomistic Simulations of Condensed Matter Systems. WileyInterdiscip. Rev.: Comput. Mol. Sci.2014,4,15–25.
- [2] Perdew J P, Burke K, Ernzerhof M. Generalized gradient approximation made simple[J]. Physical review letters, 1996, 77(18), 3865.
- [3] Hartwigsen, C.; Goedecker, S.; Hutter, J. Relativistic Separable Dual-space Gaussian Pseudopotentials from H to Rn.Phys. Rev. B:Condens. Matter Mater. Phys.1998,58, 3641.
- [4] Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-space Gaussian Pseudopotentials.Phys. Rev. B: Condens. Matter Mater. Phys.1996,54, 1703.
- [5] Wang V, Xu N, Liu J C, et al. VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code. Computer Physics Communications, 2021, 267, 108033.