

Supplementary Materials

Electrode Preparation

Material

Polyvinylidene fluoride (PVDF, MW = 1,000,000) was purchased from Duoduo Chemical Reagent. Melamine (MA) was purchased from Sinopharm Chemical Reagent Co., Ltd. The graphite (G) material was provided by Hunan Rongli New Material Technology Co., Ltd. All chemicals and reagents are used directly without further purification.

Preparation of G@FN Material and Electrode Preparation

The G@FN anode material was synthesized via ball-milling followed by a segmented high-temperature carbonization process (Fig. S1). Firstly, 0.75 g of PVDF, 0.5 g of MA, and 3 g of graphite (G) were mixed, placed in a ball-milling jar and co-milled for 6 hours. The ball-milling parameters included a ball-to-powder ratio of 20:1, a rotation speed of 300 rpm, and the rotation direction was alternated (clockwise/counter-clockwise) every 10 minutes. The resulting powder was subsequently dried in an oven at 60 °C for 4 hours. This dried powder was then subjected to heat treatment under an argon atmosphere. The temperature was first raised to 400 °C and held at this temperature for 120 minutes. Subsequently, it was further heated to 600 °C and maintained for another 120 minutes. At 400 °C, the formation of an initial carbon skeleton begins. Around 600 °C, the electrical conductivity of carbon materials undergoes a qualitative improvement. Holding at this temperature enables the coating layer to form a continuous conductive network while retaining sufficient

flexibility to buffer subsequent volume changes at higher temperatures. Finally, the powder, after being cooled to room temperature, was ground using a mortar to obtain the F/N co-doped carbon-coated graphite anode material (G@FN). For comparison, an F-doped carbon-coated graphite sample, denoted as G@F, was also prepared using the identical procedure but by adding only 0.75 g of PVDF without any MA. The active materials (G@FN) and conductive carbon black (Super P) were ground together at a mass ratio of 8:1:1 (G@FN: Super P: CMC). The half-cell assembly process was completed within a glove box filled with argon gas (oxygen and moisture levels were maintained below 0.1 ppm). The negative pole piece was placed in the center of the positive shell using the positive and negative shells of the CR2025 coin cell. Then a 12 mm lithium piece was used as the counter electrode to assemble the CR2025 coin-type half cells, which was sealed with the battery sealing machine.

Electrochemical Measurement and Characterization

The cells underwent charge/discharge tests within a voltage range of 0.005-2 V (vs Li/Li⁺), utilizing a battery testing system (NEWARE, Shenzhen, China). Cyclic voltammetry measurements and electrochemical impedance spectroscopy (EIS, 0.01-105 Hz) were performed on the cells at a CHI600E electrochemical workstation (Chenhua, Shanghai, China). The surface morphological characteristics of the materials were examined using a scanning electron microscope (SEM, S-4800, Japan) and a transmission electron microscope (TEM, Titan G2 60-300). The elemental distribution in the sample was analyzed using Energy-dispersive X-ray Spectroscopy (EDS). The X-ray diffraction analysis (XRD, Shimadzu 7000S/L type 40 kV, Cu K α) and Raman

spectrometry (Raman, Thermo Fisher Nicolet iS10) characterized the chemical structure of the materials. The full-spectrum and high-resolution scans were completed using X-ray Photoelectron Spectroscopy (XPS, Al K α).

Supplementary Equation

Supplementary Equation S1

Determination of the degree of graphitization by XRD: first determine the graphite (002) crystal layer spacing $d_{(002)}$.

$$n\lambda = 2d\sin\theta$$

$$d = \frac{n\lambda}{2\sin\theta}$$

In the above equation: λ is the wavelength of X-rays, $\lambda = 1.54056 \text{ \AA}$; θ is the position of the diffraction peak in radians; n is the number of diffraction steps, $n = 1$.

The degree of graphitization can be calculated by substituting the Mering-Maire formula (also known as the Franklin formula):

$$G = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100\%$$

In the above equation: G is the degree of graphitization; 0.3440 is the layer spacing of non-graphitized carbon, nm; 0.3354 is the layer spacing of ideal graphite crystals, nm; and d_{002} is the layer spacing of the crystalline surface of carbon material (002), nm.

Supplementary Equation S2

The diffusion coefficient of Li^+ was measured using GITT with a pulse current of 0.1C for 10 min and a rest interval of 40 min. The lithium ion diffusion coefficient can be calculated according to the simplified Fick's Second Law by using the following

equation:

$$D_{Li^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

In the above equation: τ is the pulse duration, s; m_B is the mass of the active substance; V_M is the molar volume, cm^3/mol ; M_B is the molar mass, g/mol ; S is the interfacial area of electrode/electrolyte, cm^2 ; ΔE_S is the steady-state voltage range (V) induced by the current pulse; ΔE_τ is the voltage change (V) during the constant current pulse.

Supplementary Equation S3

Electrochemical impedance spectroscopy is an important tool to study the diffusion kinetics of lithium ions in electrode materials and to obtain the internal diffusion coefficient of the charge transfer resistance of Li^+ at the electrode interface.

The formula for testing the lithium ion diffusion coefficient by EIS is as follows:

$$D_{Li^+} = 0.5 \left(\frac{RT}{An^2 F^2 C \sigma} \right)^2$$

$$\left(\omega \gg \frac{D_{Li^+}}{L^2} \right)$$

In the above equation: D_{Li^+} is the lithium ion diffusion coefficient to be calculated, cm^2/s ; R is the gas constant, $\text{J}/(\text{mol}\cdot\text{K})$; T is the absolute temperature; A is the electrode area, cm^2 ; n is the number of electrons transferred during the reaction; F is the Faraday constant, C/mol ; C is the lithium ion concentration, mol/cm^3 ; σ is the Warburg coefficient. The Warburg coefficient σ is calculated as follows:

$$Z' = R_s + R_{ct} + \sigma \omega^{-\frac{1}{2}}$$

$$(\omega = 2\pi f)$$

In the above equation: ω is the angular frequency; f is the frequency; Z' is the real

part impedance; the Warburg coefficient σ can be obtained from the slope of the linear fit between Z' and $\omega^{-1/2}$.

Supplementary Equation S4

The exchange current density j_0 is calculated as follows:

$$j_0 = \frac{RT}{nFR_{ct}A}$$

In the above equation: j_0 is the exchange current density, A/cm²; R is the gas constant, J/(mol·K); T is the absolute temperature, tested at room temperature 25°C; A is the area of the electrode/electrolyte interface, cm²; n is the number of electrons per molecule during the reaction; F is the Faraday constant, C/mol; R_{ct} is the charge transfer resistance.

Supplementary figures

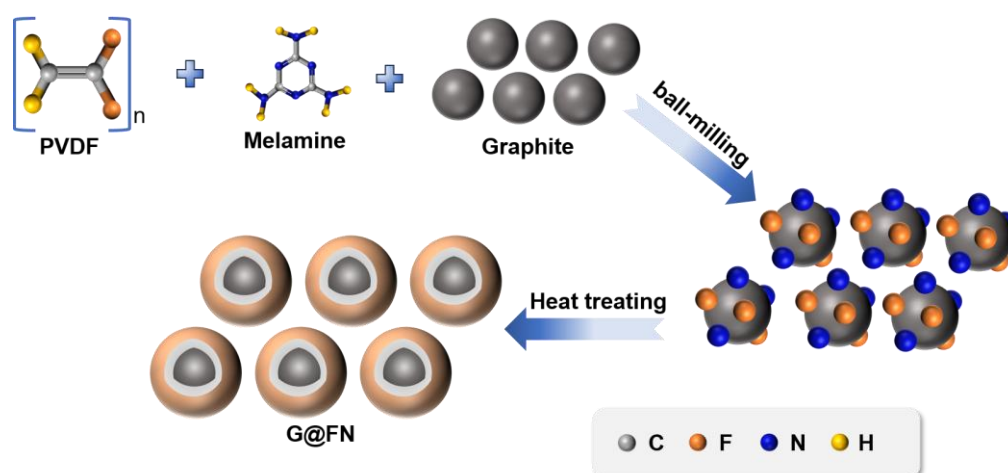


Figure S1 Schematic illustration of the synthesis process for the F/N co-doped carbon-coated graphite anode material.

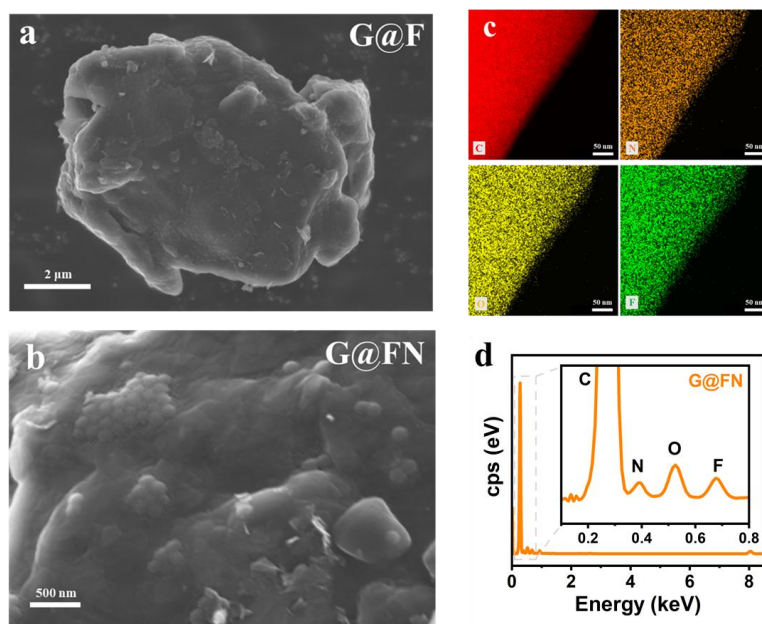


Figure S2 (a) SEM images of G@F; (b) SEM images of the local area of G@FN; (c) EDS elemental mapping of G@FN; (d) EDS spectrum of G@FN.

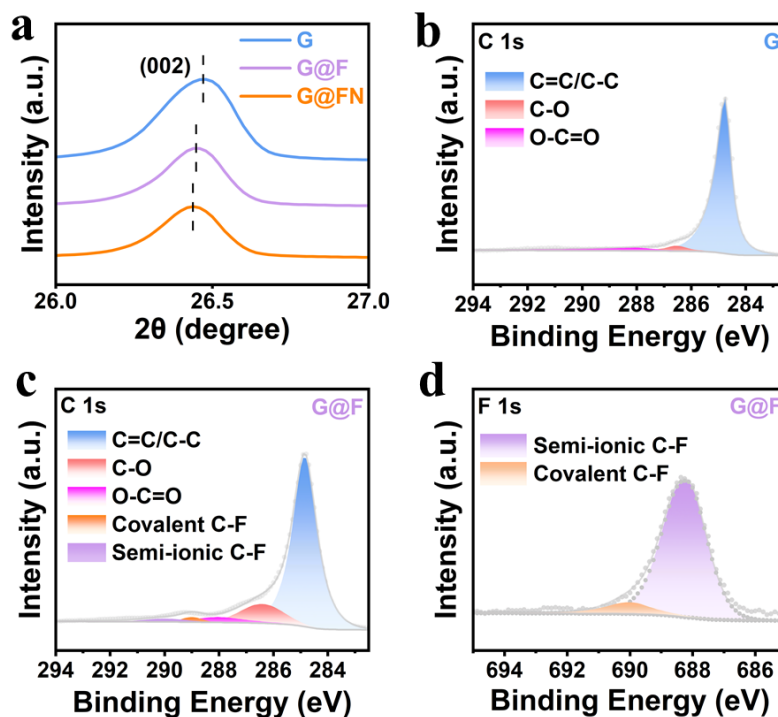


Figure S3 (a) Comparison of the graphite (002) diffraction peaks in the XRD patterns of G, G@F and G@FN materials; (b) C 1s spectrum of G; (c) C 1s spectra of G@F; (d) F 1s spectrum of G@F.

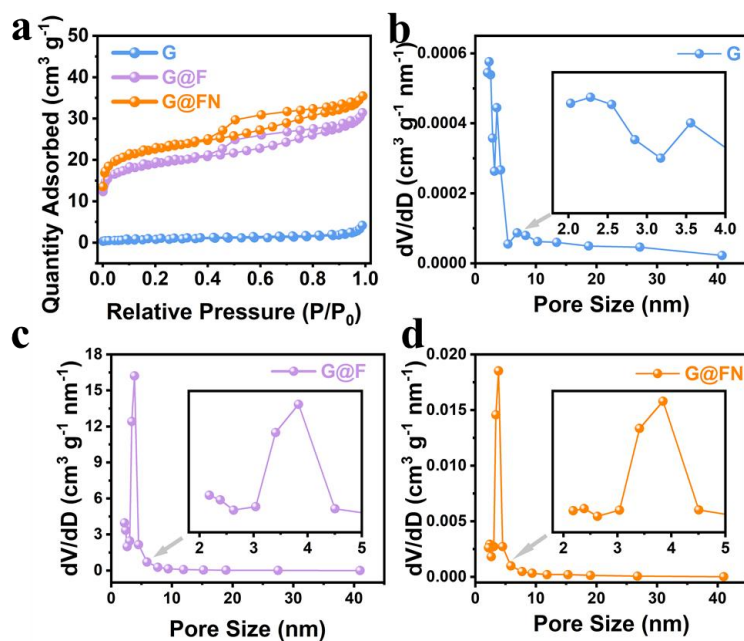


Figure S4 (a) N₂ adsorption/desorption isotherms of G, G@F and G@FN; (b-d) Pore size distributions of G, G@F and G@FN.

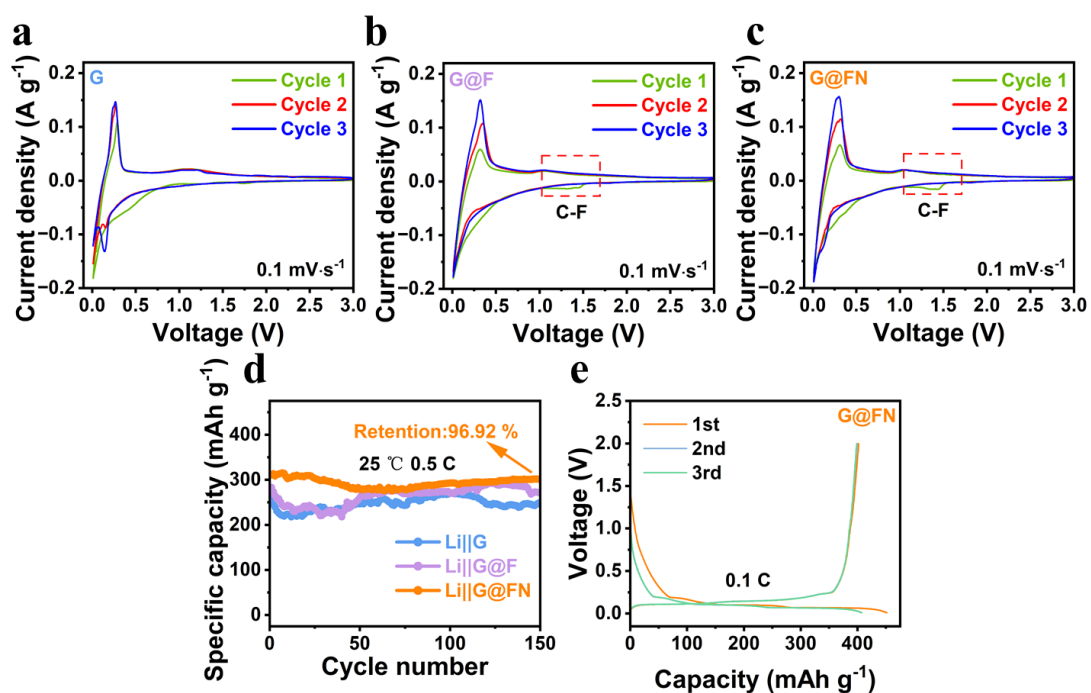


Figure S5 (a-c) CV curves of G, G@F and G@FN at 0.1 mV s⁻¹; (d) Cycling performance at 0.5 C; (e) Constant current charge/discharge curves of G@FN in the first three cycles at 0.1C.

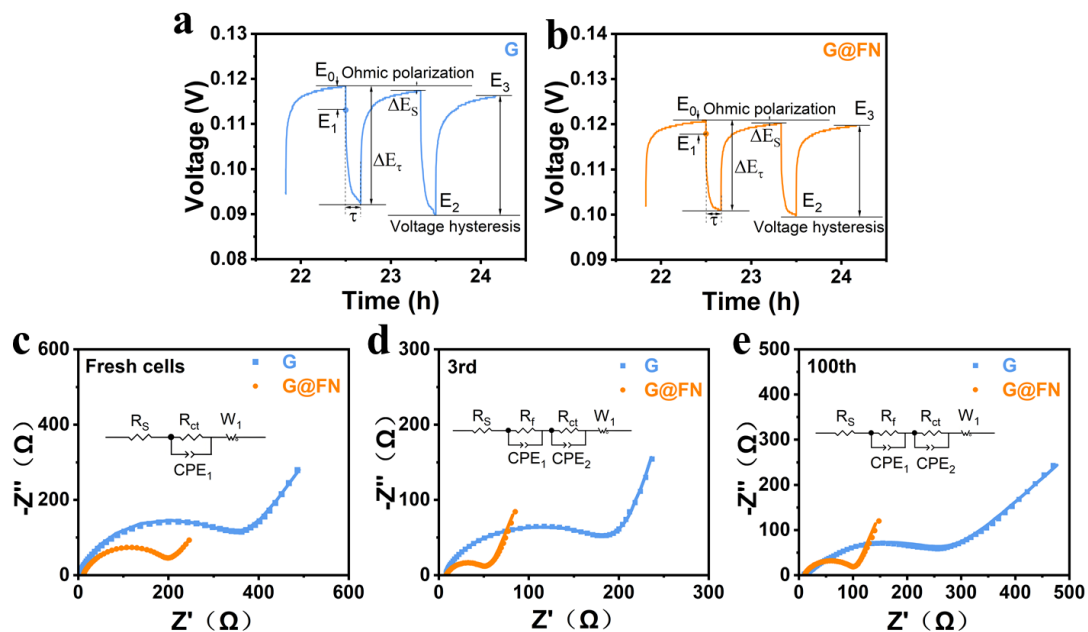


Figure S6 (a, b) Voltage vs. time curve of G and G@FN anode measured by GITT; (c-e) EIS curves after 0, 3, and 100 cycles.

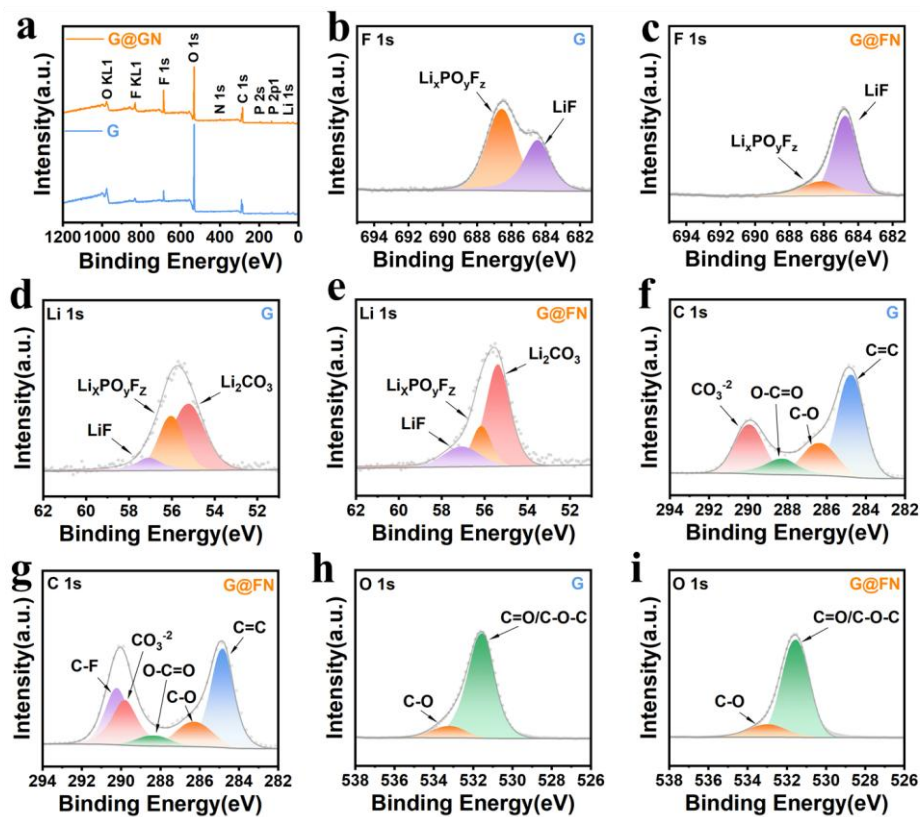


Figure S7 (a) Comparison plot of the total spectrum of XPS spectra after 100 cycles; (b, c) XPS F 1s spectra of G and G@FN after 100 cycles; (d, e) XPS Li 1s spectra of G

and G@FN after 100 cycles; (f, g) XPS C 1s spectra of G and G@FN after 100 cycles; (h, i) XPS O 1s spectra of G and G@FN after 100 cycles.

Supplementary Table

Supplementary Table S1 Comparison of layer spacing and graphitization degree between G, G@F and G@FN.

Sample	$2\theta(^{\circ})$	$d_{002}(\text{nm})$	G(% _{100%})
G	26.47156	0.33642	88.13
G@F	26.44907	0.33670	84.88
G@FN	26.43981	0.33682	83.48

Supplementary Table S2 The atomic ratios of C, O, F and N elements in the prepared anode materials were determined by XPS.

Sample	C (at.%)	O (at.%)	F (at.%)	N (at.%)
G	98.39	1.61	\	\
G@F	90.54	3.53	5.93	\
G@FN	88.38	3.35	5.04	3.23

Supplementary Table S3 N 1s spectra data of G@FN.

G@FN N 1s	Pyridinic- N	Pyrrolic- N	Graphitic- N	Oxidized- N	Fluorinated- N
Binding Energy(eV)	398.18	400.28	402.36	405.18	408.01
Content(%)	38.40	35.26	16.72	6.73	2.87

Supplementary Table S4 The specific surface areas, porosities and average pore diameters of G, G@F and G@FN.

Sample	specific surface area (m ² /g)	porosity (cm ³ /g)	average pore diameter (nm)
G	2.8506	0.0064	10.0617
G@F	70.9343	0.0486	5.0527
G@FN	84.5031	0.0548	4.5587

Supplementary Table S5 Comparison of the interlayer spacing and degree of graphitization of G, G@F and G@FN materials before and after cycling.

Sample	2 θ (°)	d ₀₀₂ (nm)	G(%,100%)
G	26.47156	0.33642	88.13
G 100th	26.42448	0.33701	81.27
G@FN	26.43981	0.33682	83.48
G@FN 100th	26.43577	0.33687	82.90

Supplementary Table S6 Comparison of D and G peak positions and FWHM for G and G@FN before and after cycling.

Sample	D peak(cm ⁻¹)	D peak FWHM	G peak	G peak FWHM
G	1354.85	45.15	1578.92	25.17
G 100th	1356.64	94.12	1582.54	44.77
G@FN	1375.07	344.81	1587.74	79.89
G@FN 100th	1376.45	272.37	1588.79	82.48