

**Graphitic carbon nitride (g-C₃N₄) as an electrolyte additive boosts fast-charging
and stable cycling of graphite anodes for Li-ion batteries**

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Supporting Materials

EXPERIMENTAL

Preparation of Electrolyte

A mixture of ethylene carbonate(EC), ethyl methyl carbonate (EMC) and ethyl methyl carbonate (EMC) (1:1:1, vol %) with 1 M LiPF₆ was used as an ordinary electrolyte (OE), which from Zhangjiagang Guotai Huarong Chemical New Materials Co., LTD. The modified electrolyte was prepared by adding g-C₃N₄ (from Shanghai Maclin Biochemical Technology Co., LTD) to the OE with a mass ratio of 0.5 wt%, and followed by stirring the mixture for 24 h, the modified electrolyte is denoted as O-CN.

Preparation of Batteries and the Electrochemical Tests

All electrochemical performances of the samples were tested in Neware CR2025 coin cells. The graphite electrodes including active materials (80wt %), carbon black (10wt %), and polyvinylidene fluoride (10wt %) were added in N-methyl pyrrolidinone (NMP), and then the slurry was casted on Cu foil. After drying at 80 °C for 12 h, the electrodes were reserved in a glovebox filled with argon. The lithium sheet was used as the counter and reference electrode in the cell, and Celgard 2400 was used as separator. Based on the amount of separator and active material used, 70 μL electrolyte was added to each cell. The cells were placed on the LAND Test System (LAND 2001 CT Wuhan China) equipment for an electrochemical performance test at room temperature. CV

plots were recorded on an electrochemical workstation (CHI604 Chenhua, Shanghai) and the scanning rate of cyclic voltammetry (CV) curves was 0.1 mV s⁻¹ in the voltage range of 0.01-2 V. The Nyquist diagrams were recorded utilizing an alternating current (AC) oscillation with a magnitude of 5 millivolts, within a frequency sweep from 100 kilohertz to 0.01 hertz, in the temperature range of 293 K to 323 K. Aiming at the changes of the components in the SEI film mentioned above, we used the Arrhenius equation to fit the impedance curves of graphite||Li cells at different temperatures after five cycles. The activation energies to overcome SEI film resistance and charge transfer were analyzed.

$$\frac{1}{R_{SEI/ct}} = A \exp\left(\frac{Ea}{RT}\right)$$

The formula can also be converted into :

$$\ln\left(\frac{1}{R_{SEI/ct}}\right) = \ln A - \frac{Ea}{RT}$$

where $R_{SEI/ct}$ is the SEI resistance or charge transfer resistance, A is the frequency coefficient, R is the ideal gas constant, T is the reaction temperature, and Ea is the reaction activation energy. In addition, $R_{SEI/ct}$ can be fitted from the impedance results of the electrochemical workstation test, and T refers to the thermodynamic temperature, so the slope $-Ea/R$ can be obtained by graphical fitting with $1000/T$ as the x-axis and $\ln(1/R_{SEI/ct})$ as the y-axis, where R refers to the ideal gas constant of 8.314 J (mol·K)⁻¹, and thus the value of Ea can be obtained.

The Li⁺ transference number (t_{Li^+}) was calculated using the Bruce–Vincent method:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where I_0 and I_s are initial-state and steady-state current, respectively. R_0 and R_s are resistance values measured at initial-state and steady state conditions, respectively. ΔV is the applied constant potential of 10 mV during the polarization process. All above tests were carried out by using Li/Li symmetric cells on a Solartron Analytical Electrochemical Workstation at RT.

Material Characterization

Morphologies of graphite electrodes were observed by using SEM (S 4800). The graphite electrode was obtained via disassembling the graphite||Li cell cycled for 5 times, followed by rinsed in dimethyl carbonate and dried in an argon-filled glovebox. The crystallographic structure was analyzed by X-ray diffractometer (XRD, D/MAX-IIA, Rigaku) with Cu-K α radiation ($\lambda = 0.15406$ nm) at a scanning angle (2θ) range of 10° to 90° . The ionic conductivity of different electrolytes was measured at room temperature with a Solartron Analytical Electrochemistry Workstation. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD. For the XPS test, the cell was disassembled in a glovebox, and the composite powder was collected after drying the rinsed electrode with dimethyl carbonate (DMC). Raman spectroscopy for the electrolyte structure was conducted on Horiba LabRAM HR Evolution microscope with a 735 nm excitation laser.

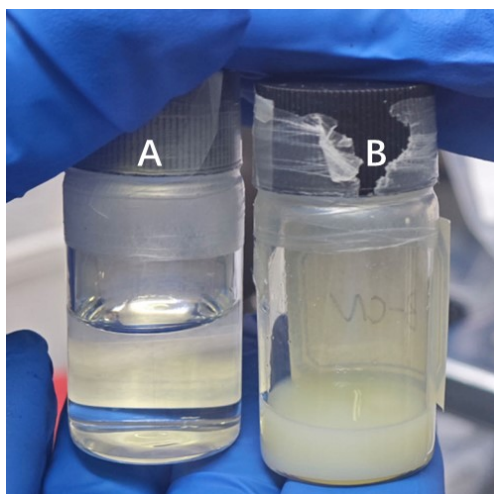


Fig. S1. The photographs of electrolytes at room temperature. A is OE electrolyte, and B is O-CN electrolyte.

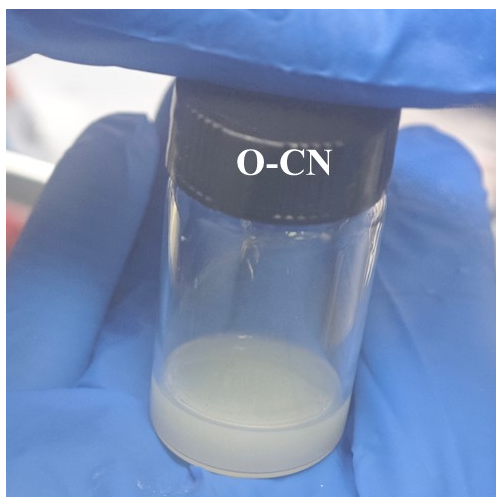


Fig. S2. The photographs of O-CN electrolyte after standing for three days.

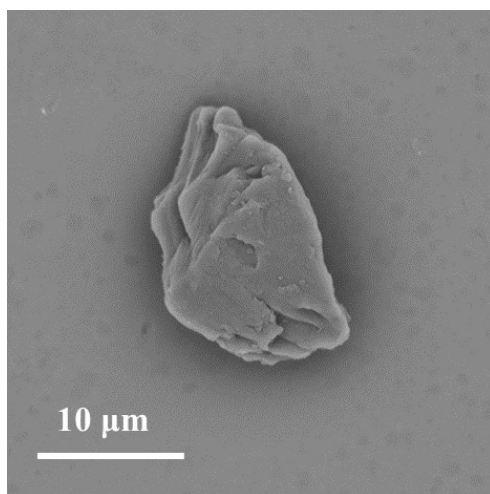


Fig. S3. SEM images of graphite powder.

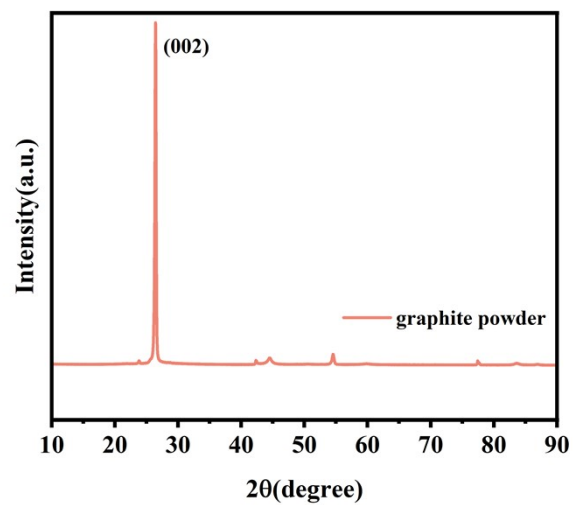


Fig. S4. XRD image of graphite powder.

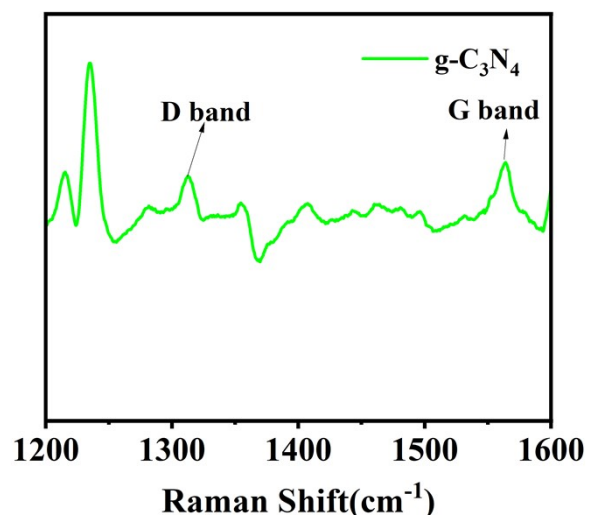


Fig. S5. Raman fitting spectra of g-C₃N₄.

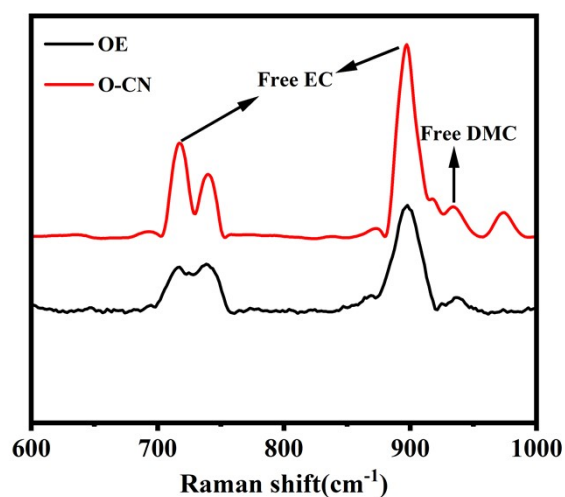


Fig. S6. Raman spectra of OE and O-CN electrolyte.

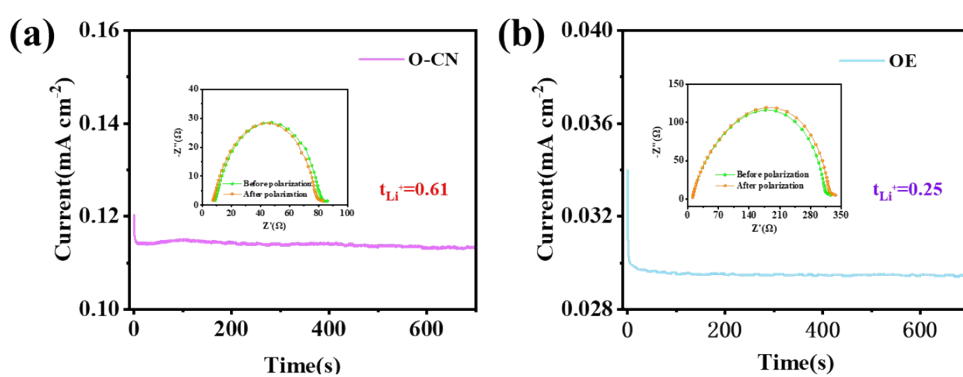


Fig. S7. Li^+ transference number measurements of (a) O-CN electrolyte and (b) OE electrolyte.

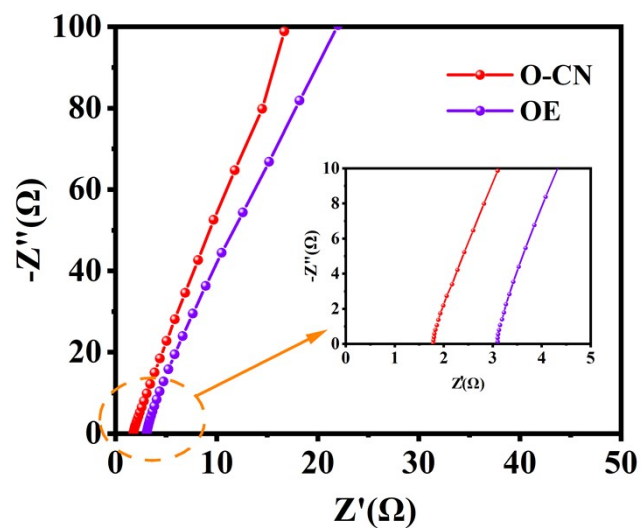


Fig. S8. The fitting results of ionic conductivity in OE and O-CN electrolyte respectively.

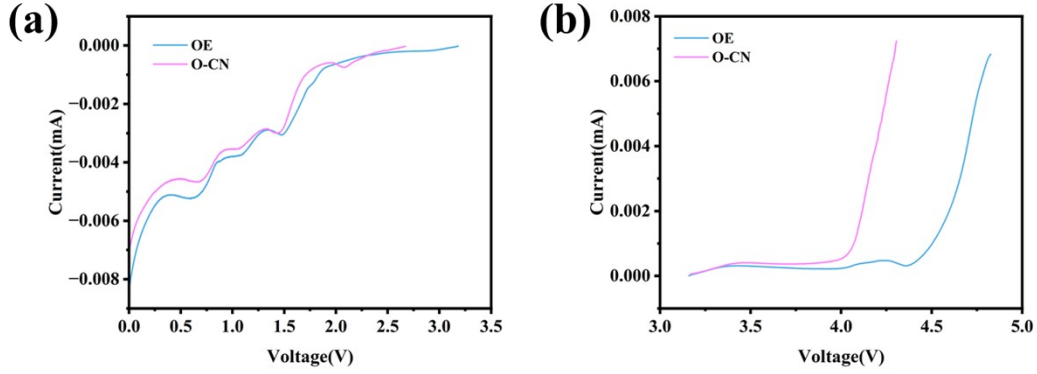


Fig. S9. LSV measurements of Li||SS cells in OE and O-CN electrolyte.

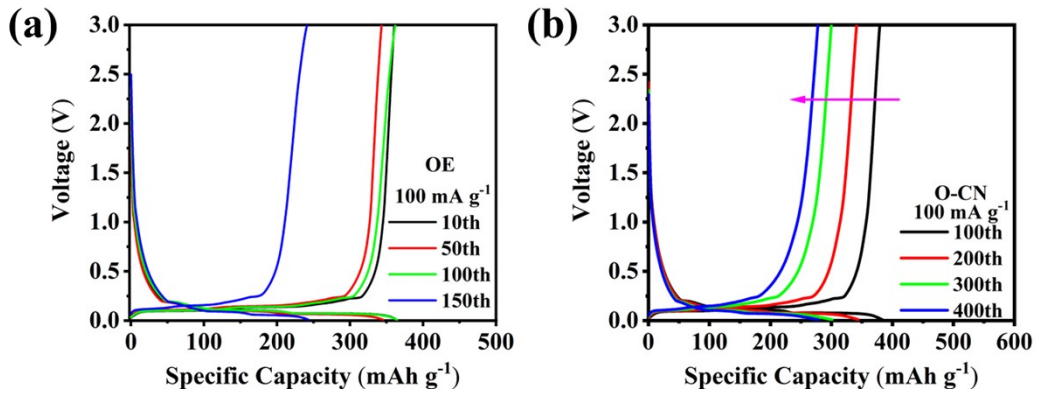


Fig. S10. Selected charge–discharge curves for the Graphite||Li cells with OE (a) and O-CN electrolyte (b).

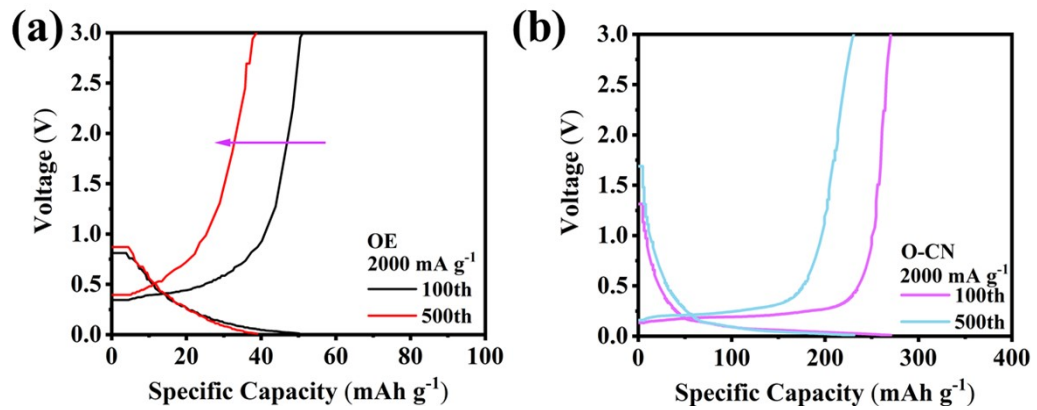


Fig. S11. Selected charge–discharge curves for the Gr||Li cells at different cycles.

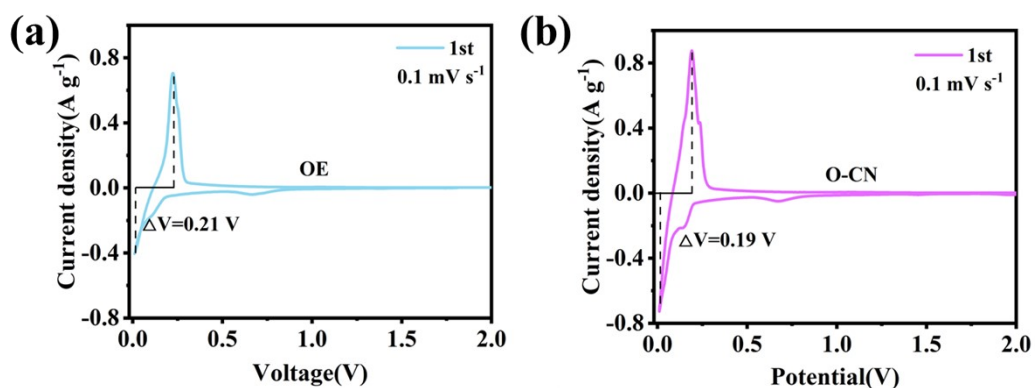


Fig. S12. CV curves of graphite||Li cells with (a) OE and (b) O-CN electrolytes at 0.1 mV s⁻¹.

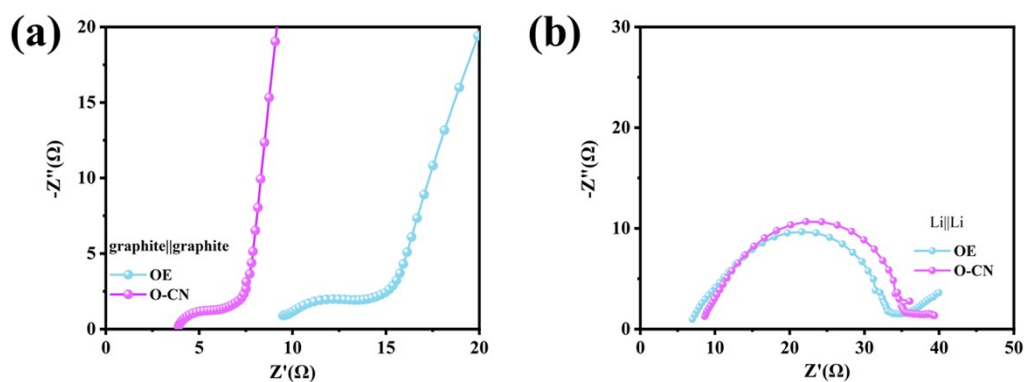


Fig. S13. The electrochemical impedance spectra of (a) graphite||graphite cells and (b) Li||Li cells with OE and O-CN electrolyte respectively.

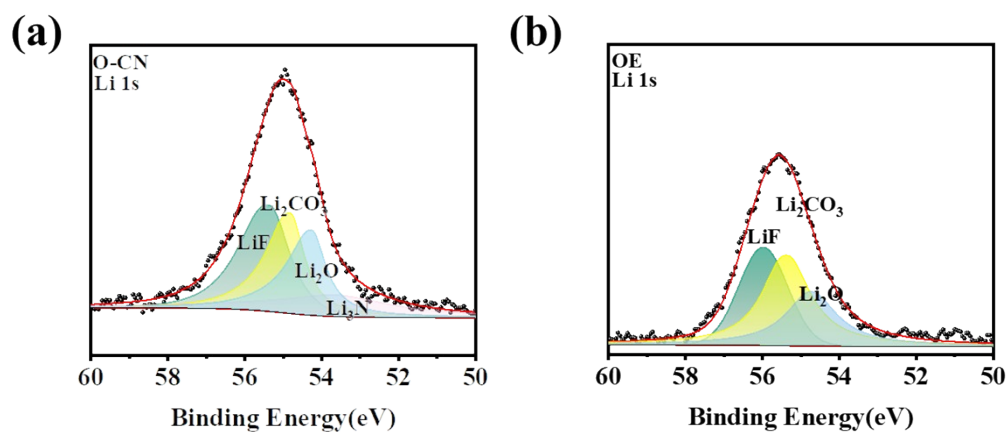


Fig. S14. XPS spectra of (a, b) Li 1s of the graphite electrode cycled in OE and O-CN for five times.

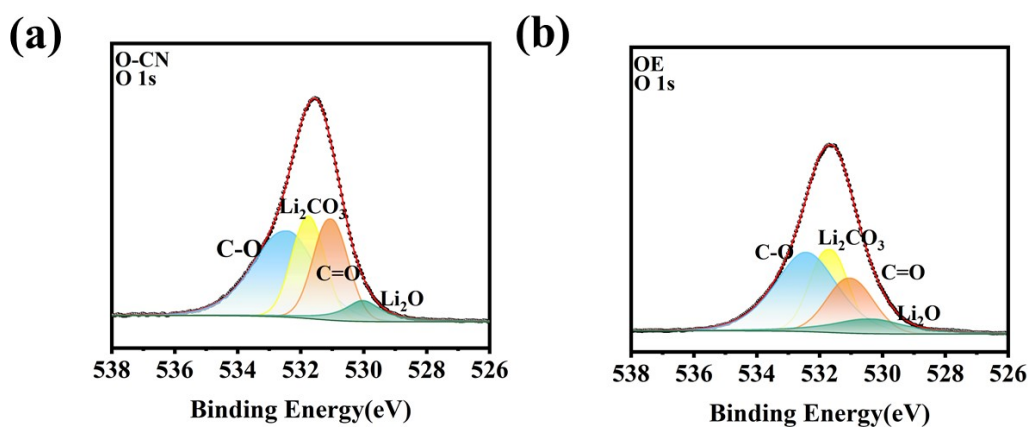


Fig. S15. XPS spectra of (a, b) O 1s of the graphite electrode cycled in OE and O-CN for five times.

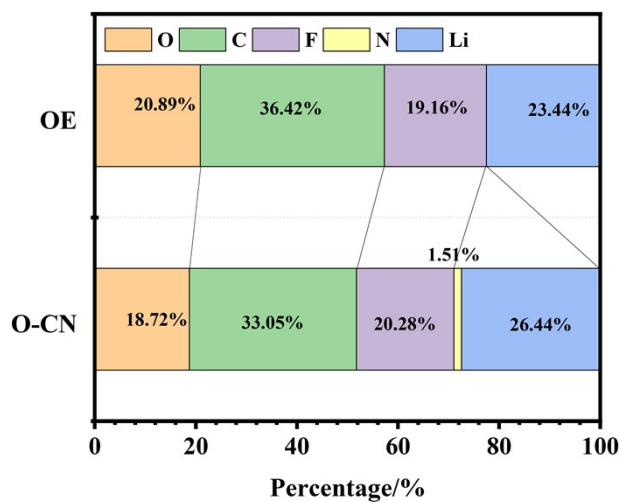


Fig. S16. Atomic ratio of different elements on the surface on graphite cycled in (a) OE and (b) O-CN at 25 °C.

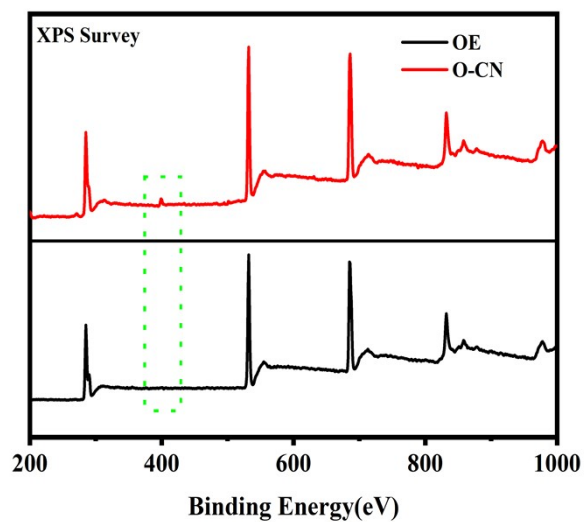


Fig. S17. XPS survey spectra of the graphite electrode cycled in OE and O-CN electrolyte for 5 times.

Table S1. The impedance values derived from the curve fitting.

	293 K		303 K		313 K		323 K	
	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	R_{SEI}	$R_{ct}(\Omega)$
OE	17.65	179.8	6.57	84.86	4.91	40.94	2.44	9.93
O-CN	5.65	104.1	3.86	46.41	2.45	22.71	1.6	11.48