Supporting Information

Riemannian Surface on Carbon Anode Enables Li-ion Storage at -35 °C

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Experimental Procedures

Chemicals

All chemicals used in this study were of analytical grade and used directly without further purification. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), multiwalled carbon nanotube (MWCNT) and diamond were obtained from Aladdin. 2-methylimidazole was supplied by Innochem. Methanol was purchased from Beijing Chemical Plant. Moreover, the separator (Celgard 2400) was purchased from Hoechst Celanese.

Materials synthesis

Preparation of ZIF-67. Typically, 350 mg Co(NO$_3$)$_2$·6H$_2$O and 765 mg 2-methylimidazole were dissolved into 30 mL of methanol, respectively, to form the pink and colorless solutions, respectively. Subsequently, the pink solution was instantly poured into the colorless solution under constant stirring. The whole mixed solution was thoroughly mixed and incubated at room temperature for 24 h. The as-obtained precipitates were collected by centrifugation, washed three times with ethanol, and finally dried under vacuum at 80 °C for 12 h to obtain purple ZIF-67 crystals.

Synthesis of O-DF and T-DF. The as-prepared purple ZIF-67 powders were heated to 425 °C with a heating rate of 5 °C min$^{-1}$ in a tube furnace and maintained for 1 h under an Ar/H$_2$ gas flow (10% H$_2$). Finally, the obtained black powders were designated as O-DF. As a control, a dodecahedral carbon framework assembled with interconnected N-doped carbon nanotubes was also synthesized by annealing the ZIF-67 precursor at 600 °C for 1 h under an Ar/H$_2$ gas flow (10% H$_2$), which was denoted as T-DF.

Characterization methods

The morphology and structure of the as-prepared products were characterized by scanning electron microscope (SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100F and ARM-200CF). X-ray diffraction (XRD) patterns were measured by using a Rigaku
Ultima III instrument with a Cu Kα radiation source (λ = 1.5406 Å) to analyze the phase composition of the samples as above mentioned. Raman spectra were measured by using Horiba Jovin Yvon T64000 Raman spectroscope (λex= 532 nm). Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) from 30 °C to 1000 °C was carried out on EXSTAR TG/DTA STK-6300 with a heating rate of 5 °C min⁻¹ under an Ar/H₂ gas flow (10% H₂). X-ray photoelectron spectroscopy (XPS) was acquired on an ESCALAB 250Xi instrument. The Brunauer-Emmett-Teller surface and nitrogen adsorption-desorption isotherms of the products were collected by using a Quantachrome Autosorb-IQ2 system at 77 K. The K-edge X-ray absorption spectra of C were collected by the surface-sensitive total electron yield (TEY, monitoring depth of about 5 nm) mode on the soft X-ray absorption near-edge structure (XANES) spectroscopy beamline at Beijing Synchrotron Radiation Facility.

**Electrochemical characterizations**

80 wt% Active materials, 10 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) were homogeneously suspended in N-methyl-pyrrolidone to produce a slurry. The resulting slurry was directly coated onto a copper foil and dried at 80 °C in vacuum for 12 h. The dried electrodes were further cut into disks with a diameter of 14 mm. The mass loading of active material was ~12.4 mg/cm². The electrolyte was consisted of 1M LiPF₆ in the ethyl carbonate (EC) and diethyl carbonate (DEC) (EC/DEC = 1:3, v/v). Li metal and polypropylene film (Celgard 2400, Hoechst Celanese) were collected as the counter electrode and the separator, respectively. The CR2025-type coin cells were assembled in an argon-filled glovebox. The galvanostatic charge-discharge tests were performed with LAND (CT2001A) in the voltage range of 0.01-3 V. Cyclic voltammetry (CV) was carried out between 0.01 and 3.0 V in the CHI 760E electrochemical workstations. Electrochemical impedance spectroscopy (EIS) was measured on a CHI 760E electrochemical workstation (Shanghai) by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 0.01 Hz to 100 kHz.

**Computational methods**
Theoretical calculations were performed with the Vienna ab initio Simulation Package (VASP) based on the plane-wave pseudopotential density functional theory (DFT) methods. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) was used as electron exchange and correlation functionals. The Kohn–Sham equations were extended using plane waves basis set with a cutoff energy of 500 eV. The energy and force convergence thresholds for the geometry optimization were set to $10^{-5}$ eV and 0.02 eV/Å, respectively. To avoid interactions between periodic images, a sufficiently large vacuum space was employed in the $z$-direction. For positive curvature, zero curvature and negative curvature graphene clusters, their lattice constants are 25×25×55 Å, 14.76×14.76×20 Å, and 30×30×25 Å, respectively.

The adsorption energy ($E_{ad}$) is calculated to examine the stability of TM/g-CN, which are defined as:

$$E_{ad} = E_{total} - E_{surface} - E_{Li}$$

where $E_{total}$, $E_{surface}$ and $E_{Li}$ represent the energy of graphene with Lithium adsorption, graphene without Lithium adsorption and isolated lithium atom, respectively. The more negative $E_{ad}$ means the stronger binding strength.

To compute the hybridization number (sp$^3$), we optimized the cluster structures at B3LYP/6-31g* level and performed the natural bonding orbital (NBO) analysis with the NBO-3.1 version implemented in Gaussian09 package.
Results and discussion

Figure S1. Side and top views and the corresponding adsorption energies of a single Li atom adsorbed on (a) zero curvature carbon, (b) negative curvature carbon and (c) positive curvature carbon.

The synthesis mechanism of O-DF

During the pyrolysis process, the coordination bonds in the ZIF-67 precursor are broken between cobalt ions and 2-methylimidazole, followed by the formation of the metallic Co nanoparticles under the reducing gas streams. Simultaneously, 2-methylimidazole is continually decomposed to produce the carbon source for the bottom-up growth of onion-like carbon nanospheres on the surface of ZIF-67 dodecahedron under the catalytic effect of the metallic Co nanoparticles.\textsuperscript{7,8}
**Figure S2.** TGA of ZIF-67 dodecahedra under an Ar/H\textsubscript{2} gas flow (10\% H\textsubscript{2}).

**Thermogravimetric analysis**

To investigate the pyrolysis behaviors of ZIF-67, TG tests were carried out under an Ar/H\textsubscript{2} gas flow (Figure S2). The ZIF-67 nanoparticles remain a slow weight loss before around 425 °C, which could be attributed to the decomposition of partial 2-methylimidazole after breaking the coordination bonds between cobalt ions and 2-methylimidazole. With a higher pyrolysis temperature of 425 °C, a large number of 2-methylimidazole decompose rapidly, where five-membered ring structures of 2-methylimidazole are disorganized thoroughly to reconstitute the sp\textsuperscript{2} hexagonal carbon framework. Therefore, controlling the pyrolysis temperature at 425 °C ensures that one partial 2-methylimidazole proceeds to the decomposition behavior and the other retains five-membered ring structures to inset the hexagonal lattices for the formation of positive structure.
**Figure S3.** Schematic illustration of the synthesis process of T-DF
**Figure S4.** SEM images of ZIF-67 (a-c), O-DF (d-f) and T-DF (g-i) with different magnifications.
Figure S5. TEM images of T-DF with different magnifications. The inset of the corresponding SAED images of T-DF.
Figure S6. HRTEM image of O-DF.
Figure S7. CV curves of T-DF for -20 °C at 0.1 mV s⁻¹ compared with the corresponding curves for room temperature.
Figure S8. Long-term cycles and Coulombic efficiency of O-DF, T-DF, MWCNT and graphite for different temperatures at 0.1 A g\(^{-1}\).
Figure S9. XRD patterns of O-DF, T-DF and graphite.

Analysis of XRD patterns

As shown in Figure S9, the XRD patterns of O-DF and T-DF show a broad diffraction peak near 23.8°, which is indexed to (002) planes of amorphous carbon structure,\textsuperscript{9,10} suggesting that abundant carbon intrinsic defects are determined in the carbon network of O-DF and T-DF. This broad peak shifts to a lower angle compared with the counterpart of well-ordered graphite, indicating that the disordered carbon interlayer spacings of O-DT and T-DF are larger than that of graphite, which is in close agreement with the TEM results. Three characteristic peaks at about 44.3°, 51.5°, and 75.8° are attributed to the (111), (200), and (220) lattice facets of metallic Co ((JCPDS card #15-0806), suggesting the formation of the face-centered-cubic cobalt nanoparticles.\textsuperscript{10,11}
Analysis of Raman spectra

The Raman spectra of O-DF and T-DF are illustrated in Figure S10. The G band is recognized as a characteristic feature of the graphitic layers, while the D band arises from disordered or defective structures. The relative intensity ratio of two peaks (I_D/I_G) grows in intensity with increasing the degree of the structural disorder in the graphitic structure. The calculated I_D/I_G ratio of N-DF is larger than that of T-DF (0.92 vs. 0.85), indicating that O-DF possesses higher proportion of disordered structures. Further, the D-band can be deconvoluted into three bands at about 1180 cm⁻¹, 1490 cm⁻¹ and 1200 cm⁻¹, denoted as D₁, D₃ and D₄, which are derived from a vibration mode of carbon atoms at the graphitic layer edges, amorphous carbon fraction and sp²/sp³ bonds stretching vibrations of polyene-like structures, respectively. The I_D/I_G, I_D3/I_G and I_D4/I_G ratios of O-DF are also calculated as 0.85, 0.46 and 0.42, respectively, which are higher than the corresponding ratio of T-DF (I_D/I_G = 0.81, I_D3/I_G = 0.43 and I_D4/I_G = 0.36). These results sufficiently demonstrate that the carbon framework of O-DF displays more defects compared with T-DF.
Figure S11. (a) XPS survey spectra, (b) high-resolution XPS Co 2p spectra and (c) high-resolution XPS N 1s spectra of N-DF and T-DF.
Figure S12. N\textsubscript{2} adsorption/desorption isotherms of O-DF (a) and T-DF (b), the inset is corresponding BJH pore size distribution.

Analysis of N\textsubscript{2} adsorption/desorption isotherms
As shown in Figure S12, the typical nitrogen adsorption-desorption isotherms of O-DF and T-DF exhibit the characteristics of type II isotherms confirmed by the Brunauer-Emmett-Teller (BET) method, indicating that both of which have the typical mesoporous and microporous structures. The pore size distribution curves demonstrate that the O-DF samples have a relatively wider pore size distribution range than that of T-DF. Whereas, O-DF delivers a specific surface area of 108.05 m\textsuperscript{2} g\textsuperscript{-1}, much lower than that of T-DF (143.80 m\textsuperscript{2} g\textsuperscript{-1}), indicating that the exposed atoms on the surface of O-DF are distinctly less than the counterpart of T-DF. Only when the exposed carbon atoms of Riemannian surface are more extracted as new active sites than the corresponding non-Euclidean surface for low-temperature Li-ions storage, this result is potentially consistent with the high capacity of O-DF. This refractive fact is that Riemannian surface are prone to availably tune the intrinsic structure of sp\textsuperscript{2} carbon atoms as new active sites towards low-temperature high capacity.
Figure S13. (a) PDOS of C atoms for negative curvature structure. (b) Charge density distribution with isosurface values of 0.005 e/Å³ corresponding to energy windows of negative curvature carbon in (a) near the Fermi level. (c) PDOS of C atoms for zero curvature structure. (d) Calculations of the hybridization number (sp³) for carbon atoms among the pentagonal defect in the Riemann surface.
Figure S14. CV curves of O-DF for different temperatures along with different scan rates ranging from 0.2 to 5.0 mV s⁻¹.

Quantitative analysis of electrochemical kinetics

In the case of O-DF, the total capacity can be divided into two parts: the diffusion-controlled capacity from the Li⁺ insertion process and the surface-induced capacitive capacity.⁹,¹⁰ Generally, the contribution ratios of the two mechanisms can be quantitatively analyzed according to the subsequent equation

\[ i = k_1 v + k_2 v^{1/2} \]

Herein, \( k_1 v \) and \( k_2 v^{1/2} \) represent the capacitive-controlled contribution and diffusion-controlled contribution, respectively. The values of \( k_1 \) and \( k_2 \) are determined from the slope and intercept of the \( i/v^{1/2} \) versus \( v^{1/2} \) plots.
Figure S15. Surface-controlled contribution (brown region) of O-DF for different temperatures at a scan rate of 1.0 mV s⁻¹.
Figure S16. CV curves of T-DF for different temperatures along with different scan rates ranging from 0.2 to 5.0 mV s\(^{-1}\).
Figure S17. Surface-controlled contribution (brown region) of T-DF for different temperatures at a scan rate of 1.0 mV s⁻¹.
Figure S18. Capacitive contribution ratios of T-DF along with different scan rates and temperatures.
Figure S19. Electrochemical impedance spectroscopy (EIS) of O-DF (a), T-DF (b), MWCNT (c) and graphite (d) at varying temperatures from 25 to -20 °C.

The true limitation of low-temperature performance is substantially due to the interfacial process, typically, substantially increased charge transfer resistance (R<sub>ct</sub>). The change of charge transfer resistance with temperature is largely determined by the activation energy. According to the relationship between R<sub>ct</sub> and E<sub>a</sub>:

\[
\frac{1}{R_{ct}} = A_o e^{-E_a/RT}
\]

where \(A_o\) is the pre-exponential factor, \(E_a\) represents the activation energy, \(T\) means the temperature in Kelvin and \(R\) is known as the gas constant. The value of activation energy (\(E_a\)
of the charge transfer process could be obtained from the slope of a log(1/R_{ct}) versus the inverse of temperature (1/T) plot.

Figure S20. (a) Before and after discharge C K-edge XANES spectra of O-DF. (b) TEM image of O-DF after 100 cycles at -20 °C.
Table S1. The atomic contents of total N, pyridinic-N, graphitic-N, and pyrrolic-N for O-DF and T-DF obtained from N 1s XPS results.

| Samples | Total N | Graphitic-N | Pyridinic-N | Pyrrolic-N |
|---------|---------|-------------|-------------|------------|
| O-DF    | 2.88%   | 1.00%       | 0.97%       | 0.91%      |
| T-DF    | 2.41%   | 0.81%       | 0.96%       | 0.64%      |
**Table S2.** Fitting results of charge transfer resistance (R_{ct}) of O-DF, T-DF, MWCNT and graphite at varied temperatures from 25 to -20 °C.

| Temperature (°C) | O-DF | T-DF | MWCNT | Graphite |
|------------------|------|------|--------|----------|
|                  | R_{ct} (Ω) | Error% | R_{ct} (Ω) | Error% | R_{ct} (Ω) | Error% | R_{ct} (Ω) | Error% |
| 25               | 81.2 | 3.71 | 91.4 | 4.07 | 111.1 | 3.89 | 83.0 | 4.42 |
| 10               | 178.5 | 3.49 | 220.7 | 1.73 | 312.7 | 1.21 | 260.4 | 2.51 |
| 0                | 450.8 | 1.22 | 512.2 | 1.54 | 924.4 | 0.99 | 850.1 | 2.89 |
| -10              | 1023.1 | 2.78 | 1348.0 | 1.57 | 2148.0 | 0.82 | 2914.0 | 1.23 |
| -20              | 2752.0 | 2.64 | 3682.0 | 1.83 | 7554.0 | 1.54 | 12218.0 | 0.97 |
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