

# Facilitating Low-Temperature Li<sup>+</sup> Storage via a Riemannian Surface

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**A Riemannian surface with positive curvature effectively tunes sluggish Li<sup>+</sup> desolvation and reduces the energy barrier for charge transfer at low temperatures.**

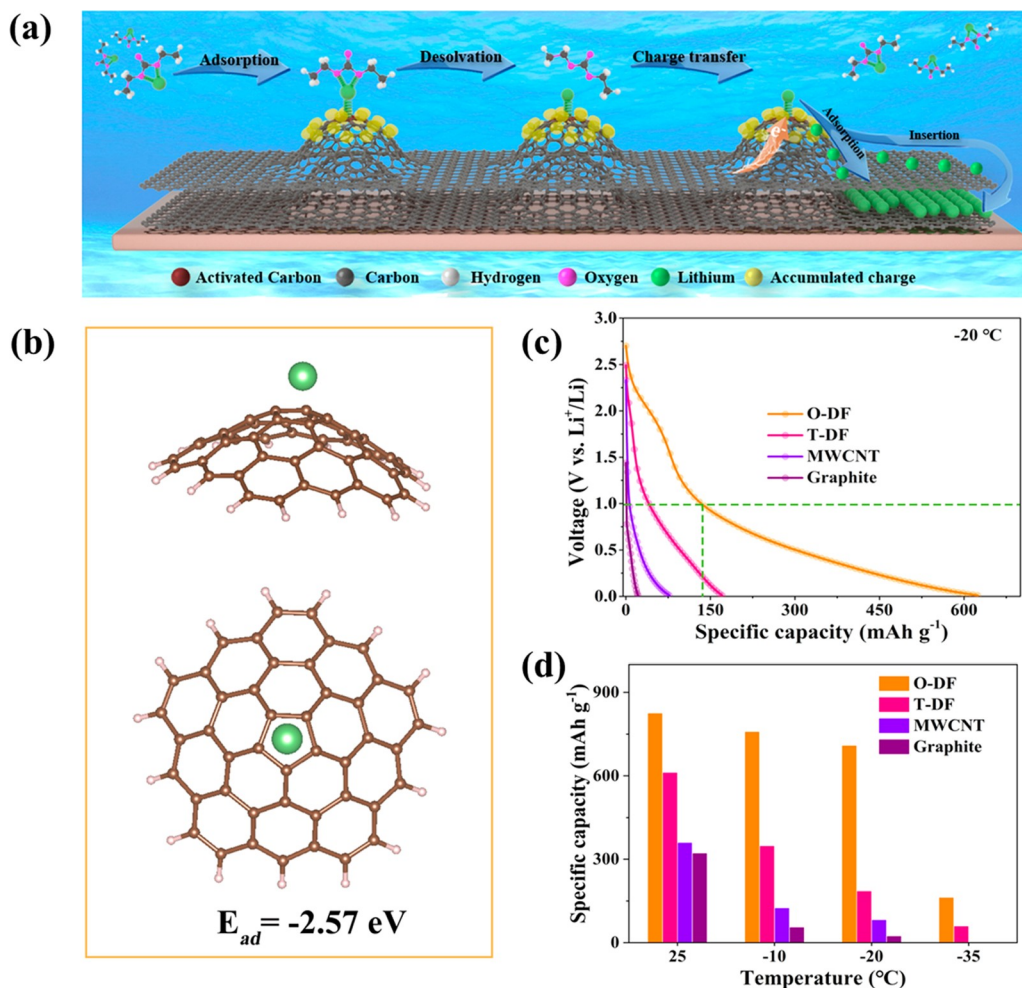
Commercialized lithium-ion batteries (LIBs) have harvested great success in many applications under mild conditions, and their brilliance was recognized with the Nobel Prize for Chemistry in 2019. However, severe energy/power degradation with decreasing temperature remains a challenge, limiting their adaptability to cold environments. Improvements have been achieved by tuning electrolytes and electrodes to satisfy ion transport at low temperatures; however, the graphite anode, the commonly used anode in commercial LIBs, remains a prohibitive factor. Here, sluggish Li<sup>+</sup> desolvation and huge resistance at the interphase result in insufficient Li<sup>+</sup> intercalation into bulk graphite, leading to a failure to charge LIBs at low temperatures. In this issue of *ACS Central Science*, Xi Wang and Jiannian Yao's group report on an enhanced Li<sup>+</sup> storage capacity at subzero temperatures with a strategically constructed carbon anode, consisting of a Riemannian surface with positive curvature on the curved carbon. This design reduces the energy barrier for charge transfer by facilitating Li<sup>+</sup> desolvation at the electrode–electrolyte interface at low temperatures.<sup>1</sup>

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The conventional graphite anode suffers from severe capacity loss as temperature declines and only shows a capacity of 12 mA h g<sup>-1</sup> at -20 °C.<sup>2</sup> This is due to the sharp increase in charge transfer resistance, which involves the transformation of solvated Li<sup>+</sup> into LiC<sub>x</sub> via electron accepting in the graphite anode.<sup>3,4</sup> In the liquid electrolyte of LIBs, lithium ions are generally solvated with polar solvents and anions in the solvation sheath. The sheath must be stripped off before the intercalation of naked Li<sup>+</sup> into electrodes, i.e., the well-known desolvation process. Such a process is energy-consuming and contributes greatly to the charge transfer impedance, which becomes more dominant at subzero temperatures.<sup>3–5</sup> Therefore, a method to tame desolvation is greatly required to reduce the energy barrier for the charge transfer process. Much attention has been paid to tuning the solvation structure via weakly solvated solvents or by increasing the salt concentration.<sup>6,7</sup> Nevertheless, desolvating the solvated Li<sup>+</sup> ions not only depends on the affinity between Li<sup>+</sup> ions and the solvent molecules but also correlates with the surface structure of the electrode where the solvated ions are primarily adsorbed.<sup>8,9</sup> The commonly used graphite is a planar layer-stacked structure with sp<sup>2</sup> hybridized carbon sites with a conjugated π-electron system. Strengthening the adhesion of solvated Li<sup>+</sup> with the carbon sites would possibly help get rid of the solvation sheath and thus lower the energy barrier for charge transfer in the Li<sup>+</sup> storage process (Figure 1a).

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**Figure 1.** (a) Schematic illustration of the process for tuning solvated  $\text{Li}^+$  before intercalation into the electrode, including the adsorption of solvated  $\text{Li}^+$  on the curved surface, the desolvation process, and the subsequent formation of  $\text{Li}-\text{C}$  coordinated bonds. (b) Side and top views as well as the adsorption energies of a Li atom adsorbed on positively curved carbon. (c) Discharge curves for  $\text{Li}^+$  storage and (d) capacity comparison with different carbon anodes. Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.

Desolvating the solvated  $\text{Li}^+$  ions not only depends on the affinity between  $\text{Li}^+$  ions and the solvent molecules but also correlates with the surface structure of the electrode where the solvated ions are primarily adsorbed

In their work, the authors ingeniously designed a carbon anode possessing a non-coplanar Riemannian surface with positive curvature.<sup>1</sup> They took a zeolitic imidazolate framework-67 (ZIF-67) as the precursor, whose pentagonal structures could be pyrolyzed into many pentagonal defects embedded in the planar  $\text{sp}^2$  hexagonal lattice. The obtained carbon nanospheres (O-DF) exhibited highly curved fullerene-like multishell structures on their edge, indicating the non-coplanar  $\text{sp}^x$  hybridization of coordination-unsaturated carbon atoms. Such a curved structure can effectively tune the

distribution of electrons and offer locally accumulated charges that preferentially donate electrons to acceptors (Figure 1b). Therefore, these sites serve as a stable adsorption active center for the solvated  $\text{Li}^+$ , and the adsorbed solvated  $\text{Li}^+$  on the curved surface can easily break the interaction of  $\text{Li}^+$  with solvent molecules. This represents an interesting trade-off to facilitate the desolvation process. These enriched charges on the Riemannian surface significantly reduce the energy barrier for charge transfer between solvated  $\text{Li}^+$  and surface carbon atoms (54.2 kJ/mol for O-DF vs 65.0 kJ/mol for conventional graphite). The unique structure of the curved carbon not only contributes a high specific capacity of  $823 \text{ mA h g}^{-1}$  at room temperature but also outputs a distinguished  $\text{Li}^+$  storage capacity of  $624 \text{ mA h g}^{-1}$  at  $-20 \text{ }^\circ\text{C}$  (Figure 1c). As a comparison, the graphite anode only has a capacity of  $19 \text{ mA h g}^{-1}$ , which is about 5% of its theoretical capacity ( $372 \text{ mA h g}^{-1}$ ). Even at a much lower temperature of  $-35 \text{ }^\circ\text{C}$ , the reversible capacity of the curved carbon can reach as high as  $160 \text{ mA h g}^{-1}$  (Figure 1d). Such excellent

tolerance to low temperatures demonstrates the superiority of the authors' design, which opens up a new pathway for the design of advanced low-temperature carbon-based anodes. Moreover, this is the first report to focus on the link between the low-temperature performance of Li<sup>+</sup> storage and the geometric architectures of carbon allotropes with positive and negative curvature through the manipulation of electron configurations. A Riemannian surface with positive curvature represents an exciting strategy for electronic structure regulation of carbon-based anodes for LIBs in extremely cold environments.

These sites serve as a stable adsorption active center for the solvated Li<sup>+</sup>, and the adsorbed solvated Li<sup>+</sup> on the curved surface can easily break the interaction of Li<sup>+</sup> with solvent molecules.

The work presented by Xi Wang and Jiannian Yao's group provides an effective solution for improving sluggish Li<sup>+</sup> desolvation at low temperatures by designing positive-curvature structures on the surface of carbon-based anodes to induce local charge accumulation. The much-improved performance will encourage researchers to design better low-temperature batteries. We anticipate that Li<sup>+</sup> storage will be further accelerated if the curved carbon is combined with a tamed low-temperature electrolyte. Meanwhile, studies are still needed to achieve precise structural control, universal characterization, and large-scale controllable synthesis of carbon allotropes with positive or negative curvature. We further expect that the construction of full cells for a deep evaluation of the realizable performance will pave the way for commercial applications of all-weather LIB-powered devices.

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