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The Reconstruction of Helmholtz Plane Enables Robust F-Rich Interface for Long-Life and High-Safe Sodium-Ion Batteries

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Carbonate-based electrolytes still retain their top preference in sodium-ion battery (SIB) as in lithium-ion battery (LIBs) owing to their cost-effectiveness and accessibility. However, extensive studies have consistently demonstrated a mismatch between the hard carbon (HC) anode and carbonate-based electrolytes[1,2]. Specifically, as for low-concentration carbonate-based electrolytes (LCEs), the composition of solid electrolyte interphase (SEI) primarily comprises organic species, such as sodium dicarbonates ($(ROCO_2Na)_2$), semicarbonates ($ROCO_2Na$)[3,4]. These components can offer flexibility and favorable conductivity, whereas their poor mechanical property renders them susceptible to crushing during cycling. Moreover, the significant solubility of organic species results in continuous decomposition of electrolytes and the formation of new SEI film during cycling. These side reactions would lead to substantial gas evolution and a subpar cycling performance.

As well recognized, the robust and uniform SEI is the key to maintaining the compatibility of the electrode/electrolyte interface, while the properties of SEI depend on its composition. Inorganic species like NaF and NaN_xO_y (arising from the decomposition of anions) have been identified with low solubility in organic electrolytes, thereby enhanc-

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ing the integrity and stability of the SEI layer[5,6]. Given the poor solubility of nitrates in esters, constructing an electrode/electrolyte interface rich in fluorine seems to be a reliable approach to stabilize the long cycle life of SIBs. Approaches such as developing high-concentration electrolytes (HCEs) or high molar ratio electrolytes (HMREs) have been demonstrated the effectiveness in forming an anion-derived fluorinated (F)-rich SEI. However, the high viscosity and low ionic conductivity of HCEs and HMREs trigger sluggish Na^+ kinetics and significantly worsen rate/cycle performance. How to reconcile the swift ion transport kinetics observed in LCEs with the excellent interfacial properties in HCEs remains a significant challenge.

To address the above-mentioned issues, an in-depth understanding of the incompatibility between HC anode and LCEs becomes imperative. The electron-rich surface of the HC anode during discharge tends to push the anions to the outer Helmholtz layer due to the Coulomb repulsion, instead the linear solvent with weaker polarity remains in the inner Helmholtz plane (IHP) and decomposes as the root component, resulting in solvent-derived SEI film and poor cycle life[7].

Hence, Chen *et al*[8] proposed a novel strategy to reconstruct the IHP of the HC anode (as shown in Fig. 1(a)). Firstly, introducing solvent that could preferentially absorb on HC surface into the electrolyte system, subsequently, leveraging its strong interaction with anions to draw anions into IHP, optimizing the Helmholtz layer and consequently forming an anion-induced F-rich interface (Fig. 1(b)). Moreover, the solvent is also expected to own flame-retardant characteristics so as to enhance the battery safety. As a proof of concept, tris(2,2,2-trifluoroethyl) phosphate (TFEP) was selected from eleven typical flame-retardant solvents by density functional theory methods with two key factors PFBE (PF_6^- binding energy) and CAE (carbon absorption energy) (Fig. 2(a)-(c)). As expected, the introduction of TFEP effectively reconstructs the IHP (Fig. 2(d)-(f)) and promotes the formation of a robust and thin F-rich SEI film on the surface of the HC anode (Fig. 2(g)-(i)), which manifests greatly enhanced mechanical stability, reduced SEI solubility, and accelerated Na^+ ion diffusion kinetics, as evidenced by galvanostatic intermittent titration technique (GITT), time-of-flight secondary ion mass spectrometry (TOF-SIMS), atomic force microscope (AFM) and electrochemical impendence spectrum (EIS).

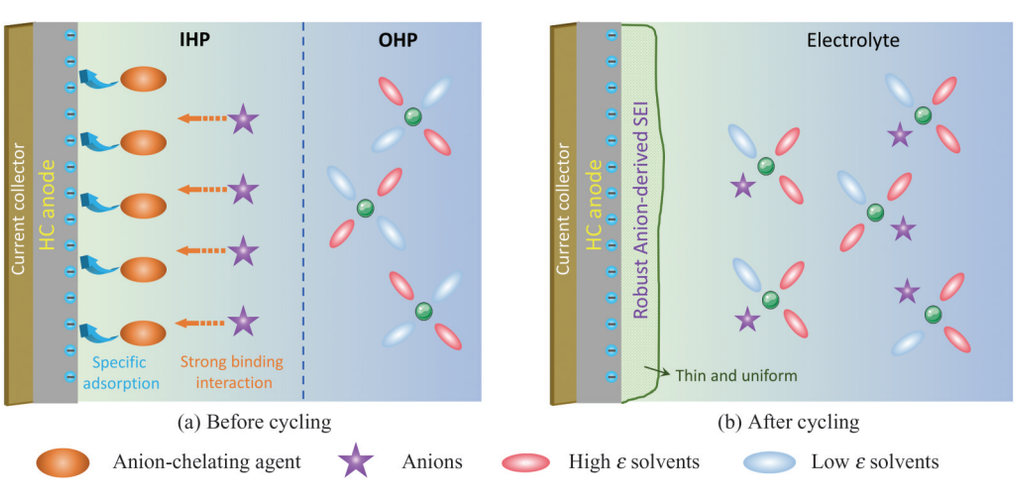

Fig. 1 Strategy for the reconstruction of Helmholtz plane[8]

In conclusion, Prof Chen's group[8] realizes the reconstruction of Helmholtz plane of HC and greatly optimizes the property of electrode/electrolyte and electrochemical compatibility with ester-based electrolytes (*Angew Chem Int Ed*, 2024, e202407717). It is believed this novel understanding of regulating interfacial properties will provide guidance for the design of compatible LCEs and promote the development of low-cost, long-life and high-safe sodium-ion batteries.

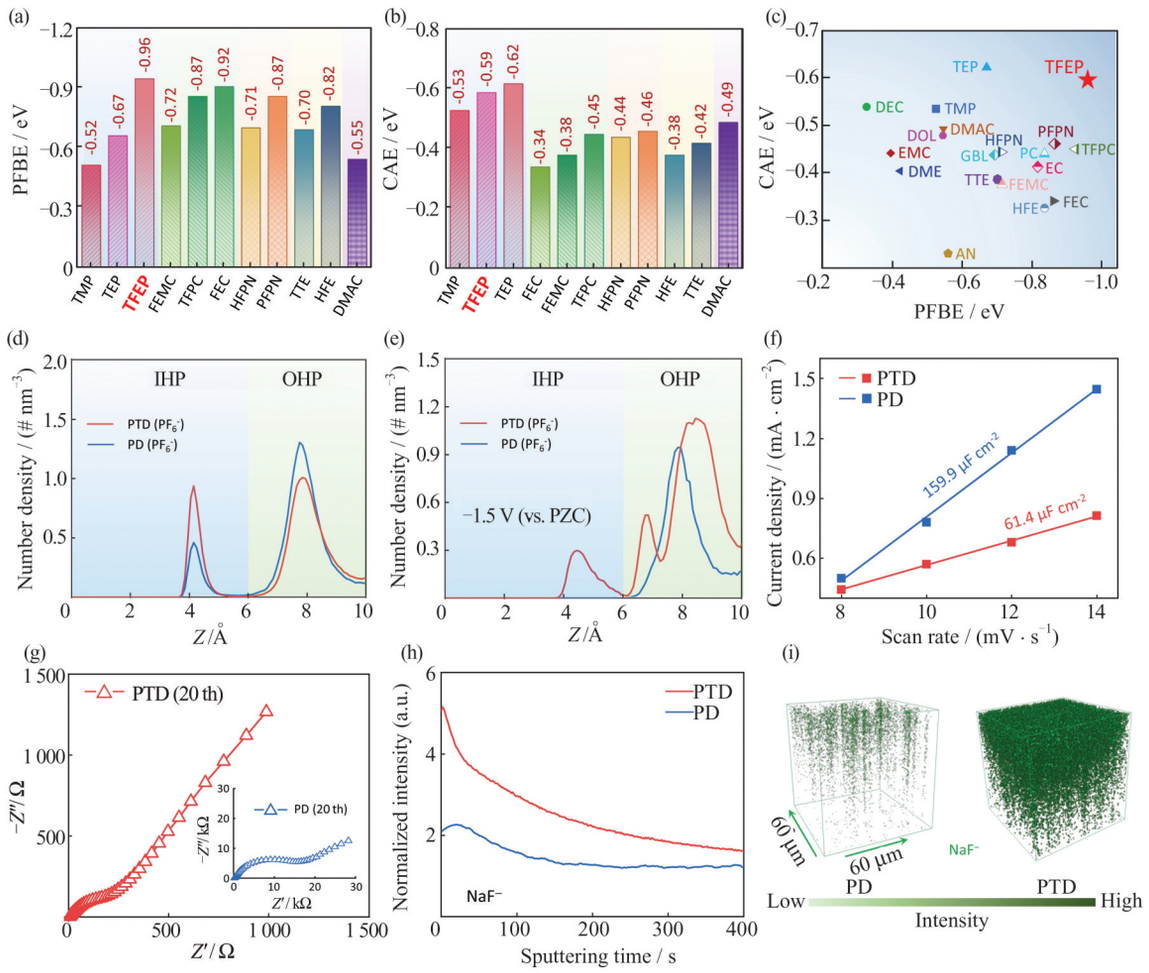

Fig. 2 (a-c) Solvent selection results, (d-f) The differences of Helmholtz plane and EDLC in different electrolytes, (g-i) The properties of F-rich electrode/electrolyte in PD and PTD[8]

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重构亥姆霍兹层构建稳定的富氟界面实现长寿命、高安全钠离子电池

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摘要: 由于电池运行时负极处存在负电场,会对亥姆霍兹平面(HP)上的分子排布产生影响,阴离子被库仑力排斥出内层(IHP), 而极性较低的链状酯类滞留在内层并分解为SEI膜的根组分, 导致较差的界面性质。想要改善界面性质,进而提高硬碳与酯基电解液的兼容性,必须要优化负电场条件下亥姆霍兹层中的离子/溶剂分子排布。近期,本研究团队提出了一种重构硬碳表面IHP 的新策略。首先, 在电解液中引入能够优先吸附在HC表面的溶剂, 然后利用溶剂与阴离子间的强相互作用将阴离子拉入IHP, 进而构筑阴离子诱导的稳固富氟界面。基于此思想, 作者确定了PFBE(阴离子结合能)和CAE(碳吸附能)两个重要指标, 并以此进行溶剂筛选, 确定了TFEP为最佳溶剂。合理设计的PTD电解液使Na||HC半电池和2.8 Ah HC||$Na_4Fe_3(PO_4)_2P_2O_7$软包电池具有优异的倍率性能、长循环寿命、高安全性和低温适应性。

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