

Title: Universal Cathode Design Strategies to Engineer Cathode Electrolyte Interfaces for High Performance All Solid-State Batteries

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Metal-ion batteries (e.g., lithium and sodium ion batteries) are the promising power sources for portable electronics, electric vehicles, and smart grids. Recent metal-ion batteries with organic liquid electrolytes still suffer from safety issues regarding inflammability and insufficient lifetime.¹ As the next generation energy storage devices, all-solid-state batteries (ASSBs) have promising potentials for the improved safety, higher energy density, and longer cycle life than conventional Li-ion batteries.² The nonflammable solid electrolytes (SEs), where only Li ions are mobile, could prevent battery combustion and explosion since the side reactions that cause safety issues as well as degradation of the battery performance are largely suppressed.

However, their practical application is hampered by the high resistance arising at the solid–solid electrode–electrolyte interface (including cathode-electrolyte interface and anode-electrolyte interface).³ Several methods have been introduced to optimize the contact capability as well as the electrochemical/chemical stability between the metal anodes (i.e.: Li and Na) and the SEs, which exhibited decent results in decreasing the charge transfer resistance and broadening the range of the stable energy window (i.e., lowering the chemical potential of metal anode below the highest occupied molecular orbital of the SEs).⁴ Nevertheless, mitigation for the cathode in ASSB is tardily developed because: (1) the porous structure of the cathode is hard to be infiltrated by SEs;⁵ (2) SEs would be oxidized and decomposed by the high valence state elements at the surface of the cathode at high state of charge.⁵

Herein, we demonstrate a universal cathode design strategy to achieve superior contact capability and high electrochemical/chemical stability with SEs. Stereolithography is adopted as a manufacturing technique to realize a hierarchical three-dimensional (HTD) electrode architecture with micro-size channels, which is expected to provide larger contact areas with SEs. Then, the manufactured cathode is sintered at 700 °C in a reducing atmosphere (e.g.: H₂) to accomplish the carbonization of the resin, delivering sufficiently high electronic conductivity for the cathode. To avoid the direct exposure of the cathode active materials to the SEs, oxidative chemical vapor deposition technique (oCVD) is leveraged to build conformal and highly conducting poly(3,4-ethylenedioxythiophene) (PEDOT) on the surface of the HTD cathode.⁶ To demonstrate our design strategy, both NCM811 and Na₃V₂(PO₄)₃ is selected as active materials in the HTD cathode, then each cathode is paired with organic (polyacrylonitrile-based) and inorganic (sulfur-based) SEs assembled into two batteries (total four batteries). SEM and TEM reveal the micro-size HTD structure with built-in channels. Featured by the HTD architecture, the intrinsic kinetic and thermodynamic conditions will be enhanced by larger surface contact areas, more active sites, improved infusion and electrolyte ion accessibility, and larger volume expansion capability. Disclosed by X-ray computed tomography, the interface between cathode and SEs in the four modified samples demonstrates higher homogeneity at the interface between the cathode and SEs than that of all other pristine samples. Atomic force microscopy is employed to measure the potential image of the cross-sectional interface by the peak force tapping mode. The average potential of

modified samples is lower than that of pristine samples, which confirms a weakened space charge layer by the enhanced contact capability. In addition, through Electron Energy Loss Spectroscopy coupled with Scanning Transmission Electron Microscopy, the preserved interface between HTD cathode and SE is identified; however, the decomposing of the pristine cathode is clearly observed. In addition, Finite element method simulations validate that the diffusion dynamics of lithium ions is favored by HTD structure. Such a demonstrated universal strategy provides a new guideline to engineer cathode electrolyte interface by reconstructing electrode structures that can be applicable to all solid-state batteries in a wide range of chemical conditions.

References:

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