High-temperature lithium-sulfur batteries with commercial paper-derived solid-state electrolyte

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Abstract

Solid-state lithium-sulfur (Li-S) battery technologies could power future electric mobility due to their potential high energy density. However, the current solid-state Li-S batteries face several challenges, such as high internal impedance at the electrode/electrolyte interfaces, shuttling of lithium polysulfides, and Li dendrite formation. Herein, we introduced a novel Li- rich cellulose-based solid-state electrolyte in combination with sulfurized polyacrylonitrile (SPAN, 36.5 wt.% S) cathode, leading to durable Li-S batteries for high-temperature applications. We utilized SPAN due to its reasonable conductivity, high reversible capacity, and stable cycling performance. The solid-state electrolyte in this study was prepared by infusing Li ions (Li^+) into a copper-coordinated cellulosic paper. The infusion of Li^+ was carried out by soaking the copper-treated paper in a 1 M LiTFSI in $EC_{0.5}DME_{0.25}DOL_{0.25}$ solution (where subscripts indicate the volume fraction), followed by complete evaporation of the solvents. Three types of cellulosic paper were explored, from which the commercial copy paper resulted in the highest area-normalized conductance of 24.4 mS cm^{-2} and Li-ion transference number of 0.76 at 50 °C. At this temperature, the Li-SPAN cells with paper-based electrolyte delivered an initial reversible capacity of 1536 mAh g^{-1} at 168 mA g^{-1} (0.1C). After high-temperature cycling for 150 cycles at 0.5C, the Li-SPAN cells exhibited an exceptional capacity retention of 82.2% (from 982 to 807 mAh g$_s^{-1}$). The conformability of the paper-based electrolyte ensures good interfacial contact with the SPAN and Li electrodes. As a result, when this solid-state Li-S battery was subjected to fast charging/discharging (1C) at 50 °C, it delivered a reversible capacity of 670 mAh g$_s^{-1}$. In this talk, we will outline the results from our electron microscopy, X-ray diffraction measurements, electrochemical impedance spectroscopy, and cyclic voltammetry studies on Li-S cells to unravel the superior performance of paper-based Li-S batteries at high temperatures.

Concentrated Solution Theory for Nano-porous Electrodes and Separators

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Abstract

Due to high reductive/oxidative stability, low volatility, high thermal stability, and high carrier density, there has been a shift in the battery community towards highly concentrated electrolytes. The cationic flux determines battery performance in a lithium-ion battery, as cations are active species and contribute to energy storage. Cationic conductivity, which determines cation migration flux, is the product of total conductivity and cationic transference number. Assuming electroneutrality, the cationic-transference number is defined as the ratio of current carried by cations to the total current in the absence of diffusion and convection fluxes. For ideal dilute electrolytes (i.e., ideal solutions of non-interacting ions), the Nernst−Einstein relation implies that the transference number is equal to the ratio of the self-diffusion coefficient of cations and the total self-diffusion coefficient of cations and anions. The transference number of ideal dilute electrolytes may be obtained experimentally via the pulsed-field gradient NMR technique.

Unlike dilute electrolytes, the ion-ion correlations cannot be neglected for highly concentrated electrolytes. In such cases, the total ionic conductivity equals the sum of self-conductivity and distinct conductivity for both cations and anions. Using Onsager reciprocal relations, potentiostatic polarization technique, and the assumption of electroneutrality, the equations for the transference number of highly concentrated electrolytes have been reported in the literature. However, recent reports indicate an anomalous increase in charge screening length for ionic liquids and concentrated electrolytes. The screening length is of the order of a few nanometers. A recent push towards using nano-porous electrodes and separators implies that the assumption of local electroneutrality (inside nano-pores) for highly concentrated electrolytes and ionic liquids (which fill up the nano-pores in separators and electrodes) may not be valid. Further, the state-of-the-art concentrated solution theory has been found to fail in correctly predicting the observed concentration profile. Since electrolyte properties significantly affect the battery performance, this necessitates the development of a concentrated solution theory without the assumption of electroneutrality. Additionally, electroneutrality breakdown within nano-pores implies the presence of local electric fields within the electrolyte in nano-pores, which is expected to bring electrokinetic effects and, hence, a non-zero convective flux into play.

In this talk, we will delineate the governing equations, the boundary conditions, and the concentration profiles obtained using the novel concentrated solution theory for nano-porous

electrodes and separators. Moreover, we are designing an electrochemical cell to obtain experimental concentration profiles inside nano-pores of a nano-porous separator using operando Raman spectroscopy. We will finally compare the theoretical and experimental results to validate our model.

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Fundamental electrochemical mechanisms in sulfurized polymer cathode-based Li-S batteries

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Introduction: Sulfurized polymer (SPAN) is a promising cathode material for Li-S batteries due to its unique ability to electrochemically react with Li+ without the formation of long-chain lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) [1]. Despite the recent advances in SPAN based Li-S batteries [1-5], the structure, the fundamental electrochemical mechanism, and the nature of solid-electrolyte interfaces of SPAN still remain unclear.

Methodology: We systematically controlled the sulfur content in SPAN from 0-33 wt. % to experimentally investigate the effects of local S bonding environment on the electrochemical behavior of SPAN. We used CHSNO elemental analysis, thermogravimetry, and x-ray photoemission spectroscopy (XPS) to determine the sulfur content and bonding environment.
The electrochemical performance of SPAN cathodes with varying S content was analyzed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and gravimetric charge-discharge behavior. We derived the redox density of states of SPAN with 0-33 wt. % S using EIS. We performed in-situ micro-Raman spectroscopy and detailed ex-situ angle-resolved XPS to gain new insights into the electrochemistry of SPAN and solid-electrolyte interface formation.

Results: The SPAN cathode with ideal (33 wt. %) sulfur content showed a capacity around 1400 mAh/g. At lower sulfur content, we observed a concomitant decrease in the specific capacity. We performed scan-rate dependent CV (scan rates ranging from 0.1mV/s to 2.0 mV/s) to decouple the redox and capacitive contributions. Using the EIS data, we derived the redox density of states which show a distinct peak ~2.2-2.5 V window overlapping with the sulfur oxidation potential. We performed angle resolved XPS on cathodes with different S content after 1, 10, and 100 cycles. We observed interesting trends in the evolution in C 1s and S 2p spectra of SPAN cathodes compared to the conventional S_8 cathodes.

Conclusions: The specific capacity of SPAN cathodes (0-33wt.% S content) has a significant capacitive contribution. The electrochemical redox peaks in SPAN cathode differ from S8 suggesting a different mechanism that does not involve polysulfide formation. Our in-situ Raman spectroscopy results show significant structural changes in the carbon backbone of SPAN, which concurred with angle resolved XPS spectra suggesting that sulfur is present as short chains attached to the carbon backbone.