Porous Carbon-Based Composites for Lithium-Sulfur Batteries

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Chapter 7

Summary and outlook

7.1 Summary

In this dissertation, different porous carbon materials and their composites were developed and configurated as different components in Li-S batteries. Considerable progresses including optimization of sulfur/porous carbon composites cathodes, configuration of porous carbon nanofibers (CNFs) based interlayers, and stabilization of Li-metal anodes using CNFs based current collectors, have been made to address the challenges of the Li-S cells and greatly improve the electrochemical performance.

In chapter 2, the preparation of hierarchical porous carbons (HPCs) and their functions as different components in Li-S batteries were comprehensively reviewed. The review started with synthetic methods for the preparation of HPCs, including hard-templating method, soft-templating method, self-templating method, hard & soft templating method, and templating & activation method. Then, HPCs based high-performance sulfur cathodes were emphasized, the correlation between structures (pore volume, specific surface area, degree of pores, and heteroatom-doping) of HPCs and the electrochemical performance of S@HPCs cathodes was also elaborated. Next, the configurations of HPCs based coating layers/interlayers for functionalizing separators and current collectors in supressing the polysulfide migration and stabilizing Li anodes were discussed, respectively. Finally, a discussion on the challenges that associated with Li-S batteries was provided.

Then, the aspect ratio of ordered mesoporous carbon (OMC)-based sulfur host was optimized in chapter 3. OMCs with variable sizes were synthesized through the reverse replication with the help of ordered mesoporous silica (OMS) hard templates. Then, the corresponding S@OMCs cathodes were obtained by melting method. After systematic electrochemical measurements (cyclic voltammetry, electrochemical impedance, galvanostatic intermittent titration technique, and galvanostatic charge-discharge) and characterizations (electron microscopy and small-angle X-ray scattering), it was demonstrated that S@OMC-1.2 with moderate length and largest width exhibited best electrochemical performance as more discharged product generated.

Next, to endow the sulfur host with chemisorption toward polysulfides and further improve the sulfur content and electrochemical performance, cobalt/carbon spheres were introduced into CNTs (Co-C-CNTs) in chapter 4. The hierarchical porous carbon frameworks with large pore volume and high specific surface area (SSA) alleviated the volume exchange and physically restricted the polysulfides. The partially remained cobalt nanoparticles were beneficial for the chemical adsorption and redox reaction of polysulfides. With the synergetic effects of physical barrier and chemical adsorption toward polysulfides, the obtained S@Co-C-CNTs cathodes presented ultrahigh discharge capacity (1568 mAh g^{-1} at 0.1C) as well as enhanced cyclic stability.

Beside optimization of sulfur hosts, configuration of interlayers between sulfur cathodes and separators is also effective in suppressing the escape of polysulfides and serving as second current collectors. In chapter 5, the crystallinities of titanium nitride (TiN) film on copper-embedded carbon nanofibers (Cu-CNFs) were tuned and the nanofibers were inserted in Li-S batteries as interlayers. Low-crystalline titanium nitride coated Cu-CNFs (L-TiN-Cu-CNFs) interlayer was systematically compared with its highly-crystalline counterpart (H-TiN-Cu-CNFs). The L-TiN coating not only strengthened the chemical adsorption toward polysulfides, but also greatly facilitated the redox conversions of polysulfides. Attributed to robust porous carbon frameworks and enhanced kinetics, impressive high-rate performance at 2C (913 mAh g^{-1}) as well as remarkable cyclic stability up to 300 cycles (626 mAh g^{-1}) were achieved. Moreover, the L-TiN-Cu-CNFs interlayer equipped Li-S cells (sulfur loading: 3.8 mg cm^{-2}) exhibited high areal capacity (4.35 mA cm^{-2}), which was 2.2 times higher than that of commercial $LiCoO_2$ ($LiCoO_2$ loading: 14.4 mg cm^{-2}) cathode.

In order to protect lithium-metal anodes from dangerous dendritic growth and degradation, chapter 6 presented the elaborate design and large-area fabrication of a 3D current collector consisting of nitrogen-doped porous carbon fibers featuring abundant copper-based Cu/Cu_3P heterostructure decorations (Cu/Cu_3P-N-CNFs). The 3D hierarchical porous structure alleviated the huge volume variation during Li plating/stripping processes and reduced the local current density. The lithiophilic nitrogen-doped carbon sites and the embedded functional Cu/Cu_3P heterostructure endowed ultralow nucleation overpotential and small polarization. Thus, Cu/Cu_3P-N-CNFs electrodes exhibited high Coulombic efficiency (~94%) for 500 cycles at 1 mA cm^{-2} with the capacity of 1 mAh cm^{-2}. More significant, excellent electrochemical performances were realized for both symmetrical cells and Li-S full cells by the developed Li@Cu/Cu_3P-N-CNFs anodes.

7.2 Outlook

To overcome the above obstacles, the future development of porous carbon for Li-S batteries can benefit from focusing on the following aspects. First, developing scalable and cost-effective strategies for producing porous carbon still requires more

efforts. The properties such as pore volume, specific surface area (SSA), and electrical conductivity, heteroatom-doping and microstructures should be comprehensively controlled to meet the requirements for sulfur/carbon composites cathodes with practically needed sulfur contents, loadings, and utilizations.

Second, correlations between electrochemical performances of cathodes and several key parameters such as high sulfur contents, electrodes capacity, areal sulfur loadings, and low electrolyte/sulfur (E/S) ratio require more investigations. More efforts also need to be devoted toward exploring novel porous carbon architectures to facilitate the reaction kinetics and improve the power densities. For example, surface chemistry such as heteroatom-doping to improve the sulfiphilicity can further suppress the polysulfide migration through chemisorption. Decoration of porous carbon with catalysts can accelerate the chemical conversion of active materials, reducing the overpotential and improving power densities of batteries. Simulations on mass transfer within electrodes and electrode reactions, and density functional theory (DFT) calculations of the interaction between polysulfides and surface functional groups such as N or O heteroatoms and catalysts are highly recommended for guiding experimental studies.

Third, separators/interlayers functionalized with porous carbon could effectively enhance the conductivity and suppress the migration of polysulfides, playing an important role in the operation of high-sulfur-loading batteries. According to the abovementioned challenges, the following pathways can be taken in to account: first, based on experiments, simulation and calculations, the picture of permeable behaviors of polysulfides need to be well drew. Under the practical metrics, investigations on the reduction of the thickness of coating layers without sacrificing the capacity and effect of suppressing the polysulfide shuttle can be performed. To develop facile and scalable routes such as roll-to-roll printing and other coating techniques adoptable in industry for producing a large-area and uniform coatings/interlayers is meaningful.

In addition, the freestanding sulfur/porous carbon cathodes or Li/porous carbon anodes can reduce the ratio of inactive materials. HPCs can be tailored as lightweight current collectors with areal density below 1 mg cm^{-1} for 50 μm thick to replace the traditional current collectors of copper foil (>8.5 mg cm^{-2} for 9 μm thick) and aluminum foil (>3.0 mg cm^{-2} for 12 μm thick), to this end, leading to a remarkable increase of the energy density of Li-S cells. Although a number of progresses have been made, corresponding researches are still of significance and need to be conducted more in the future with respect to the electrode mechanical stability, flexibility, high loadings of active materials, electrodes/battery performances, durability, thin electrodes production technologies, scalability and so forth.

Last but not the least, the configurations of integrating the different components (porous carbon functionalized sulfur cathode, separators/interlayers, Li anodes) into one Li-S cell can simultaneously alleviate the problems of the sulfur cathodes and lithium anodes. Furthermore, more research attention needs to be paid to theoretical simulations and in-situ characterizations, which can deepen the understanding of the role and working mechanism during battery operation and in turn guide optimizing the structures of porous carbon. Despite there are still lots of formidable obstacles that hinder the practical application and survival of Li-S batteries, the recent progresses demonstrate that rationally designed porous carbon with high pore volume and SSA, ordered structures, and optimal heteroatom-doping can be one of the most desirable materials to promote the development for this promising energy storage system.