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Abstract

This doctoral thesis centers on the synthesis and application of heteroatom-doped hard carbons derived from bio-based polymers as anode materials for both lithium-ion and sodium-ion batteries.

Chapter 1: Introduction

Energy storage has become increasingly vital in today's world which is highly dependent on technology. Traditionally, fossil fuels have served as the primary energy source for transportation and various systems; however, concerns over resource depletion and environmental impact have accelerated the shift toward cleaner and more sustainable alternatives. In response, a range of energy storage technologies—including fuel cells, batteries, and capacitors—are being actively developed and improved. This chapter provides an overview of key energy storage devices, including capacitors, fuel cells, primary batteries, and rechargeable (secondary) batteries. Sodium-ion batteries, an emerging energy storage technology is also receiving increasing attention owing to the low cost and widespread availability of sodium. This chapter also outlines the fundamental components of batteries—cathode, anode, and electrolyte—with a focus on their roles in both lithium-ion and sodium-ion systems. Finally, the chapter introduces the material design strategies explored in this thesis, setting the foundation for the subsequent chapters.

Chapter 2: Bio-based poly(benzimidazole-co-amide) derived N, O co-doped carbons as fast-charging anodes for lithium-ion batteries

This chapter presents the synthesis and electrochemical evaluation of nitrogen and oxygen co-doped hard carbons (HCs) derived from bio-based copolymers, specifically poly(benzimidazole-co-amide), as potential anode materials for lithium-ion batteries (LIBs). The study addresses the growing demand for LIBs that support

fast charging and deliver high capacity, particularly for electric vehicle applications. To explore the effect of precursor composition on electrochemical performance, poly(benzimidazole-co-amide) copolymers were synthesized with varying ratios of benzimidazole to amide units—8.5:1.5, 7:3, and 5:5. These copolymers were then pyrolyzed under a nitrogen atmosphere to yield nitrogen and oxygen dual-doped hard carbons, referred to as PYPBIPA8.5-1.5, PYPBIPA7-3, and PYPBIPA5-5. The copolymers acted as single-source precursors for carbon, nitrogen, and oxygen, resulting in materials with nitrogen contents ranging from 12.1 to 8.0 atomic percent and oxygen contents between 11.8 and 25.0 atomic percent. Coin cells were fabricated using the obtained carbon materials as anodes, and rate capability tests were conducted to assess their performance. Among the three, PYPBIPA8.5-1.5 exhibited the best rate performance, especially under high current densities. Motivated by these results, extended cycling studies were carried out at a high current density of 4.0 A/g. Remarkably, PYPBIPA8.5-1.5 maintained a delithiation capacity of 135 mAh/g, compared to 100 mAh/g and 60 mAh/g for PYPBIPA7-3 and PYPBIPA5-5, respectively. It also showed excellent cycling stability, retaining 90% of its capacity even after 3000 cycles.

Chapter 3: Bio-based poly(benzothiazole) derived N, S co-doped carbons as fast-charging anodes for sodium-ion batteries

Sodium-ion batteries (SIBs) have gained attention as a promising alternative to lithium-ion batteries (LIBs) for next-generation energy storage, thanks to the abundance and low cost of sodium. However, enabling fast-charging in SIBs remains a key challenge, largely due to the sluggish diffusion kinetics of sodium ions. This limitation often appears as a pronounced low-potential plateau in the charge-discharge profiles, which hampers high-rate performance. To overcome this, various strategies have been explored, with heteroatom doping emerging as a particularly effective approach. Nitrogen doping is well-known for enhancing electronic conductivity and promoting surface adsorption through pseudocapacitive mechanisms. Sulfur doping, especially relevant for SIB anodes, provides additional benefits due to its larger atomic radius, which increases interlayer spacing and allows for extra sodium-ion storage through non-faradaic interactions. In this study, a nitrogen and sulfur co-doped hard carbon material derived from the bio-based polymer polybenzothiazole is investigated as a potential anode for sodium-ion batteries. The hard carbon samples were synthesized via pyrolysis at two different temperatures to systematically assess the influence of structural and compositional variations on their fast-charging performance.

Chapter 4: Conclusions

This chapter presents a comprehensive summary of the key findings and discussions outlined in the preceding chapters. It revisits the main objectives of the thesis and highlights how each chapter contributed to addressing these goals. A concise overview of the topics explored throughout the study is provided, emphasizing the significance of the results in the context of the broader research field. Additionally, this chapter explores the potential future directions for research involving these materials, outlining possible improvements, extensions, and innovations. It also discusses the wide range of applications these materials could support across various industries, reflecting their promising potential in both current and emerging technologies.

Keywords: Bio-based, polymer, heteroatom doped carbon, energy storage, fast-charging