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論文の内容の要旨

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

論文審査の結果の要旨

本研究においては、ポリ（ベンズイミダゾール/ポリアミド）共重合体及びポリ（ベンズチアゾール）をそれぞれ前駆体として焼成することによって得た各種ヘテロ元素ドープカーボンを合成し、前者をリチウムイオン二次電池用負極活物質として、後者をナトリウムイオン二次電池用負極活物質としてそれぞれ検討しつつ、活物質の構造と電池特性との相関についてそれぞれ検討している。

学位申請者は以前に修士論文研究においてバイオベースのポリベンズイミダゾールを焼成することによって得た高濃度窒素ドープカーボンが、リチウムイオン二次電池の負極活物質としての採用時に急速充放電能の発現を促すことを見出し報告していた。

博士論文研究においては、これをいっそう発展させるべく、ポリ（ベンズイミダゾール/ポリアミド）の焼成により窒素及び酸素をドープしたカーボン材料を合成した。以前に報告したポリベンズイミダゾールを焼成した系と比較して、ポリ（ベンズイミダゾール/ポリアミド）の焼成系では層間距離がさらに長くなることが見出された。前駆体ポリマーのベンズイミダゾールユニットとアミドユニットの比を検討したところ、85:15 の系において層間距離は最長の 3.8Å となった。本材料を負極活物質としたリチウムイオン二次電池のアノード型ハーフセルにおいては、4000 mAg^{-1} の急速充放電条件において 137 $mAhg^{-1}$ の放電容量を 3000 サイクル時点で示し、95%の容量維持率を示すなど、卓越した特性を示した。また、LiNCAO を正極としたフルセルも良好に駆動した。

また、ポリベンズチアゾールを前駆体として焼成することによって得た N、S デュアルドープカーボンを負極活物質としたナトリウムイオン二次電池のアノード型ハーフセルに関しても検討した。800oC で焼成した活物質においては、2000 mAg^{-1} の急速充放電条件においても 100 $mAhg^{-1}$ の放電容量を示した。高いヘテロ元素ドープ量は、系内の構造欠陥を増加させて層間距離を増加させ、イオン輸送の活性化エネルギーの低下、ひいてはスムーズなイオン拡散につながることが示された。

以上のように、本論文は、耐熱性高分子前駆体を用いて調整した各種ヘテロ元素ドープカーボンの金属イオン二次電池負極活物質としての適用時における構造特性相関について検討したものであり、学術的及び実学的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。