

Title	高官能基密度を有するポリメチレン系高分子の電解質及び バインダーとしての金属イオン二次電池への応用
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Abstract

Batteries are crucial in advancing efficient energy storage technology amid the global transition to renewable energies for carbon-free transportation and stationary energy storage. They are essential for decarbonizing the transport and energy sectors, while also finding applications in aerospace, medical devices, automotive, power grids, wearable electronics, and robotics. Li-ion and Na-ion batteries (LIB, SIB), with their high energy and power density, are preferred for hybrid/all-electric vehicles, power tools, and portable electronic devices, promising significant reductions in greenhouse gas emissions. Their potential extends to improving energy efficiency and quality from renewable sources in power grid applications. However, challenges loom regarding their long-term viability, cost effectiveness, availability of materials, and safety concerns such as fires, explosions, and problems that need addressing. A deeper understanding of metal-ion battery performance under adverse conditions is crucial for ensuring safer cells and their continued contribution to a sustainable energy economy.

The present doctoral work mainly focuses on synthesizing dense functional group polymers through cost-effective and non-toxic materials aiming to mitigate the abovementioned issues, divided into chapters 2,3, 4, 5, and 6 in the doctoral thesis.

In Chapter 2, LIBs are crucial for various applications, but their electrolytes' carbonate-based liquid solvents face challenges of flammability and lithium-ion movement dynamics. Poly (ethoxycarbonylmethylene) (PECM) with a high density of ester groups was explored as a polymer electrolyte to tackle these issues. PECM exhibited polar aprotic properties, enhanced cation solvation, and a glass transition temperature of 10–33 °C when combined with LiTFSI. Ionic conductivity ranged from 9.76×10^{-5} to 3.08×10^{-4} S cm⁻¹ at 51 °C, with lithium-ion transference numbers between 0.80 and 0.98 and diffusion activation energies of 27.4–43.0 kJ mol⁻¹. The PECM-based cathodic half-cell displayed excellent rate capacity and long-cycle performance, retaining 80% capacity at 0.2 C for over 100 cycles. These findings highlight PECM's potential as an alternative electrolyte material for future LIB applications.

In Chapter 3, poly(fumaric acid) (PFA) as a binder in LIBs shows exceptional Li⁺ diffusion kinetics. Studies, including activation energy and diffusion coefficient assessments, confirm this. The PFA binder demonstrates impressive reversible specific capacities ranging from 343 to 65 mAhg⁻¹ across various current densities of graphite electrode. At a 1C rate during extended cycling, the PFA binder maintains remarkable performance, achieving a reversible specific capacity of 325 mAhg⁻¹ with an impressive 79% capacity retention at 710th cycle. Additionally, under rapid 5C charging, the PFA

binder reduces polarization, ensuring a specific capacity of 54 mAhg^{-1} in just 1.5 minutes. Impedance studies reveal a low-resistance solid electrolyte interphase (R_{SEI}) value, facilitating the smooth passage of Li^+ ions. Postmortem investigations confirm the PFA binder's effectiveness, forming a uniform SEI on the electrode surface, devoid of exfoliation or cracks. This highlights the binder's role in enhancing LIB performance.

In Chapter 4, SIB with PFA binder for hard carbon anodes exhibit exceptional performance. They achieve an impressive initial coulombic efficiency of 80.8% and outperform PAA and PVDF binders in terms of reversible rate capacities at various current densities, with PFA binder showing capacities ranging from 332 to 119 mAhg^{-1} . PFA binder also demonstrates excellent capacity retention, retaining 85.4% of its reversible specific capacity over 250 cycles at a higher current density of 60 mA g^{-1} , reaching a maximum capacity of 288 mAhg^{-1} . Moreover, PFA binder enhances sodium ion kinetics by modifying SEI, resulting in a lower activation energy, a higher sodium ion diffusion coefficient, and reduced resistance compared to PAA and PVDF binders.

In chapter 5, Poly(oxycarbonylmethylene 1-allyl-3-methylimidazolium) (PMAI), exhibits excellent electrochemical performance for graphite in LIB, achieving 80% capacity retention at 750 cycles with a specific capacity of 298 mAhg^{-1} at 1C compared to PVDF binder. At 5C rate, PMAI/Gr delivers a higher discharge capacity of 85 mAhg^{-1} than PVDF/Gr (47 mAh g^{-1}). Postmortem analysis reveals noticeable electrode degradation containing PVDF binder, characterized by high charge transfer resistance and thick organic species at SEI. In contrast, when PMAI serve as binders, high content of inorganic species in SEI and crack-less electrode is observed, resulting in reduced overpotential, lower activation energy and enhanced Li^+ diffusion.

In Chapter 6, PMAI binder for hard carbon in SIB is shown to be reduced during cyclic voltammetry and charge/discharge at 0.9 V vs. Na^+/Na , leading to better adhesion with electrode components and formation of functionalized SEI. The PMAI/HC's initial coulombic efficiency is 74% and a maximum specific capacity of 254 mAhg^{-1} with a capacity retention of 96.2% was observed after 200 cycles at 60 mA g^{-1} . PMAI-containing electrodes showed better rate capability at different current densities than PVDF binder. PMAI/HC electrode exhibits an enhanced Na^+ diffusion coefficient, low R_{SEI} and R_{CT} and decreased activation energy of desolvation, which is ascribed to densely polar ionic liquid groups along the binder, enhancing the ion conductivity in electrode, influencing the Na^+ diffusion kinetics at the surface and formation of functionalized SEI due to binder reduction.

Keywords: binder for carbon anode, lithium-ion batteries, poly(ionic liquid), sodium-ion batteries, water-soluble binder