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
Author(s)	Amarshi, Patra
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Description	supervisor: 松見 紀佳, 先端科学技術研究科, 博士

氏　　　　　名	AMARSHI PATRA
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論 文 題 目	Polymethylene Polymers with High-Density Functional Groups as Electrolyte and Binders for Metal Ion Secondary Batteries
論文審査委員	松見　紀佳　　北陸先端科学技術大学院大学　教授
	長尾　祐樹　　同　教授
	谷池　俊明　　同　教授
	松村　和明　　同　教授
	上野　和英　　横浜国立大学　准教授

論文の内容の要旨

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 710^{th} 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 mAg^{-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-methyimidazolium) (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 $mAhg^{-1}$). 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 mAg^{-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

論文審査の結果の要旨

今日、リチウムイオン二次電池、ナトリウムイオン二次電池分野においては、電解質やバインダー用途としてイオン拡散能に優れた材料系が探索されている。そのような背景のもと、本研究ではフマル酸誘導体の電池材料としての応用が詳細に検討された。従来型の汎用バインダーの一つであるポリアクリル酸の場合には、高分子主鎖において炭素原子ひとつおきに官能基としてのカルボン酸を有しているが、ポリフマル酸においては主鎖を構成するすべての炭素原子上にカルボン酸を有し、高官能基密度高分子となっている。このようなポリフマル酸の構造的特質は、多点相互作用による集電体へのより強固な接着を促すとともに、高密度なイオンホッピングサイトによる高い金属カチオン拡散性をもたらすと期待できる。加えて、フマル酸はバイオベース化合物であり、バイオベースポリマーとしてのポリフマル酸の広範な活用は低炭素化技術としても魅力的である。フマル酸エステルのラジカル重合により得たポリフマル酸エステルの加水分解により、ポリフマル酸を得た。

ポリフマル酸エステルにLiTFSI を溶解させ､イオン伝導特性を評価したところ､51℃において 9.76×10^{-5} to 3.08×10^{-4} S cm^{-1} のイオン伝導度を示し、0.80-0.98 のリチウムイオン輸率が観測された。また、高分子のセグメント運動性と高度にデカップルしたイオン伝導挙動が観測された点も興味深い。

また、ポリフマル酸はリチウムイオン二次電池、ナトリウムイオン二次電池の負極バインダーとして優れた特性を示した。例えば、ナトリウムイオン二次電池の充放電試験においては、ハードカーボン負極型ハーフセルは30 mAg^{-1} 及び60 mAg^{-1} の電流密度においてそれぞれ288 $mAhg^{-1}$ 及び254$mAhg^{-1}$ の放電容量を示し、PVDF 系やポリアクリル酸系と比較して顕著に優れた性能を示した。また、長期サイクル耐久性においても優れていた。負極におけるナトリウムイオン拡散係数はポリフマル酸/ハードカーボン系では $1.90 \times 10^{-13} cm^2/s$、ポリアクリル酸/ハードカーボン系では $1.75 \times 10^{-13} cm^2/s$、PVDF/ハードカーポン系では $8.88 \times 10^{-14} cm^2/s$ であった。さらに、フマル酸から高密度にイオン液体構造を有する新規高分子化イオン液体の合成に成功している。電池向けのバインダーとしての有効性が示されたほか、多様なデバイスへの波及効果が期待される。

成果は学術的、実学的に共に有意義と考えられ、博士学位論文として十分に価値を有すると認めた。