学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Organophosphate-Based Self-Assembled Electrolytes for Electroactive Actuators
（有機リン酸エステル系自己組織化電解質を用いた電気活性アクチュエータ）

This doctoral thesis delves into the development of electrolytes with self-assembling ion pathways, offering significant advantages in ion transport efficiency and applications in electrochemical devices. The primary focus lies on creating novel organophosphate-based liquid crystals with ion transport pathways and their integration into free-standing liquid crystal–polymer composite electrolytes to fabricate high-frequency response actuators for haptic applications. While ionic electroactive polymer (iEAP) actuators show promise in producing bending deformation and stable force output at low voltages (< 4 V), their conventional iEAP actuators result in limited frequency response (< 30 Hz) and small amplitude actitation due to inefficient ion transfer in randomized ion-hopping sites. Moreover, fire hazard risks upon short circuits pose significant challenges for practical applications. Recent our advancements in photocured liquid crystal (LC) polymer electrolytes have demonstrated potential for high performance iEAP actuators with durable bendability and high force generation. However, their frequency responses do not meet the requirements for haptic applications, emphasizing the need for new design strategies for nanostructured electrolytes. Liquid organophosphates emerge as promising candidates for flame retardant electrolytes for lithium-ion batteries, assuming their long-range ordered arrangements could facilitate fast ion transport, leading to high frequency actuations.

Chapter 1 provides a comprehensive overview of flexible actuators, covering electrode and electrolyte materials used in iEAP actuators, their working mechanisms, and the potential applications of liquid crystal electrolytes.

Chapter 2 focuses on the design strategy of a diethylphosphate-based liquid crystal and its polymer composites, forming 2D lithium-ion transport pathways. The self-assembly of an equimolar mixture of phosphate, a room temperature liquid, and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) through ion–dipole interactions produced a layered smectic A liquid-crystalline phase, exhibiting high ionic conductivity of 10^{-4} S cm^{-1}. Through screening of blended polymers, the combination of the phosphate with 15 wt% polyvinyl chloride and 5 wt% poly(vinylidene fluoride-co-hexafluoropropylene) provided a free-standing, flexible LC–polymer composite film. This composite demonstrated mechanically stable and flat film-forming ability while maintaining high ion conductivity comparable to the LC electrolyte. The fabrication of actuators composed of this composite electrolyte, sandwiched between two pieces of the conducting polymer, poly(3,4-ethylenedioxythiophene) doped with poly(stylenesulfonic acid) (PEDOT:PSS), successfully achieved a high bending strain (0.63%), a maximum frequency response of up to 80 Hz, and an output force of 0.35

mN at 2 V and 0.1 Hz. The actuation was primarily driven by the Faradaic reaction of PEDOT:PSS cathode through the insertion of lithium cation as well as by the electric double layer capacitance.

Chapter 3 explores novel 2D liquid crystal assemblies employing a less hindered dimethylphosphate-based mesogenic molecule instead of diethylphosphate. This compound, combined with LiTFSI and an ionic liquid ($BMImPF_6$), demonstrating enhanced thermal stability and actuation response. The study elucidates the impacts of electrodes and ions on the actuator' s performance. The LiTFSI-based LC composite exhibited superior performance with PEDOT:PSS electrodes, achieving a maximum bending strain of 0.68% and an actuation response of up to 110 Hz, while also demonstrating a novel ring-shaped haptic interface. Conversely, the $BMImPF_6$-based LC composite showed potential with active carbon electrodes, addressing back relaxation phenomena observed for the LiTFSI systems.

Chapter 4 focuses on designing columnar LC electrolytes with 3D interconnected pathways for efficient lithium-ion transport. This design was accomplished through the self-assembly of a novel wedge-shaped phosphate molecule and lithium salts. Fine-tuning the lithium salts and mixing ratio resulted in a thermally stable columnar LC phase exhibiting high conductivity, reaching 10^{-4} S cm^{-1} at room temperature. Additionally, the integration of the columnar LC electrolytes into a commercially available microporous polyethylene membrane simplifies iEAP actuator processing, offering advantages in scalability, cost-effectiveness, and manufacturability. Coupled with PEDOT:PSS electrodes, the LC-infused electrolyte demonstrated promising performance metrics, including a bending strain of 0.52% at ± 2 V and 0.01 Hz, a maximum frequency response up to 50 Hz, and a output force of 0.5 mN at 0.1 Hz.

Chapter 5 proposed an iEAP actuator featuring high strain and rapid response, utilizing a fluorinated layered LC–polymer composite. Actuators fabricated with LC electrolytes from different ionic liquids showed improved strain, response frequency, and output force, reaching 0.70%, 130 Hz, 0.8 mN, respectively.

Chapter 6 concludes by summarizing the benefits of organophosphate-based LC–polymer composite electrolytes in iEAP actuators and outlining future prospects for improving these materials, highlighting their potential for significant advancements in ionics and electrochemical devices.