学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　呉　哲豪

学 位 論 文 題 名

Development of Photocured Liquid-Crystalline Electrolytes with Ion-Transport Pathways and their Application to Electroactive Actuators
（イオン輸送パスを有する光硬化液晶電解質の開発と電気活性アクチュエータへの応用）

The self-assembly of ionic molecules into hierarchically ordered structures is a promising route for the development of new solid electrolytes that enhance ion transport. This thesis focuses on presenting a series of ionic liquid-crystalline (LC) membrane electrolytes with commercial poly(3,4–ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) electrodes to create a novel class of ionic electroactive polymer (iEAP) actuators. Generally, iEAP actuators have the capability to produce bending deformation and deliver stable force output at low voltages (< 4 V), making them promising candidates for the next generation of soft robots and haptic sensors. However, conventional iEAP actuators, which rely on amorphous ion gels and hydrated ionic polymer films, suffer from limitations such as low force generation and poor durability during long-term actuation in the open air. These limitations mainly arise from the lack of mechanical robustness and electrolyte leakage. Therefore, the author’ s objective is to address these issues by utilizing the self-assembly of polymerizable LC molecules to design lightweight and robust LC polymer electrolytes specifically tailored for deformable actuators. The dimensionality of the ion diffusion pathways within the nanostructured electrolyte plays a crucial role in facilitating fast ion migration and reducing the energy barrier. With this in mind, the author conducts a comprehensive investigation into the relationship between LC nanostructures and actuation performance by exploring diverse designs of the LC molecules.

Chapter 1 provides a general introduction to iEAP actuators, including their working mechanism, the materials currently used in actuators, and the potential applications of ionic LC membranes.

Chapter 2 primarily focuses on an iEAP actuator based on the integration of ionic liquid (IL) into a one-dimensional (1D) ion-conductive free-standing LC polymer film. This film is formed through the columnar LC self-assembly and subsequent polymerization of polymerizable fan-shaped imidazolium LC molecules and ILs. The presence of inner ionophilic channels within this columnar LC structure enables fast ion migration compared to an amorphous structure. The correlation between the nanostructures and actuation performances is revealed through measurements of ionic conductivity as well as displacement and force of the actuators. The resulting columnar LC film actuator exhibits a bending strain of 0.2 % (at 2 V and 0.01 Hz) and generates a force of 0.3 mN, surpassing the performance of the corresponding amorphous film. This enhancement can be attributed to the efficient ion transport and the mechanical robustness of the ordered columnar structure. The concept of nanosegregation, characterized by the coexistence of liquid and anisotropic rigid domains, opens up a promising pathway for the design of electroactive actuators.

Achieving macroscopic alignment of the 1D ion-pathways that bridge between electrodes is a crucial technology for enhancing mass transport and electromechanical actuation. However, columnar LC materials often exhibit polydomain formation, posing a challenge to achieve vertical alignment of cylinders over large areas. In Chapter 3, the author presents a study on the self-assembly of a new environmentally benign biomolecular itaconate ionic amphiphile and a non-volatile IL, resulting in layer, bicontinuous cubic, and columnar LC structures. Through *in-situ* photopolymerization of these mixtures with a cross-linker, mechanically tough polymer electrolytes with layered ion transport pathways are obtained. The shear-aligned layered structure demonstrates enhanced ion transport and Young’ s modulus, making these robust

ionic LC electrolytes suitable for application in soft actuators. The results indicate that the aligned layer electrolyte enhances the bending strain (0.29 % at 2 V, 0.1 Hz) and generation force (0.7 mN at 2 V, 0.1 Hz) of the actuators. Moreover, the photocured itaconate ionic amphiphile can be used to fabricate actuators with specific shape using printing technology. Finally, the biodegradability of the itaconate LC polymer film has been confirmed through soil burial experiments. This materials design concept contributes to the development of sustainable soft electronics.

Moving beyond the construction of effective ion channels with 1D or 2D connectivity within the electrolytes, an intriguing design is to extend this concept to create alignment-free 3D ion transport pathways. In Chapter 4, the author introduces novel nanostructured polymer membrane electrolytes that contain 3D interconnected ion transport pathways. These lightweight and mechanically tough polymer films are obtained through a supramolecular columnar LC self-assembly of tapered ionic amphiphiles and a low content of IL (5.6 wt%), followed by photopolymerization. Leveraging the efficient and fast ion migration through the 3D ionic pathways in the solid matrix, nanostructured polymer actuators with flexible PEDOT:PSS electrodes exhibit excellent actuation performance (0.35 % at 2 V, 0.1 Hz) under low input voltages. The author demonstrates that this new type of actuator holds promise for applications in tactile sensor arrays, artificial muscles, and soft robots.

In order to further expand the design concept of 3D ionic pathways in electrolytes, the utilization of periodically ordered cubic structures proves to be an attractive option due to their interconnected ionic network and high viscoelastic characteristics. In Chapter 5, a micellar cubic electrolyte membrane with continuous ion pathways is introduced. This cubic electrolyte empowers the iEAP actuator to achieve both high bending strain (0.63 %) and high blocking force (2.7 mN) under low input voltage (2 V, 0.1 Hz). To construct this electrolyte membrane, the ionophilic domain within the inverse columnar structure, composed by wedge-shaped ionic LC molecules is further expanded to an inverse spherical symmetrical structure through the addition of an IL. The micellar cubic structure exhibits higher dynamic modulus, viscosity, and Young's modulus, both in its monomer state and as a polymer film. The author successfully demonstrates that the iEAP actuator based on the cubic LC membrane combines high-power output with large strain motion, enabling it to carry objects up to 40 times its own weight.

In Chapter 6, the author summarizes the benefit of using ionic LC electrolytes in iEAP actuators, discusses their overall performance, and explores future prospects for improving the reported materials and driving their real application. Through this dissertation, the author highlights the significance of advancing LC membrane and molecular design to comprehend the mechanical properties and actuation behavior of the designed iEAP actuators. The innovative concept of combining photocured molecular design with nanoscale channels offers a new opportunity for significant advancements in the fields of soft electronics.