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Title	高プロトン伝導性スルホン化ポリイミド薄膜におけるリオトロ ピック液晶性、組織構造と圧力応答性
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## Abstract

The catalyst layer (LC) is an important part of the polymer electrolyte membrane fuel cells (PEMFCs), where the hydrogen oxidation and oxygen reduction reactions (ORR) take place. Therefore, the efficiency of the LC has a profound effect on the performance of PEMFCs. The CL is a multi-scale composite structure composed of platinum group metal catalysts, carbon supports, ionomer materials and pores. The ionomers are used as binder and proton conduction network, carbon supports are applied to electron conduction, and pores provide mass transport channels for reactants and products. Studies have shown that the ionomer coverage on the catalyst particles decreases the ORR activity and increases the difficulty of oxygen diffusion to Pt surface, which seriously affects cell performance. Although reducing the thickness of the ionomers and low proton transport efficiency. Hence, it is necessary to develop ionomer thin film materials with high proton conductivity.

After decades of research, designing polymers with efficient proton transport channels based on well-defined phase segregation is a basic principle for development of high-performance proton-conducting materials. The alkyl-sulfonated polyimides (ASPIs) are a kind of high proton-conducting materials that can form ordered structure under humidified conditions driven by lyotropic liquid crystalline (LC) properties. Previous studies have systematically explored the lyotropic LC properties of fully aromatic ASPIs. However, the reports on sulfonated semi-alicyclic polyimides are still rare. Therefore, this study mainly focused on exploring the influence of semi-alicyclic structure on the ordered structure driven by lyotropic LC properties and proton conductivity of ASPI thin films. In addition, the potential of ASPIs as pressure-sensitive materials was explored.

Firstly, a sulfonated semi-alicyclic polyimide (BSPA-BOEDA) with a dienophile structure in backbone was newly synthesized. A facile cross-linking reaction was carried out via Fe3<sup>+</sup>-catalyzed Diels–Alder (D-A) reaction between BSPA-BOEDA and silica nanoparticles modified by (3-cyclopentadienylpropyl) triethoxyslane (CPTS). Compared

with BSPA-BOEDA, the cross-linked BSPA-BPEDA-NPs membrane and thin film showed better stability in water. Because of the nonlinear molecular conformation of neither BSPA-BOEDA nor BSPA-BPEDA-NPs can form well-defined ordered structures but only form phase separation. The proton conductivity of BSPA-BPEDA-NPs thin film is lower than that of BSPA-BOEDA thin film due to the cross-linking, reaching maxima value of 0.01 and 0.04 S cm<sup>-1</sup> at 25 °C and 95% RH, respectively.

Secondly, a sulfonated semi-alicyclic oligoimide (BSPA-CPDA) with a linear molecular conformation was newly synthesized. Benefiting from this conformation, the BSPA-CPDA thin film forms a lamellar structure similar to that of fully aromatic alkyl sulfonated polyimides driven by lyotropic liquid crystal properties, even the molecular weight is significantly lower. The BSPA-CPDA thin film exhibits a high proton conductivity of 0.2 S cm<sup>-1</sup> at 25 °C and 95% RH, which is the highest value among reported alkyl sulfonated polyimides with comparable molecular weight.

Finally, the basic pressure sensitivity of three ASPIs (ASPI-1, ASPI-2 and APOS-PMDA) was investigated. The results show that ASPI-1 has no pressure sensitivity, while ASPI-2 and APOS-PMDA show reproducible pressure sensitivity under humidified conditions. Particularly, the resistance of ASPI-2 thin film increases linearly with increasing the pressure between 0.1 and 0.2 MPa and the calculated sensitivity is 24 MPa<sup>-1</sup>.

**Keyword:** Sulfonated imide ionomer, Proton-conductive thin film, Lyotropic liquid crystal, Pressure sensor