新規ナトリウム型スルホン化ポリイミドの合成および組織構造と イオン伝導度のカチオン依存性

(北陸先端大¹・信大アクア・リジェネレーション機構²)

○山本有真¹・青木健太郎¹・是津信行²・長尾祐樹¹

Synthesis of a Novel Sodium-type Sulfonated Polyimide and Cation Dependence of Organized Structure and Ion Conductivity

(¹Japan Advanced Institute of Science and Technology, ²Institute for Aqua-Regeneration, Shinshu University) OYuma Yamamoto,¹ Kentaro Aoki,¹ Nobuyuki Zettsu,² Yuki Nagao¹

We have performed the structural and electrochemical characterization of highly organized sulfonated polyimides (SPI) thin films as polymer electrolytes layer, protonated SPI (SPI-1-H) and lithiated SPI (SPI-1-Li) were revealed to form a lamellar structure derived from their lyotropic liquid crystal natures. Moreover, the degree of structural ordering increased with humidification, leading to enhanced ion conductivity. In this study, we expanded same analogy to Na-ion conductive SPI-1-Na and compared the organized structure and ion conductivity with H- and Li-type SPI compounds. Grazing-incidence X-ray scattering (GIXRS) showed that SPI-1-Na thin film formed a lamellar structure at more than 60% relative humidity (RH), while the extension of the lamellar distance (*d*) with humidification was smaller than SPI-1-H and SPI-1-Li. Furthermore, we found SPI-1-Na exhibited higher ion conductivity than SPI-1-Li at lower RH range, however this trend reversed at higher humidity (≥ 80% RH).

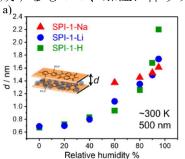
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高分子電解質であるスルホン化ポリイミド(SPI)において、カチオン X を H および Li とした SPI-1-X(Fig. 1)はリオトロピック液晶性に起因したラメラ構造を形成し、含水に伴いその周期性が向上することで、高いイオン伝導

Fig.1 Structure of SPI-1-X.

性を示すことが報告されている $^{1)}$ 。今回我々は X=Na とした SPI-1-Na を新規に合成し、アルカリ金属イオンを系統的に変化させた SPI-1 薄膜における組織構造とイオン 伝導度のカチオン依存性を検討した。斜入射 X 線散乱測定の結果、Na 体は相対湿度 60%以上でラメラ構造を形成するものの、加湿に伴うラメラ層間距離 d の伸長は H

体やLi体よりも小さいことを見出した(Fig. 2 a)。また、インピーダンス測定の結果、低湿度側ではNa体はLi体よりも高いイオン伝導度を示すが、相対湿度80%以上でこの傾向が逆転した(Fig. 2 b)。



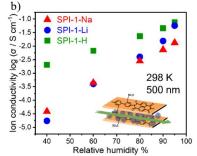


Fig. 2 a) Lamellar distance d and b) ion conductivity of SPI-1-X thin films.

1) T. Honbo et al., ACS Appl. Polym. Mater., 2010, 6, 13217.