Electrolyte characterization of ion conductive polymer nanofiber composite membrane

Ph. D Thesis

Presented to

TOKYO METROPOLITAN UNIVERSITY

Tsukasa WATANABE

In this thesis, the author describes ion conductive polymer nanofibers and their composite membranes, and evaluation their electrolyte and battery performances. The characteristics of these materials and a number of conclusions emerging from this study are summarized.

Chapter 2 Fabrication and electrolyte characterization of uniaxially-aligned anion conductive polymer nanofibers

(1) Uniaxially-aligned anion conductive Q-PAES nanofibers have been fabricated using the ES method and evaluated their anion conductive characteristics under various conditions.

(2) The aligned nanofibers had 10–15 times higher conductivity (up to 160 mS cm^{-1} at 90 °C and 95% RH) and lower activation energy (23–25 kJ mol^{-1}) than the corresponding membranes, even though the nanofibers showed lower water uptake than the corresponding membranes. The nanofibers prepared using a higher V_2 voltage had better anion conductive characteristics.

(3) TEM observation demonstrated a phase-separated structure inside the nanofibers. Well-aligned structure of polymer chain in nanofibers were confirmed by ATR-FT-IR. From these results (1-3), improvement of the anion conductive properties was able to lead to effective ion transport pathways in the nanofibers. By the preparation of high anion conductive polymer nanofibers, the nanofiber electrolyte materials will solve several problems such as low conductivity and high ion transport resistance.

Chapter 3 Anion conductive polymer nanofiber composite membrane: effects of nanofibers on polymer electrolyte characteristics

(1) Anion conductive electrospun nanofibers composite membranes have been prepared and evaluated their electrolyte performances. The incorporation of Q-PAES nanofibers was shown to be an efficient method to obtain effective performance for AEMFCs. As a result, the anion conductivity increased in the composite membrane compared to the membrane without nanofibers. (2) The conductivity of the

nanofibers in the composite membrane was also calculated to reveal that this value almost matched the intrinsic anion conductivity of the nanofibers themselves.

(3) Besides the effective ion conductive properties of the composite membrane, membrane stability such as the reductive degradation resistance and the mechanical strength was also much improved, and the gas barrier property of the composite membrane was enhanced compared to the membrane without nanofibers. These results indicated that the excellent properties of the nanofiber were maintained even in the matrix, and the composite membranes promise to have potential applications in future anion conductive devices.

Chapter 4 Fabrication and electrolyte characterization of lithium ion conductive nanofibers consisting of PEO-based polymers

(1) Lithium ion conductive polymer nanofibers have been prepared by ES method to reveal their electrolyte performances. Electrospun PEO with LiTFSI nanofibers were successfully fabricated, and the ion conductivity at room temperature indicated higher than the corresponding membrane.

(2) At the high PEO ratio over 50%, PI/PEO blend nanofibers indicated higher ion conductivity than the membrane. These high conductivities were ascribed to effective ion transport channel formed on hydrophilic nanofiber surface.

(3) PI-g-PEO with various grafting ratio and PEO chain length were synthesized by chemical imidization and ester reaction. PI-g-PEO nanofibers indicated higher thermal stability than PEO and PI/PEO blend nanofibers. The ion conductivity of PI-g-PEO nanofibers were dramatically changed by grafting ratio and PEO chain length. These electrolytes nanofibers with excellent electrochemical properties are considered to be potential candidates for all-solid-state lithium ion battery.

Chapter 5 Lithium ion conductive nanofibers framework: High-performance polymer electrolyte for all-solid-state secondary batteries

(1) Lithium ion conductive novel polymer (PI-g-PEO) nanofibers containing LiTFSI were prepared by

electrospinning process. The fabricated composite membranes showed superior ion conductivity and activation energy than the membrane without nanofiber.

(2) The degree of PEO crystallinity measured by DSC was suppressed by nanofibers composition. It was considered that crystal growth in PEO matrix was reduced due to restricted nano-scale area of nanofibers. Thin membrane formability and mechanical strength of the composite membrane improved due to rigid nanofibers network.

(3) The fabricated CR 2032 $LiFePO_4$/polymer electrolyte/Li all-solid-state coin cell using the composite electrolyte membrane delivered a good discharge capacity and stable cycle performance. This is an important step in expanding applications of lithium ion batteries and future devices.