

論文の内容の要旨

論文題目 STUDY ON STRUCTURE-PROPERTY RELATIONSHIP OF GRAFT-TYPE
FLUORINATED POLYMER ELECTROLYTE MEMBRANES USING QUANTUM BEAMS
(量子ビームを利用したグラフト型フッ素系高分子電解質膜の
構造 / 機能相関に関する研究)

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Polymer electrolyte fuel cells (PEFCs) have attracted much interest for solving environmental problems because their clean and efficient high-power generation is expected to reduce fossil fuel consumption and CO₂ emission which is the main source of the greenhouse effects. Polymer electrolyte membranes (PEMs) have been considered as one of the key components of a PEM fuel cell because their properties required for high fuel cell performance, such as ionic conductance, mechanical strength, chemical and thermal stability, are directly related to their power generation efficiency and durability under severe operating conditions.

In order to improve the cost, performance, and durability of PEM fuel cell, the fundamental understanding of the structure-property relationship of PEM is indispensable. The main current concern of structure-property relationships of PEM is to develop the PEM materials which possess higher proton conductivity at low relative humidity (RH) (<50% RH) and high temperatures (>80 °C) and superior mechanical properties under humid conditions via higher ionic content and/or improvement of proton transport pathway, without excessive swelling with water. The graft-type PEM which is prepared by irradiating polymer substrates using a quantum beam, immersing them in a monomer solution for graft polymerization, and subsequent sulfonation of the graft polymers is one of the promising candidates to solve the above problems because such material comprises the substrate films having mechanically tough crystalline phase and various functional grafted polymer phases directly bond to the polymer main chain. In addition, graft-type PEM materials prepared by the introduction of sulfonated graft side chains in polymer main chain is an excellent way to control the ion exchange capacity (IEC) values by a grafting degree (GD) and well-defined phase-separation between the hydrophilic/hydrophobic domains by sulfonation. The partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE) film comprised hydrocarbon and fluorocarbon segments has a strong radiation resistance which makes it possible to highly quantum beam irradiated for subsequent grafting and robust mechanical strength for long time durability of fuel cell operation. Thus, the structure-property relationship of poly(styrenesulfonic acid) grafted

poly(ethylene-*co*-tetrafluoroethylene) (ETFE-PEM) which is a promising candidate for fuel cell application was investigated in this work. Above mentions were presented in **Chapter 1**.

In **Chapter 2**, the detail procedure preparations of ETFE-PEM using pre-irradiation-induced graft polymerization are described. Then, the standard procedures of water uptake, *IEC*, thermal stability, and crystallinity measurements are also addressed. We focus on the measurement of effects of RH on the conductance and mechanical properties of ETFE-PEMs. Finally, the procedure measurements of small-angle scattering method using small- and ultra-small angle X-ray scattering (SAXS/USAXS), and field emission scanning electron microscope (FE-SEM) are presented. Note that a combination of SAXS and USAXS has displayed a powerful tool to observe a wide length scale of higher-order structures of PEM from nano- to micrometers which is not accessible using only conventional laboratory X-ray sources. Unlike SAXS measurement in which the bulk structures of specimens are analyzed, direct microscopic imaging such as FE-SEM provide the information of morphology and structures of the specimen's surface. Thus, in order to investigate fully the structure of PEM, both imaging and scattering methods are necessary.

In **Chapter 3**, the effects of RH on the conductance and mechanical properties (tensile strength, elongation at break) of ETFE-PEMs as a function of *IEC* (0–3.3 mmol/g) are discussed in comparison to Nafion-212. Thermal stability and crystallinity were also evaluated using thermo gravimetric analysis, and differential scanning calorimetry. We focused on proton conductivity at low RH (30% RH) and mechanical properties at high RH (100% RH), which are the main concerns for PEMs because they govern the power efficiency and durability under severe operating conditions in fuel cell systems. ETFE-PEM proton conductivity ranges for *IECs* of 1.3–2.9 mmol/g at 30% and 98% RH were 0.001–0.013 and 0.16–0.52 S/cm, respectively. Unlike aromatic hydrocarbon type PEMs, ETFE-PEMs have proton conductivities that are less dependent on RH because hydrophilic grafted polymers show clearer phase separation from the hydrophobic ETFE substrate, thereby maintaining conducting channels even under dry conditions. ETFE-PEM tensile strengths increased in the range of *IEC* > 2.0 mmol/g at 0% RH, but gradually decreased with increasing *IEC* at 100% RH and 80 °C. Moreover, ETFE-PEMs with *IEC* < 2.4 mmol/g showed higher tensile strengths compared to Nafion-212 at 100% RH. DSC measurements revealed that graft polymerization did not affect the crystallinity of ETFE-PEM, although sulfonation induced some damage in the crystalline domains. Further, the ETFE-PEM mechanical strength and proton conductivity were clearly related to PEM crystallinities. ETFE-PEMs with *IEC* > 2.7 mmol/g exhibited higher conductivity (>0.009 S/cm) at 30% RH and showed compatible tensile strengths of approximately 10 MPa at 100% RH and 80 °C.

In **Chapter 4**, the hierarchical structures of ETFE-PEMs under dry and hydrated states in wide *GDs* of 0–117% (*IECs* of 0–3.1 mmol/g) were investigated using a wide *q* observation ($4 \times 10^{-3} \text{ nm}^{-1} \leq q \leq 3 \text{ nm}^{-1}$) in SAXS/USAXS. By comparing the SAXS profiles of ETFE-PEMs with those of precursor original ETFE and polystyrene-grafted film (grafted-ETFE) as well as based on the variation of SAXS profiles with *GD* (*IEC*), two distinct scattering features can be observed in *q*-region I ($1.5 \times 10^{-1} \text{ nm}^{-1} \leq q \leq 3 \text{ nm}^{-1}$) and *q*-region II ($4 \times 10^{-3} \text{ nm}^{-1} \leq q \leq 1.5 \times 10^{-1}$

nm⁻¹).

In a q -region I, the pristine ETFE possesses the maximum peak (at q -position of 0.328 nm⁻¹) with d -spacing of 19.0 nm, originated from lamellar period. The grafted-ETFE with a GD of 59 % and the corresponding ETFE-PEM ($IEC = 2.4$ mmol/g) showed shoulder-like peaks (at q -positions of 0.219 and 0.216 nm⁻¹) with d -spacing of 28.7, and 29.1 nm, respectively. The lamellar periods increased with increasing GD ($\leq 59\%$) and then kept constant in a GD range of 59–117%, indicating that new phases consisting of polystyrene grafts (PS) and poly (styrene sulfonic acid) (PSSA) grafts generated around lamellar crystals with increasing the GD (IEC) up to 59% (2.4 mmol/g).

In a q -region II, the pristine ETFE film exhibited no appreciable scattering, while the grafted-ETFE films and ETFE-PEMs with GD of 19–59% showed discernible shoulder-like features, which assigned to the cylindrical crystallites (lamellar grains) with 185–320 nm in diameter and 701–769 nm in length, respectively, determined by profile fitting. These membranes with $DG \geq 81$ % showed shoulder-like peaks with less than half of scattering intensity than those of the membranes with $DG \leq 59\%$ and totally different scattering features, assigned to a new phase of structure with the length of a crystallite above the observed q region (> 1.6 μm). These discontinuous changes in a q -region II strongly indicate the phase transition from cylindrical-like shape to new phase crystallite structure between GD s of 59–81%.

The SAXS observation in the entire q -regions indicate that the ion-channels consisting of PSSA grafts located locally around the lamellar crystals in the membranes with $GD \leq 59\%$ and expands to out of the crystallites (lamellar grains) to have higher interconnection for $GD \geq 81\%$. In addition, the hydrophilic/hydrophobic boundary was less clear and the ordering of lamellar stacks and lamellar crystals still remained under hydrated state even at very high GD ($GD > 59\%$). The ion-conducting layers and lamellar structures with d -spacing around 29.1 nm in ETFE-PEM can be confirmed by SEM observation.

There have been some researches for structural analysis for the graft-type PEMs using SAXS and SANS. However, most of the papers did not concern the background effects due to thermal scattering (also known as liquid scattering) and amorphous phase scattering especially in high- q region (short correlation distances) even though ionomer peaks, which is one of the most important structures, are located in the this region. Thus, in **Chapter 5**, the hierarchical structures of ETFE-PEM with GD of 19% were investigated by SAXS in terms of background scattering ($I_B(q)$) correction in the high- q range ($2 \text{ nm}^{-1} < q < 10.5 \text{ nm}^{-1}$).

A simple procedure using a newly defined contribution factor for reliable background correction has been proposed for avoiding the overestimation of $I_B(q)$ to show the effects of background behavior in the high q range. The precisely estimated $I_B(q)$ indicates that the structures of interfacial thicknesses and intra-structures of the PS graft domains, appearing in the high- q range, were dramatically affected by background correction. Moreover, the new method for background correction dramatically affects the value of the interfacial thickness but not the correlation distance of the grafted polymers in the graft domain. In particular, the lamellar periods ($19.1 \text{ nm} \leq d_L \leq 26.0 \text{ nm}$) in the lower- q range were not altered by $I_B(q)$, whereas the interfacial thickness ($0.97 \text{ nm} \leq E \leq 1.11 \text{ nm}$) or ($1.46 \text{ nm} \leq E \leq 1.83 \text{ nm}$) using

Vonk's method with $n = 4$ or 6 in the higher- q range was only obtained (from the negative deviation of Porod's law) after determining the background-corrected scattering intensity. The scattering peak of the grafted-ETFE film ($d = 0.9$ nm) only appeared after background correction (and was independent of the background correction methods), whereas the ETFE-PEM still did not appear. After background correction, the negative deviation from Porod's law increases from the original ETFE to the grafted-ETFE and ETFE-PEM, and this increase indicates a relatively sharp boundary between the crystallite and amorphous layers within the lamellar structures of the grafted-ETFE and ETFE-PEM. The above results indicate that the hierarchical structures of graft-type PEMs in the high- q range were strongly affected by background correction.

In **Chapter 6**, study on structure-property relationship of ETFE-PEM revealed that the ETFE-PEM with high $IECs$ (>2.7 mmol/g) exhibited higher conductivity (> 0.009 S/cm) at 30% RH and compatible tensile strengths (approximately 10 MPa) at 100% RH at 80 °C, compared with those of Nafion, should result from the well interconnected ion-channels around the lamellar crystallites and the remaining of the lamellar stacks as well as lamellar crystallites (lamellar grains) in the PEMs, respectively. In addition, when GD increased beyond 59% ($IEC > 2.4$ mmol/g), the hydrophilic/hydrophobic boundary was less clear due to the miscible of PSSA grafts with polymer substrates which was found by Porod's law in SAXS measurement. This behavior prevented the stress degradation at the boundary induced by the swelling and thus, kept inherent crystallinity and mechanical properties of ETFE-PEM.

In **Chapter 7**, it is concluded that ETFE-PEMs showed high level of conductivity under low RH (30% RH) and excellent mechanical property under high RH (100%RH) at 80 °C should result from the well interconnected ion-channels around the lamellar crystallites and the remaining of the lamellar stacks as well as lamellar crystallites in the PEMs, respectively. In addition, the membranes kept inherent crystallinity and mechanical properties of ETFE-PEM even under high absorbed water conditions is due to the less clear boundary between the hydrophilic/hydrophobic domains with higher IEC ($IEC \geq 2.4$ mmol/g) which prevented the stress degradation at the boundary. The organization of lamellar stacks and lamellar crystallites (size, shape, connectivity) plays an important role to impact on the effective route comprising PSSA grafts for higher proton transportation through membrane while keep the inherent mechanical property and crystallinity of membranes. This is the first systematic and comprehensive understanding of structure-property relationship of graft-type PEM at high IEC ($IEC > 2.4$ mmol/g) under severe operation conditions for fuel cell applications. From these achievements, it is no doubt that ETFE-PEM with IEC around 2.4 – 2.7 mmol/g exhibited the promising electrochemical and mechanical properties for fuel cell applications, especially for clean electric source of vehicles. These achievements will offer optimization of higher-order structures and proper production processing of graft-type PEMs for high fuel cell performance as well as provide the fundamental understand of structure-property relationship of graft-type PEMs.