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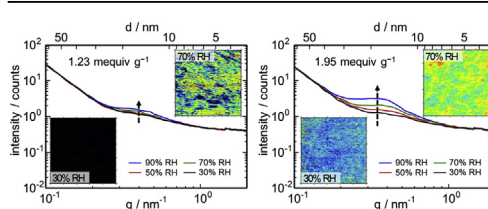
Phase separation and ion conductivity in the bulk and at the surface of anion exchange membranes with different ion exchange capacities at different humidities

Taro Kimura ^a, Ryo Akiyama ^b, Kenji Miyatake ^{b, c, *}, Junji Inukai ^{b, c, **}^a Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan^b Fuel Cell Nanomaterials Center, University of Yamanashi, 6-43 Miyamae-cho, Kofu 400-0021, Japan^c Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan

HIGHLIGHTS

- Bulk and surface structures of anion exchange membranes were investigated.
- Periodic structures inside the membranes were developed by water molecules.
- Surface anion conductive regions became homogeneous with increasing RHs and IECs.
- Increasing IEC gave different influences on phase separations in bulk and on surface.

GRAPHICAL ABSTRACT



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ABSTRACT

For higher performances of anion exchange membrane (AEM) fuel cells, understanding the phase-separated structures inside AEMs is essential, as well as those at the catalyst layer/membrane interfaces. The AEMs based on quaternized aromatic semi-block copolymers with different ion exchange capacities (IECs) were systematically investigated. With IECs of 1.23 and 1.95 mequiv g⁻¹, the water uptakes at room temperature were 37% and 98%, and the anion conductivities 23.6 and 71.4 mS cm⁻¹, respectively. The increases were not proportional to the IEC. Images obtained by transmission electron microscopy in vacuum were similar with both IEC values, but the development of a clear phase separation in humidified nitrogen was observed in the profiles only with 1.95 mequiv g⁻¹ obtained by small-angle X-ray scattering. At the temperature of 40 °C and the relative humidity (RH) of 30%, the average currents observed at the tip apex by current-sensing atomic force microscopy were <0.5 and 10 pA with 1.23 and 1.95 mequiv g⁻¹, respectively, and those at 70% RH were 10 and 15 pA, respectively. The humidity gave a larger influence on the bulk structure with 1.95 mequiv g⁻¹, whereas a larger influence on the surface conductivity with 1.23 mequiv g⁻¹.

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* Corresponding author. Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan.

** Corresponding author. Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan.

E-mail addresses: miyatake@yamanashi.ac.jp (K. Miyatake), jinukai@yamanashi.ac.jp (J. Inukai).

1. Introduction

Fuel cells have been receiving considerable attention as clean energy conversion devices due to their high efficiency and low emission [1,2]. Proton exchange membrane fuel cells (PEMFCs)

have now been commercialized as the electrochemical power-generating devices for stationary and automotive applications. Recently, anion exchange membrane fuel cells (AEMFCs) have been actively studied because of the potential use of non-precious metal catalysts and the enhancement of oxygen reduction kinetics on non-Pt catalysts due to the operation under alkaline conditions [3–6]. Power generation by AEMFCs with non-precious metals, such as nickel, cobalt, and silver, has already been demonstrated [7–13]. To accomplish higher performance and durability of AEMFCs, the enhancement of the properties of the anion exchange membranes (AEMs) is essential, including higher chemical/mechanical stability at high temperatures under alkaline conditions and higher anion conductivity. To improve both the stability and the conductivity of AEMs, various types of main-chain structures and cationic groups in polymers have been investigated [3–6,14–18]. In our group, a series of poly (arylene ether) (PE) multiblock and semi-block copolymers, also used for proton exchange membranes (PEMs) [19,20], was applied to the main chains and functionalized with quaternary ammonium groups for AEMs such as QPE-bl-1, -3 and -9 [9,21–23]. Recently, we have synthesized a quaternized poly (arylene ether) semi-block copolymer (QPE-bl-11) composed of densely quaternized phenylene as the hydrophilic component and arylene ether sulfone as the hydrophobic block [24]. The QPE-bl-11 membranes with an ion exchange capacity (IEC) of 1.95 mequiv g⁻¹ showed a superior OH⁻ conductivity (130 mS cm⁻¹) in water at 80 °C. After an 8-h treatment with Fenton's reagent, the QPE-bl-11 membrane retained its shape and bendability. The losses of weight, IEC, and hydroxide ion conductivity were negligibly small. As a mechanical stability test, dynamic mechanical analysis was carried out; the storage moduli and loss moduli of QPE-bl-11 membranes were nearly constant from room temperature to 95 °C. The IEC values seemed to be a minor factor, with little effect on these properties. The humidity dependence was also measured, and the loss moduli decreased with increasing humidity for all the membranes due to the increased water absorption [24].

In PEMs, phase-separated structures are suggested to be organized. It has been proposed that hydrophilic groups in a hydrophobic matrix form spherically-shaped clusters, interconnected by narrow ionic channels [2,25,26]; the interconnected hydrophilic clusters in the phase-separated membrane structure function as the proton conductive networks for the proton transport. Recently, cylindrical polymer bundle models [27,28] and lamellar models [28,29] have been suggested and are being accepted. The coordination of the phase-separated structure of PEMs, such as by block copolymerization [2,19,30–32], has been attempted for enhancing the proton conductivity. Additionally, highly-dispersed ion conductive spots at the membrane surfaces (or the interfaces between the membrane and the catalyst layers) could contribute to improving the cell performance because of the improved interfacial contact in terms of the mass transport of water molecules and ions [33–36]. To investigate the proton-conducting properties on a PEM surface, current-sensing atomic force microscopy (CS-AFM) was recently applied to Nafion [34–46], and then to hydrocarbon-based membranes [50–54], which allowed a direct observation of proton-conducting paths on the surface under controlled conditions. The hydration of the membranes was revealed to impact the distribution of the proton-conductive domains on PEM surfaces [38,42,46–54]. However, for AEMFCs, only a few results have been reported on the anion-conducting behavior, both in the bulk [55] and at the surface [35,56]. Chen et al. reported that the activation energy barriers in AEMs for the hydroxide diffusion were larger than those for the proton diffusion in PEMs [55]. They also

suggested that the ion diffusion mechanism in AEMs might be potentially different from that in PEMs. He et al. reported the observation of the surface conductance on Tokuyama A-006 membranes [56]. In a recent paper, we have compared the distributions of the anion-conductive areas on two different AEMs [35]. Not only the ion conductivity of the bulk, but also the ion conductivities at the surfaces of the AEMs clearly influenced the AEMFC performances.

In this paper, of two QPE-bl-11 membranes [24] with different IECs, systematic investigations were carried out by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) for the bulk characteristics and by CS-AFM for the surface characteristics. The influence of the IEC was large both in the bulk and at the surface. The importance of water molecules absorbed in the membranes was demonstrated as well.

2. Experimental

2.1. Water uptake and ion conductivity

QPE-bl-11 membranes (Fig. 1) with IECs of 1.23 (X = 4, m: n = 1: 2.9) and 1.95 mequiv g⁻¹ (X = 4, m: n = 1: 5.4) were synthesized as reported previously [24]. The IECs were determined by ¹H nuclear magnetic resonance. The membranes were obtained by casting a dimethyl sulfoxide solution containing QPE-bl-11 on a flat glass plate. The average membrane thickness was approximately 60 μm. Water uptake ((mass of hydrated membrane – mass of dry membrane)/(mass of dry membrane) × 100%) of the membranes was measured at room temperature by use of a microbalance (water immersion for 2 h at room temperature and vacuum drying for 3 h at 80 °C). The OH⁻ conductivity of the membranes in OH⁻ form was measured in pure degassed water using a four-probe conductivity cell with an impedance spectroscopic analyzer (Solartron 1255B and 1287, Solartron, Inc.) carefully avoiding CO₂, a contaminant in air [6,35].

2.2. TEM and SAXS

For TEM observations, the membranes were ion-exchanged with PtCl₄²⁻ by immersing in a PtCl₄²⁻ aqueous solution. Then the membranes were rinsed with deionized water and dried in a vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, subsequently sectioned to 60 nm thickness with a microtome (Ultracut UCT, Leica) and placed on copper grids. TEM images were taken with a transmission electron microscope (H-9500, Hitachi) with an accelerating voltage of 200 kV.

SAXS measurements of AEMs in chloride-ion form were performed using a NANO-Viewer (Rigaku) with an environmental chamber, and Cu (Kα) was used as the X-ray source [57]. The AEMs were treated in 1 M hydrochloric acid at room temperature for 48 h and immersed in deionized, degassed water for 24 h. Then, the AEMs in chloride-ion form were placed in the environmental chamber, and each specimen was equilibrated at least for 2 h at different humidities before the SAXS measurements. The scattering

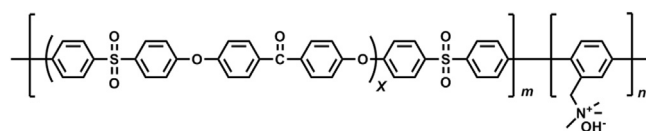


Fig. 1. Chemical structure of QPE-bl-11.

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