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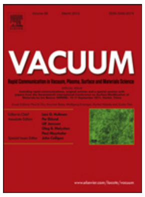

# Effects of ion beam surface modification on water absorption characteristics of perfluorosulfonic acid membranes

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ABSTRACT

The dynamic behavior of water within ion beam (10 keV $Ar^+$, 1.0 × $10^{16}$–1.2 × $10^{17}$ ions/$cm^2$) modified perfluorosulfonic acid (PFSA) membranes was investigated at room temperature by combining direct-current (DC) resistance with alternative-current (AC) impedance methods under a water-saturated air atmosphere. The bulk impedance in existing surface sulfonate groups ($SO_3^-$) decreased approximately one order of magnitude as a result of $Ar^+$ ion irradiation compared to the unirradiated membrane. The enhancement in the proton conductivity results in an improvement of the water absorption characteristics at the $Ar^+$ ion-modified surface which showed large superficies as well as hydrophilic radicals. These results can be explained in base of a relative increase in both the water content of the membrane and the change in the interactions of water molecules with sulfonate group at the interface on the proton-transfer process.

## 1. Introduction

Perfluorosulfonic acid (PFSA) polymer electrolyte membranes (PEMs), with their extremely high proton conductivity at operating temperatures (ca. 373 K) and high humidification properties, possess elevated potential as hydrogen separators in hydrogen production systems from water [1]. The absorption characteristics of water into the polymer electrolyte membranes is one of the most significant parameters determining the development of hydrogen gas production systems since it greatly contributes to the increase in the proton conductivity and re-combination rate for hydrogen molecule formation. In particular, in order to increase the amount of hydrogen produced per unit of time and to minimize the cost of producing this gas, it is necessary to improve the water dissociation on the surface of the membrane at temperatures below 373 K.

In the present study, we performed ion beam surface modification on PFSA membranes under vacuum and room temperature with the aim of modifying the water or proton-transfer processes by means of atomic displacements and ionizing effects. Additionally, with the aim of estimating the water absorption characteristics of PFSA membranes, the dynamic behaviors of water or protons within the ion-induced PEMs were in-situ investigated at pressure conditions ranging from vacuum to air atmosphere and room temperature using direct-current (DC) resistance as well as alternative-current (AC) impedance methods.

## 2. Experimental

The PFSA membranes used in the present study were Aciplex-SF-1004®, fabricated by Asahi Kasei Corporation. The dimensions of the membranes were 8.0 mm diameter and 117 μm thick. The PFSA membrane was one-faced irradiated with 10 keV $Ar^+$ ions from a colutron accelerator at room temperature of 297 K under vacuum. The incident direction of $Ar^+$ ions beam was normal to the surface of the membrane. The flux of the $Ar^+$ ions beam was approximately 6.9 × $10^{13}$ ions/$cm^2$s, while four different ion fluences (i.e., 1.0 × $10^{16}$, 5.0 × $10^{16}$, 8.4 × $10^{16}$, and 1.2 × $10^{17}$ ions/$cm^2$) were applied to the membranes. The SRIM2003 code indicated that, for 10 keV $Ar^+$ ions implantation into membranes, the projected range and the range straggling of Ar were approximately 20.8 and 7.5 nm, respectively [2]. This calculation made several assumptions: (i) a membrane composition of $C_{35}O_5F_{55}(SO_3H)$; (ii) displacement energies of H, C, O, F, and S of 10, 28, 28, 25, and 25 eV, respectively; (iii) a lattice binding energy of 3 eV for all of elements and; (iv) a membrane density of approximately 1.54 g/$cm^3$.

The surface morphology of the $Ar^+$ ion-irradiated membranes was observed by scanning electron microscopy (SEM). In addition, the structural change in the $Ar^+$ ion-irradiated membranes was investigated at room temperature and under air using transmission spectroscopy with ultraviolet (UV) and visible (Vis) wavelength ranges of

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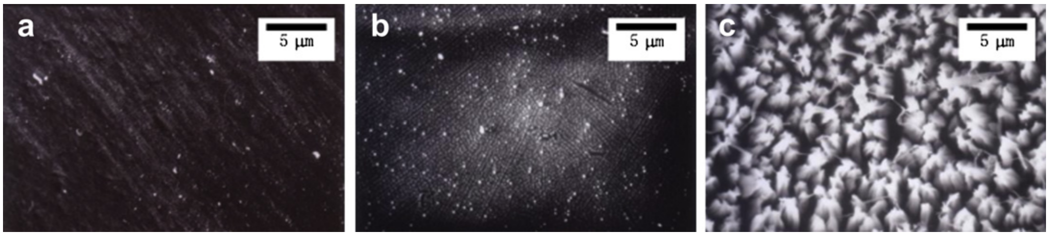

**Fig. 1.** SEM (SEI: secondary electron image) micrographs of (a) unirradiated and $Ar^+$ ion-irradiated PFSA membranes at fluences of (b) 1.0 × $10^{16}$ and (c) 1.2 × $10^{17}$ ions/$cm^2$.

190–380 and 380–760 nm, respectively, and Fourier transform infrared (FTIR) spectroscopy using the attenuated total refraction (ATR) technique for the wavenumber range 500–3600 $cm^{-1}$.

The in-situ electrical conductivity measurements were carried out by combining DC resistance with AC impedance methods. In these experiments, (Pt) central electrodes (diameter: 7.5 mm; thickness: 0.1 μm) were sputtered onto both face of the $Ar^+$ ion-irradiated membrane under vacuum using an ion-sputtering device. The membrane was mounted into a special vacuum vessel consisting of a quartz tube which was previously evacuated under a pressure of 6.0 × $10^{-5}$ Pa. The relative humidity in vacuum was assumed to be 0%. Subsequently, $Ar^+$ ion-irradiated membranes at different ion fluences (0, 1.0 × $10^{16}$, 8.4 × $10^{16}$, and 1.2 × $10^{17}$ ions/$cm^2$) were exposed to air with a relative humidity of approximately 50% and temperatures of 291, 298, 294, and 299 K, respectively. In-situ electrical conductivity measurements were carried out by applying DC-voltages of +1.0 V or AC-voltages of +0.01 V and subsequently recording the resulting DC or AC-currents during air exposure. The impedances at bulk, radical formation, and interface between the electrolyte membrane and the Pt electrode were identified by comparing DC and AC data. In the case of the AC impedance method, the frequency ranged from 4.0 to 1.0 × $10^6$ Hz.

## 3. Results and discussion

Fig. 1 shows SEM (SEI: secondary electron image) micrographs of both unirradiated and $Ar^+$ ion-irradiated PFSA membranes at several ion fluencies. The SEI image of the unirradiated PFSA membrane was almost dark since it acts as an insulator and dependent on amount of secondary electrons which are recoiled elastically by incident electrons. However, there seems to be a little intrinsic defect on the top-surface which could be produced during the preparation of the membranes. As shown in Fig. 1(b), a noticeable number of nanometric dots appeared as a consequence of the regularly arranged $Ar^+$ ion irradiation at the lowest ion fluence. At higher ion fluences (e.g., 1.2 × $10^{17}$ ions/$cm^2$), a new surface morphology consisting of large superficies with an assembly projection with a width of approximately 1.0 μm appeared. Additionally, the SEI image was extremely light. These results show the improvement of the electrical properties by changing the morphology on the top-surface.

Figs. 2 and 3 show typical UV–Vis (transmission) and ATR-FTIR (refraction) optical absorption spectra, respectively, for the unirradiated and $Ar^+$ ion-irradiated PFSA membranes. As shown in Fig. 2, the optical densities for UV–Vis optical absorption increased at wavelengths below 500 nm for 1.0 × $10^{16}$ ions/$cm^2$ and below 900 nm for 5.0 × $10^{16}$, 8.4 × $10^{16}$, and 1.2 × $10^{17}$ ions/$cm^2$. In the latter case, the optical densities at wavelengths above 700 nm further increased with the ion fluence while the optical densities at wavelengths below 200 nm decreased dramatically at a fluence of 1.2 × $10^{17}$ ions/$cm^2$. On the basis of the experimental results from the X-ray irradiation of Nafion (obtained by UV–Vis electronic absorption spectroscopy and electron paramagnetic resonance (EPR) spectroscopy), the observed increase in the optical densities at several wavelengths are inferred to be associated with fluorocarbon radicals, peroxy radicals, and carbonyl groups (R-COF), respectively [3]. The interaction of $Ar^+$ ions with the PFSA membrane constituent elements such as H, C, O, F, and S can be described in terms of photoelectric effects and Compton scattering of electrons as well as atomic displacement by elastic collisions. In particular, the atomic displacement is for the main parameter affecting the interaction of $Ar^+$ ions with the constituent elements. Consequently, the modified surface morphology, shown in Fig. 1(b) and (c), may be probably produced by ion sputtering resulting in a modified surface with no cross-links, chain scissions, and long-chain branches produced by radiolysis. The ATR-FTIR optical absorption spectrum of the unirradiated PFSA membrane (Fig. 3)

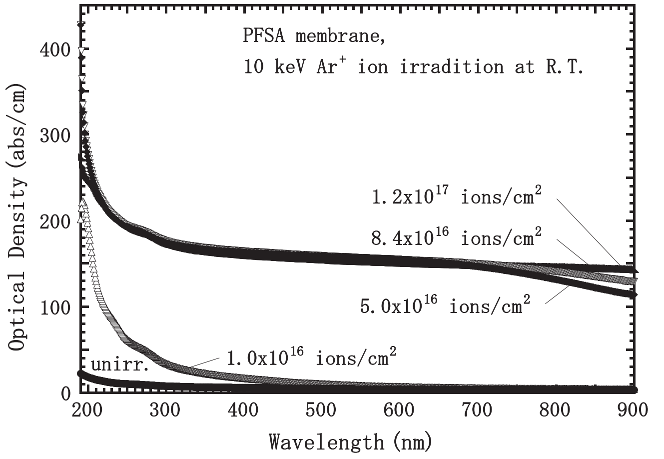

**Fig. 2.** UV–Vis optical absorption spectra of the unirradiated and $Ar^+$ ion-irradiated PFSA membranes at fluences of 1.0 × $10^{16}$, 5.0 × $10^{16}$, 8.4 × $10^{16}$, and 1.2 × $10^{17}$ ions/$cm^2$.

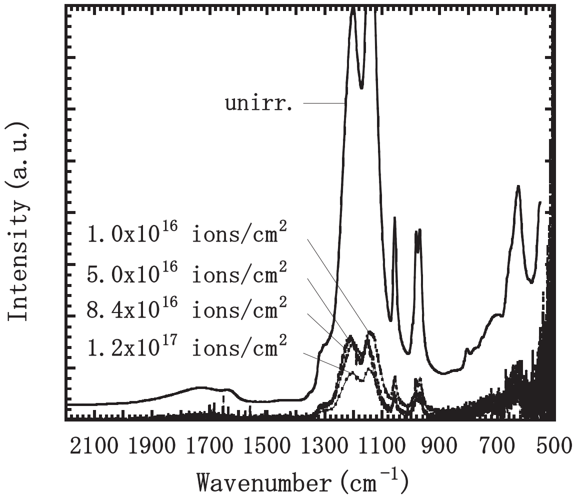

**Fig. 3.** FTIR optical absorption spectra of the unirradiated and $Ar^+$ ion-irradiated PFSA membranes at fluences of 1.0 × $10^{16}$, 5.0 × $10^{16}$, 8.4 × $10^{16}$, and 1.2 × $10^{17}$ ions/$cm^2$.