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Effects of γ-ray and neutron irradiation on electrical characteristic of proton-conducting polymer electrolyte membranes

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Abstract

Radiation effects on proton-conducting polymer, perfluorosulfonic acid (PFSA) membranes were studied as the absorbed dose dependence of the electrical characteristics. *V–I* characteristic was measured under irradiation of γ-rays and of 14 MeV neutrons. Under the neutron irradiation, the electrical conductivity of membranes decreased with an exponential form. In the case of the γ-ray irradiation, the electrical conductivity increased with increase of the dose and the membranes showed higher conductivity than before the irradiation, as much as 150 times after irradiation to a dose of more than 100 kGy. The effects on the electrical conductivity under irradiation is explained by structural changes in membranes caused by radiation effects as well as by changes at the interface between electrodes and membranes.

1. Introduction

Polymers are candidates for several use in a fusion reactor; they can be used as electrical insulators and separation membranes for hydrogen isotopes, they are inexpensive, and their reliable industrial mass-production processes are already established. However, effects of γ-ray and neutron irradiation on organic polymers have not been clearly understood. Processing of the polymers by energetic beams have been studied with visible light radiation, plasma, and penetrating radiation. However, effects of penetrating irradiations on the electrical properties of polymers are far from being adequately understood for their applications in intense radiation environments. In this paper, radiation effects in perfluorosulfonic acid (PFSA) membranes, a proton-conducting polymer, were studied. PFSA membranes, such as Nafion®, [1] Aciplex®, [2] Flemion®, [3] and Dow membranes [1], are now commercially available. They are mainly used for polymer electrolyte fuel cells (PEFCs) as ion exchanged electrolyte membranes. They can be used for hydrogen isotope separation membranes and as membranes for gas purification systems in a fusion reactor. Also, some organic polymers are candidates as inexpensive but reliable electrical insulators in instruments deployed in peripheral regions of a fusion reactor.

A large number of $-SO_3H$ in the membranes cohere, forming the inverse micellar of a few tens nano meter [2]. Water absorption into a membrane gives protons hydrated in the inverse micellar.

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[1] A Dupont registered trademark.
[2] A Asahi Kasei registered trademark.
[3] A Asahi Glass registered trademark.

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A hydrated proton moves from one $-SO_3H$ to another $-SO_3H$ in sequence [3]. Consequently, proton conduction is enhanced. The PFSA membranes have been principally studied concerning their proton conductivity with parameters such as equivalent weight (EW) [4], water uptake ratio ($\lambda = [H_2O]/SO_3^-$) [5,6], water content (relative humidity (RH)) [7], crystallinity (cluster structure involving hydrophilic and hydrophobic components) [2,3], but radiation effects on their proton conductivity have not been studied. D.C. Phillips reported comprehensively on the behavior of the electrical conductivity of organic compounds under ionizing irradiation [8]. He reported radiation induced conductivity (RIC) behavior similar to that of well-known inorganic insulators. Hydrogen isotopes will play an important role in the electrical conductivity of polymers, especially in proton conductive materials, in a fusion reactor environment but Phillips referred to the effects of hydrogen only briefly. This paper evaluates dynamic and accumulated irradiation effects on the electrical characteristic of the PFSA membranes, focusing on the role of proton conductivity.

2. Experimental

The sample used for the experiment is Aciplex s-1004® (EW = 950), whose thickness is 0.117 mm. The electrical conductivity of the surface and the volume was measured under irradiation with γ-rays from a cobalt-60 (1.17 and 1.33 MeV, 2.4×10^4 Gy/h) source in the Takasaki Research Establishment of Japan Atomic Energy Research Institute (JAERI), as well as under 14 MeV fusion neutron irradiation (4×10^{12} n/m^{2}s from the D–T reaction) in the Fusion Neutronics Source (FNS) in Tokai Research Establishment in JAERI. The accompanying γ-rays during neutron irradiation in the FNS is very small, estimated to be less than 10^{-5} Gy/s.

The irradiations were carried out at room temperature. The absorbed dose on the sample was up to 650 kGy for the γ-ray irradiation and the fluence was up to 3.3×10^{17} n/m^2 for the neutron irradiation. A schematic illustration of the measuring set-ups is shown in Fig. 1. Each cell was made of a machinable ceramic insulator. The electrodes for the volume-electrical-conductivity measurement was zirconium (Zr) plates (8 mm × 8 mm × 0.1 mm) in the case of the γ-ray irradiation and tantalum (Ta) plates (8 mm × 8 mm × 0.1 mm) in the case of the neutron irradiation. The Aciplex® membrane was sandwiched between the two plate electrodes. The electrode for the surface-electrical-conductivity measurement was a platinum (Pt) wire of 0.25 mmϕ (3 mm width with 24 mm interval). The electrical current was measured by a KEITHLEY 6517 ELECTROMETER/HIGH RESISTANCE SYSTEM, and the power source was a KEITHLEY 238 HIGH CURRENT SOURCE MEASUREMENT UNIT.

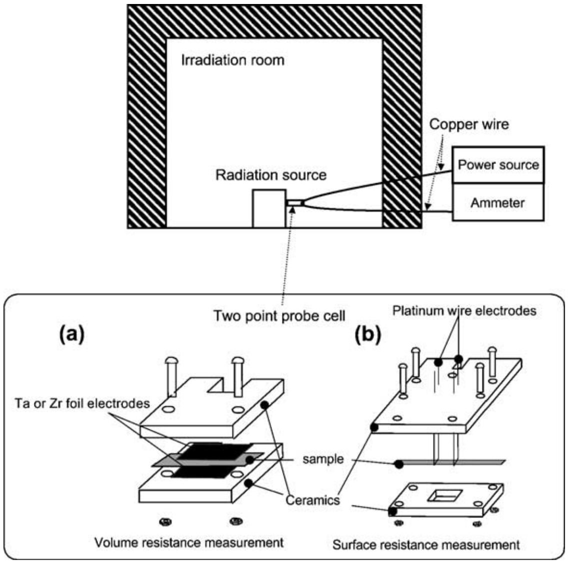

Fig. 1. Schematic illustrations of measuring setups, (a) for volume electrical conductivity, (b) for surface electrical conductivity.

3. Results and discussion

Fig. 2 shows measured electrical current through the membrane as a function of the applied voltage (*V–I* plot), (a) under γ-ray irradiation and, (b) under neutron irradiation, with parameters of absorbed dose and fluence for the γ-ray irradiation and the 14 MeV neutron irradiation, respectively. Similar *V–I* plots are shown for the surface electrical conduction in Fig. 3. The volume electrical conductivity is plotted as a function of irradiation dose in Fig. 4.

It should be noted that an abrupt increase of the electrical conductivity was not observed at the onset of the irradiation in either the γ-ray or the neutron irradiation. In general, the electrical conductivity, σ, under irradiation can be expressed as a follow [9],

$$\sigma = \sigma_0 + \sigma_{ric}. \tag{1}$$

Here, σ_0 is the intrinsic conductivity and σ_{ric} is the radiation induced conductivity (RIC). The results indicated that the RIC, σ_{ric} is very small or negligible in the present proton conductive polymer. The RIC induced by the less than 10 Gy/s in the γ-ray irradiation and less than 10^{-4} Gy/s in the neutron irradiation, even accounting for that caused by the 14 MeV neutrons, would not contribute to the total electrical conductivity, σ. Also, the surface conductivity was about the same order as the volume conductivity under the present irradiation conditions.

Among the plots shown in Figs. 2 and 3, the volume electrical conductivity under the γ-ray irradiation

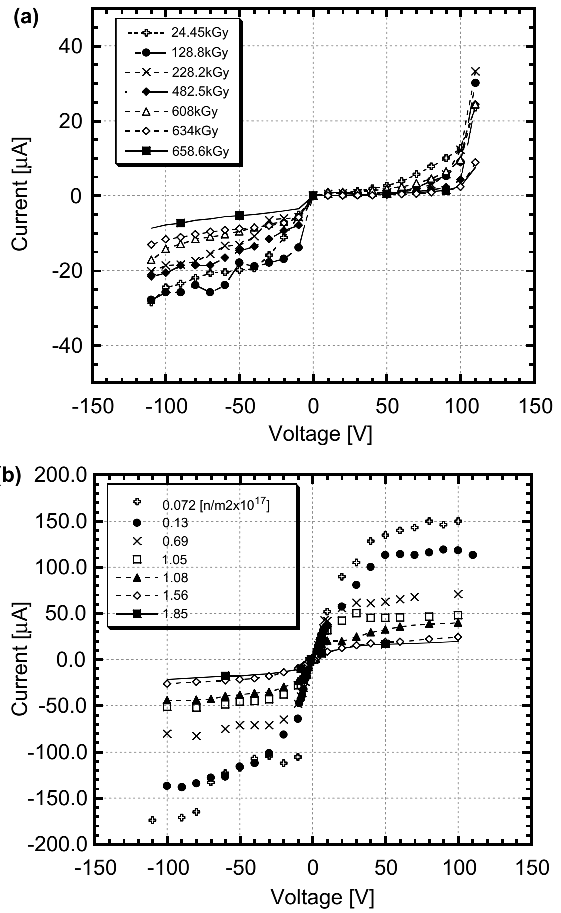

Fig. 2. *V–I* plots for volume electrical conductivity measurements, (a) γ-ray irradiation, (b) neutron irradiation.

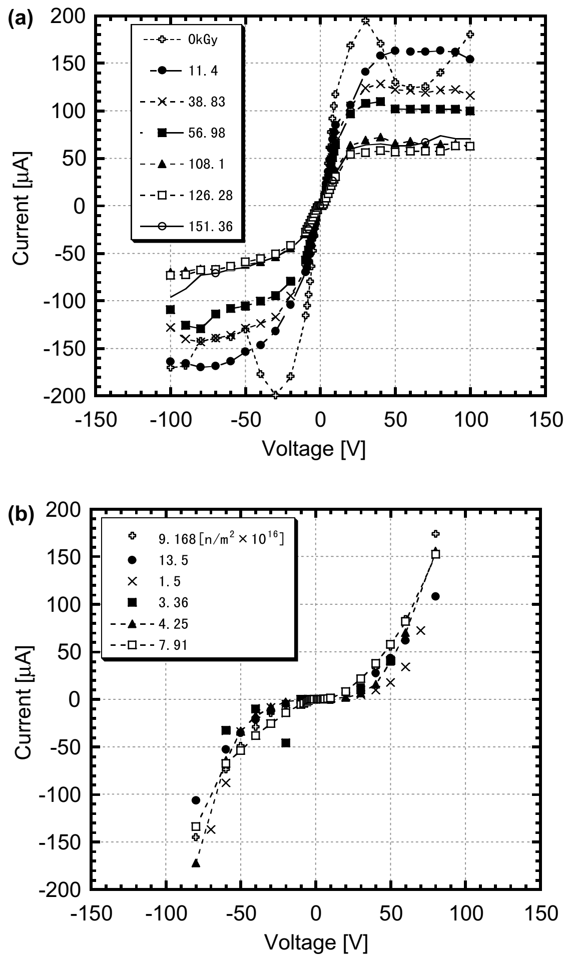

Fig. 3. *V–I* plots of surface electrical conductivity measurements, (a) γ-ray irradiation, (b) neutron irradiation.

showed a clear asymmetric polarity of the induced electrical current as a function of the applied voltage. The post irradiation examination showed that some chemical interaction took place at the interfaces between the zirconium foil and the membrane. It was found that the zirconium was more chemically sensitive to the oxidation current (an electrical current to the anode) and the reduction current (an electrical current to the cathode) than Ta and Pt. Also, effects of the electronic excitation in the γ-ray irradiation may enhance the chemical reaction between the Zr electrode and the membrane. The results clearly shows an important role of the electrode material in the electrical conductivity under irradiation.

When Fig. 3(a) and (b) as well as Fig. 4(a) and (b) are compared, it is noticed that there is a definite difference between the effects of the γ-ray and the neutron irradiation. The volume electrical conductivity of the Aciplex membrane at room temperature ranges from 10^{-4} to 10^{-10} S/m, depending on the humidity [7,10]. In the present experiments, the electrical conductivity without irradiation was 6.5×10^{-10} and 7.5×10^{-6} S/m for the γ-ray and the neutron irradiation, respectively. The relatively high electrical conductivity in the neutron irradiation will be due to the higher humidity and salt content in the environment. The 14 MeV neutron irradiation decreased the electrical conductivity of the membrane monotonically with increase of fluence. In the meantime, the γ-ray irradiation increased the electrical conductivity with dose up to 300 kGy. Above 500 kGy, the electrical conductivity decreased drastically with increase of the dose. The post irradiation measurements confirmed the increase of intrinsic conductivity, σ_0 with the dose ranges from 2 kGy to a few hundreds kGy. It is assumed that the atomic displacements caused by the 14 MeV neutron irradiation break the molecular structure of the membrane and reduce the proton conductivity. In the meantime, a moderate irradiation with γ-rays modify the structure and enhance the proton conductivity.

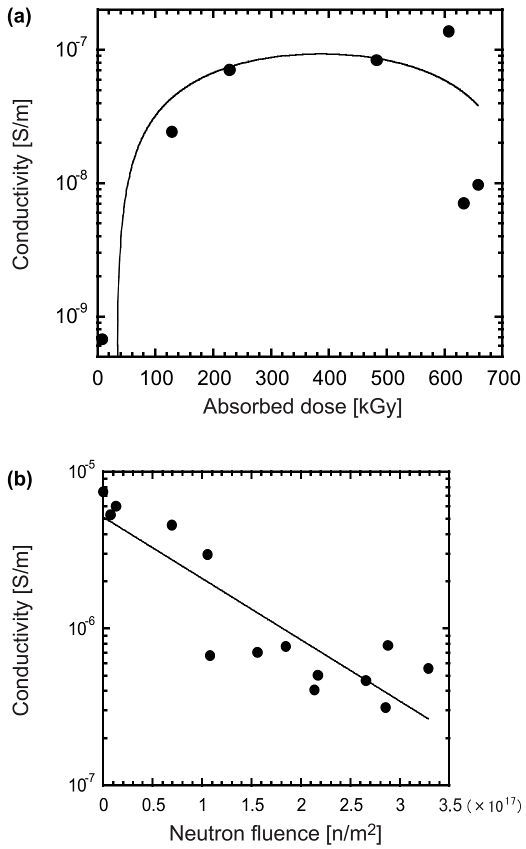

Fig. 4. Electrical conductivity as a function of, (a) absorbed dose of γ-rays, (b) neutron fluence. The solid line is provided as guide for the eyes.

It is believed that γ-ray irradiation above 500 kGy causes structural changes which reduce the proton conductivity as dose the 14 MeV neutron irradiation.

In a fusion irradiation environment, organic polymers as well as ceramics [11] will absorb large amount of hydrogen isotopes, which will affect their functional properties such as electrical conductivity under the irradiation.

4. Summary

Under γ-ray and 14 MeV neutron irradiation, electrical characteristic of PFSA proton conductive polymer films changed through structural changes caused by radiation effects. The radiation induced conductivity was negligible in the PFSA under the present irradiation conditions. The atomic displacements caused by the 14 MeV neutron break the structure and reduce the proton conductivity. At the same time, the electronic excitation effects by the γ-ray irradiation will modify the structure of membrane and enhance the proton conductivity. The interface between electrode and membrane will also play a role in radiation induced modification of the electrical properties of the PFSA.

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