

## Electronic Supplementary Information

# Surface modification of Nafion membranes by ion implantation to reduce methanol crossover in direct methanol fuel cells

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## **Experimental details**

### **1. Surface modification of Nafion membranes by ion implantation**

Nafion 115 membranes were purchased from DuPont Chemical Company and pre-treated with 1.0 M aqueous hydrochloric acid solution and deionized water. The pre-treated membranes were irradiated with 150-keV proton ions at fluences of  $1 \times 10^{14}$ ,  $1 \times 10^{15}$  and  $1 \times 10^{16}$  ions  $\text{cm}^{-2}$ . The pressure in the implanter's target chamber was  $10^{-5}$  to  $10^{-6}$  Torr, and the current density was kept about  $1 \mu\text{A cm}^{-2}$  to prevent a detrimental thermal effect on the Nafion. The ion-implanted Nafion membranes were placed in an air environment for about 1 day for oxidation.

### **1.2. Characterization of the ion-implanted Nafion membranes**

The changes in the chemical structure of the Nafion surface after ion implantation were investigated by attenuated total-reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Bruker, Tensor 37). The surface chemical composition of the original and ion-implanted Nafion membranes was investigated by using an X-ray photoelectron spectrometer (XPS, MultiLab 2000, Thermo Electron Corporation, England) with MgK X-ray source. The applied power was 14.5 keV and 20 mA, and the base pressure of the analysis chamber was less than  $10^{-9}$  mbar. The surface morphology

of the membranes was analyzed by atomic force microscopy (Bruker-Nano GmbH N8 Argos). The water contact angles of the original and ion-implanted Nafion surfaces were measured by using a Phoenix 300 contact angle analyzer (Surface Electro Optics Co., Korea) and the measurement was repeated 10 times to obtain an average value. To determine the water uptake of the membranes, the membranes were vacuum-dried at room temperature for 24 h, the water uptake of the membranes was obtained from the weight gain after they were soaked in deionized water for 24 h. The proton conductivity was measured with an impedance analyzer (Solatron SI 1260/1280) over a frequency range of 1 Hz to 106 Hz at room temperature and 100% relative humidity conditions using a four-point probe method. The proton conductivity was calculated as:

$$\sigma \text{ (S/cm)} = \frac{L}{R \times A} \quad (1)$$

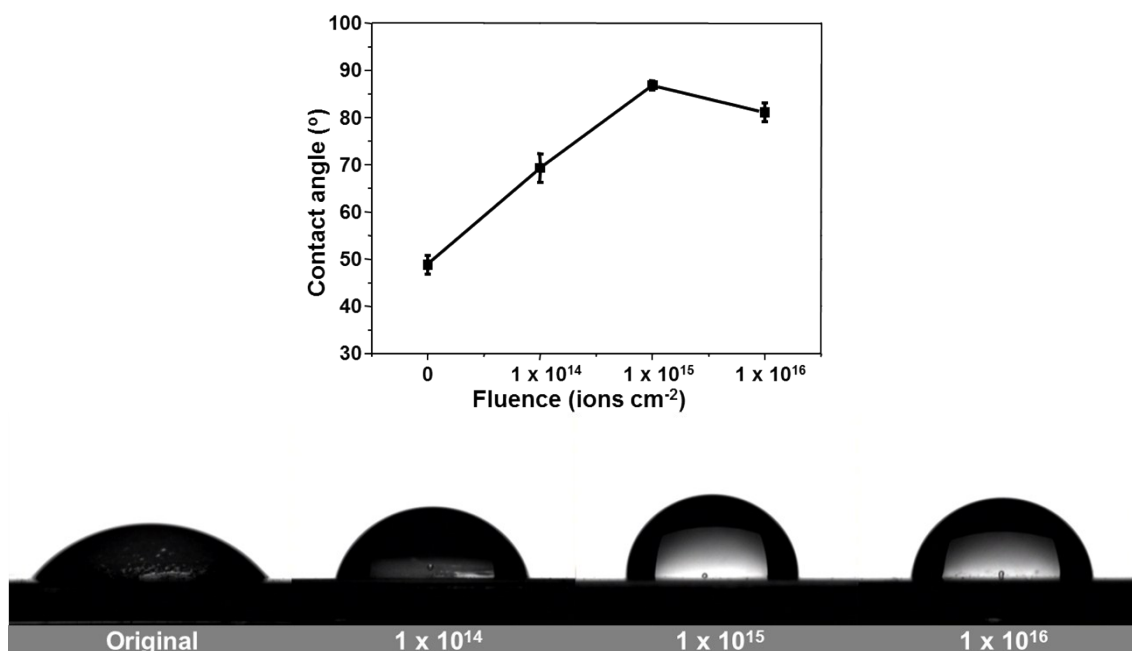
where  $\sigma$  (S/cm) is the proton conductivity,  $L$  (cm) is the distance between the two electrodes used,  $R$  ( $\Omega$ ) is the membrane resistance, and  $A$  ( $\text{cm}^2$ ) is the surface area of the membrane. The impedance of each sample was measured five times to ensure data reproducibility.

The methanol permeability ( $P$ ) was determined using a diffusion cell consisting of

two reservoirs. Reservoirs A and B were filled with 10 M methanol aqueous solution and deionized water, respectively. The reservoirs were separated by the test membrane. During the measurement, the methanol concentration in reservoir B was measured by a gas chromatograph (Shimadzu, GC-14B) equipped with a thermal conductivity detector and calculated by the following equation:

$$C_B(t) = \frac{A}{V_B} \frac{P}{L} C_A(t - t_0) \quad (2)$$

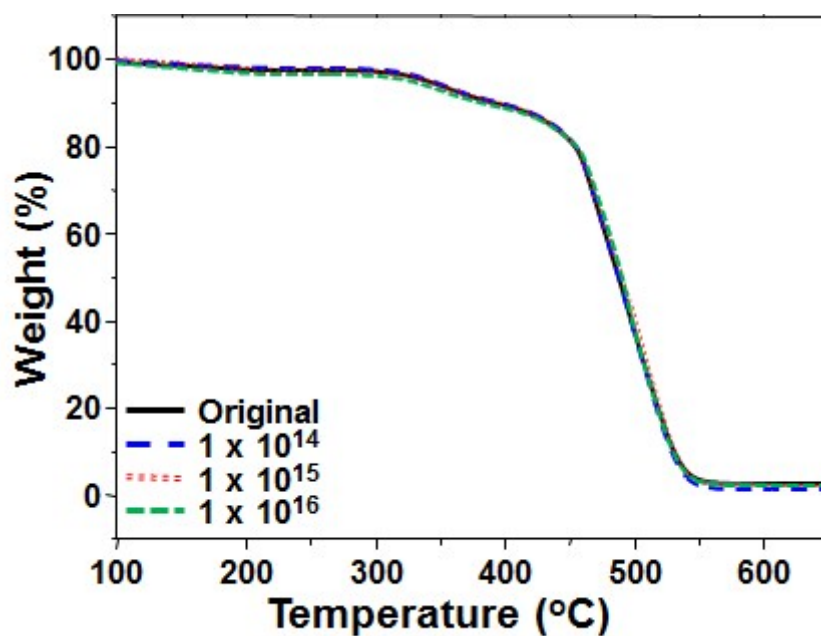
where  $C_B(t)$  is the methanol concentration in reservoir B at time  $t$ ,  $A$  ( $\text{cm}^2$ ) is the surface area of the membrane sample,  $V_B$  (mL) is the volume of deionized water in reservoir B,  $L$  (cm) is the film thickness, and  $C_A$  is the initial methanol concentration in reservoir A.



**Fig. S1.** Surface wettability of original and ion-implanted Nafion membranes at various fluences.

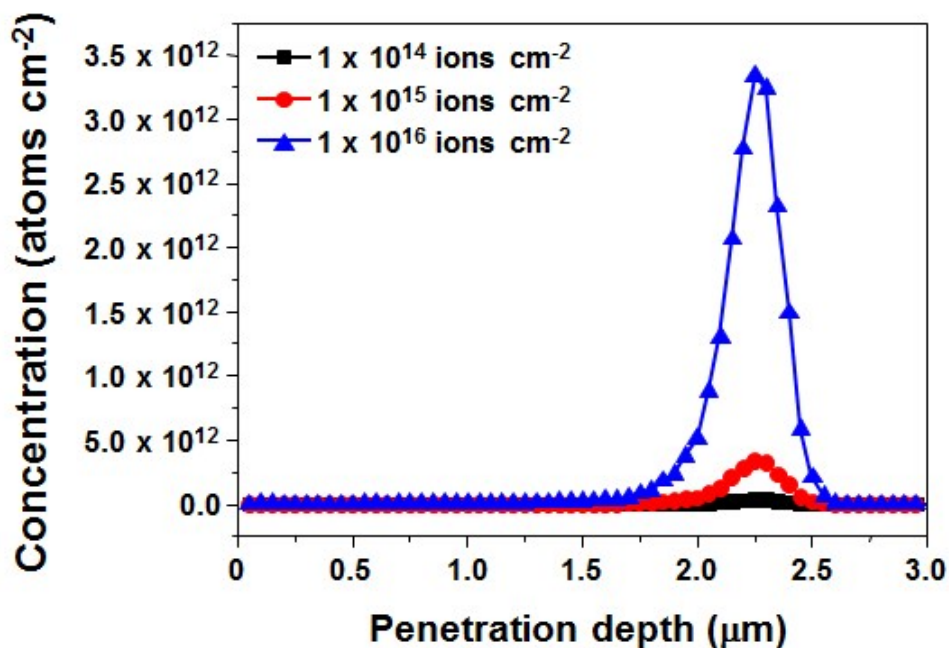
The water contact angles of the original and ion-implanted Nafion surfaces were measured by using a Phoenix 300 contact angle analyzer (Surface Electro Optics Co., Korea) and the measurement was repeated 10 times to obtain an average value. Although the ion implantation removed sulfonic acid groups on the surface, hydrophilic functional groups such as COOH, OO, CO, and OH were generated on the implanted surface. The newly generated hydrophilic functional groups helped to maintain the

hydrophilicity of the implanted Nafion surface in the dry state, but the contact angle was increased above the pristine Nafion surface. This can be attributed to the fact that the reduced sulfonic acid group concentration on the surface increased the ultimate contact angle.



**Fig. S2.** TGA thermograms of Nafion membranes implanted at various fluences.

The TGA curves for the Nafion membranes implanted at various fluences were not changed significantly compared to that of the original Nafion as shown in Figure S3. This result indicates that the surface of the Nafion membranes was successfully modified by ion implantation without any change in the bulk thermal property of the original Nafion membrane.



**Fig. S3.** Penetration depth profile of 150 keV proton ions into Nafion membranes at fluences of  $1 \times 10^{14}$ ,  $1 \times 10^{15}$ , and  $1 \times 10^{16}$  ions  $\text{cm}^{-2}$  obtained by the TRIM98 simulation program.

The penetration depth of 150 keV proton ions into Nafion membranes was estimated by using the TRIM98 simulation program, and the results are shown in Fig. S3. The maximum penetration depth of 150 keV proton ions into Nafion was around 2.5  $\mu\text{m}$ . Therefore, the ion implantation-induced surface modification of the Nafion membranes within the maximum depth of 2.5  $\mu\text{m}$  could not affect their bulk property taking consideration of the thickness of the Nafion membranes.