

Comparative Experimental Study on Ionic Polymer Metal Composite based on Nafion and Aquivion Membrane as Actuators

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Abstract. Most ionic polymer metal composites employ Nafion as the polymer matrix, Aquivion can also manufactured as ionic polymer metal composite while research was little. This paper researched on two kinds of ionic polymer metal composite based on Aquivion and Nafion matrix with palladium electrode called Aquivion-IPMC and Nafion-IPMC. The samples were fabricated by the same preparation process. The current and deformation responses of the samples were measured at voltage to characterize the mechano-electrical properties. The experimental observations revealed that shorter flexible side chains in Aquivion-IPMC provide a larger force than Nafion-IPMC, while the displacement properties were similar in two different samples. The results also showed that Aquivion membrane can also replace Nafion to reproduce IPMC application in soft robots, MEMS, and so on.

1. Introduction

An ionic polymer-metal composite (IPMCs) consists of a thin perfluorinated ionomer membrane with electrodes plated on both faces. When the membrane was hydrated, a device of this type will undergo a large bending motion as a low level electric field was applied across the two electrodes [1-3]. IPMC actuators can be readily miniaturized and typically have a low density and high mechanical flexibility, such that they showed promise for a wide variety of applications, ranging from MEMS actuators to soft robots [4-6]. One of the most common ionic polymers in use today is DuPont's Nafion developed in the 1960s and commercialized in the 1970s, since then Nafion is a Teflon TM -based polymer with pendant sulfonic acid side groups. Aquivion was known in literature as short side chain ionomer in comparison to Nafion that was indicated as long side chain ionomer developed by Solvay Solexis [7]. These perfluorosulfonate ionomers consist of a polytetrafluoroethylene (PTFE) backbone and double ether perfluoro side chains terminating in a sulfonic acid group as illustrated in figure 1. The short flexible side chain in Aquivion provides a lower equivalent (980g/mol) mass than Nafion (1100g/mol). Although in the literature, most of ionic polymer-metal composite employed Nafion as the polymer matrix, Aquivion were employed to manufacture IPMC can also be feasible, but the research was little. In this study, ionic polymer metal composite based on Nafion and Aquivion membrane with palladium-electroded were manufactured to conduct experiment called as Nafion-IPMC and Aquivion-IPMC. We focus on the different mechanical and electrical performance between Nafion-IPMC and Aquivion-IPMC under same preparation process. A series of SEM pictures on the electrodes surface and cross-section of theses samples have been captured, and the mechano-electrical responses of IPMC under DC voltage have been measured. Through experimental comparison, it is investigated the



ways that how the side chain-ionomer influenced the mechanical and electrical parameter and corresponding mechano-electrical properties. The results of this research help to explore whether the Aquivion can replace Nafion to reproduce IPMC because of Aquivion's price lower than Nafion [7].

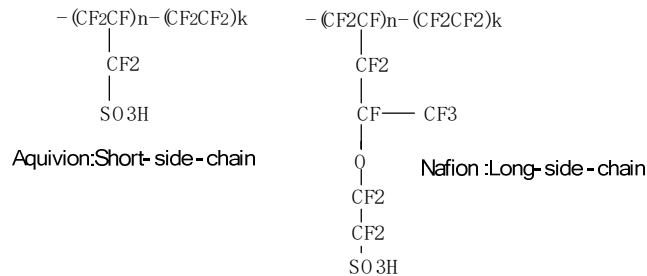


Figure 1. The molecular structure of short side chain Aquivion and long side chain Nafion.

Table 1. Comparison of Aquivion and Nafion membrane parameters [8-10].

Membrane	Equivalent mass/g/eq	Density /g/cm ³	Thickness /μm	Elastic modulus/MPa	Ionic conductivity/ms/.cm	Water content (%)
Nafion117	1100	1.97	183	249	60-140	38%
Aquivion9815S	980	1.93	150	290	>160	20%

2. Experimental

2.1. Materials preparation

Nafion-IPMC and Aquivion-IPMC was fabricated through an effective process to manufacture palladium-electroded IPMC by our lab, mainly by impregnation-reduction plating (IRP) and autocatalytic plating (ACP) [3]. In our experiment, Nafion 117 with a thickness of 180 μm, purchased from Dupont in USA, and Aquivion (EW98015S) with a thickness of 150 μm purchased from Solvay Solexis in Japan. The noble metal Pd, which has similar physical and chemical properties to Pt and is less expensive (approximately one-third cheaper), was selected as the electrode material. Na ion was exchanged into the IPMC as actuating ions, while water acted as solvent. Strip-shaped IPMCs with the dimensions of 35mm×5mm were tested and analyzed. The thickness of Aquivion-IPMC was about 0.20mm, while the Nafion-IPMC was about 0.22mm due to different thickness of membrane.

2.2. Characterization.

2.2.1 Morphology observation. The surface and cross-section morphology of samples were examined by means of SEM (TESCAN-VEGA \XMU VG3210677). Scanning electron microscopy (SEM) was performed at an accelerating voltage of 20.0kV. All sample cross-sections were obtained by low-temperature cracking, being placed in liquid nitrogen for 5min and then broken into pieces.

2.2.2. Surface resistance. The sheet resistances of the samples were measured by a low-resistivity meter with a measurement range of 10^{-2} – $10^6 \Omega$ (the Loresta-EP handheld unit with a four-pin probe). Membranes were cut into discs with a 10 mm radius size and immersed in de-ionized (DI) water for 2h prior to testing. The same samples from the same batch were tested five times and the average value was recorded. All operations were carried out at room temperature and room humidity.

2.2.3. Bending stiffness measures. The bending stiffness of fully hydrated IPMC samples with the dimensions of 5mm (width)×35 mm (free length) were estimated using the free oscillation attenuation method which were described in [3].

2.2.4. Water content measures. The two IPMC samples were soaked in DI water for 12 hours to absorb water completely. After being picked up from the DI water and cleaning the surface water, the sample were put on an electric balance. The transient mass was m_{wet} recorded until it reached the equilibrium state. Then IPMC samples were dried at 80 °C in an oven for 12 hours to sufficiently remove the inside water. After cooling its were put on the electric balance to measure the transient mass m_{dry} , the water content can be calculated by the following formula:

$$w = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

2.2.5. Electrochemical properties of IPMCs. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to evaluate the interfacial surface of the IPMC electrodes in terms of capacitance. In the (CV) and EIS measurements for the IPMC specimens, the electrochemical VersaStudio (VersaSTAT 3, Princeton, USA) was used to obtain the CV curves and Nyquist plots. The CV measurements were carried out with potential range between -1.0 and 1.0 V at a scan rate of 50 mV s^{-1} , and the EIS measurements were carried out over the frequency range from 100 kHz to 1 Hz with applied current of 100 mA . All the measurements were performed as [11]. The charging-discharging capacitance was determined from the measured cyclic voltammograms according to the relation [12]:

$$C = \frac{|I^+| + |I^-|}{2dV/dt} \quad (2)$$

where I^+ and I^- are the polarization currents at 0 V , and dV/dt is the potential scan rate.

2.2.6. Mechano-electrical properties of test. The measurement setup for mechano-electrical properties testing as shown in figure 2. IPMC samples were clamped between gold electrodes to form a cantilever. DC analog signal generated by PC was amplified by a power amplifier HM8143 to stimulate the IPMC sample. The deformation at 25 mm from the clamp was measured with a laser displacement sensor, the current was measured by a self-made circuit board. The displacement and current signals were recorded in a PC through an ADLINK DAQ2214 data acquisition card.

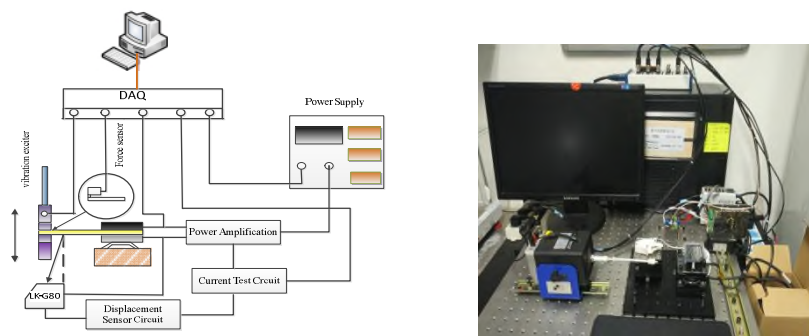


Figure 2. Measurement setup for mechano-electrical and sensing properties testing.

3. Results and discussion

3.1. Morphology of surface electrode and cross-section

From figure 3 (a), we can see that Nafion-IPMC appears as a flat, smooth and compact surface electrode with few cracks, the Pd particle distribute on the surface uniformly to form good electrical conductivity. Most of Pd ions were reduced on the surface, cross-section morphologies of sample shows that the thickness of upper and lower electrode layers is about $10 \mu\text{m}$ respectively. It's worth noting that a small number of particles penetrate into the substrate to increase the pseudo-capacitor of

Nafion-IPMC. From figure 4(a), we also know that Aquivion-IPMC with a compact surface electrode due to autocatalytic plating. The cross-section morphologies of Aquivion-IPMC in figure 3(b) gives an evidence of fewer particles penetrate into the substrate than Nafion-IPMC.

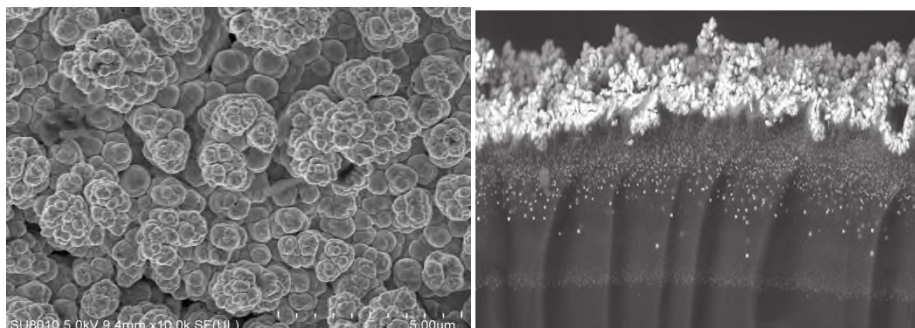


Figure 3. SEM image of Nafion-IPMC:
(left) the electrode surface morphology and cross-section morphology (right).

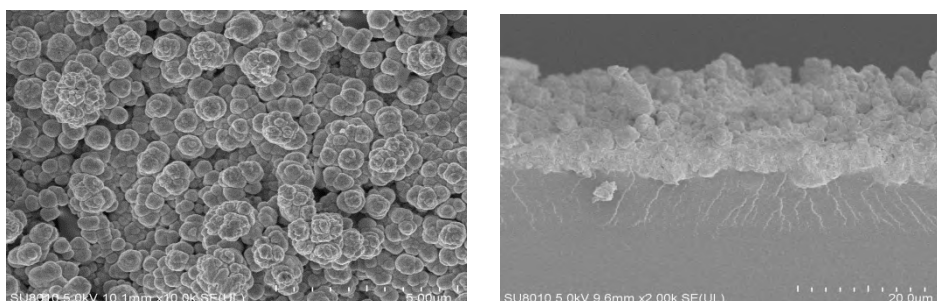


Figure 4. SEM image of Aquivion-IPMC:
(left) the electrode surface morphology and cross-section morphology (right).

3.2. Electro-mechanical parameters

Previously, we have known that some key factors such as surface resistivity, elastic modulus, water content, and specific capacitance affect the mechano-electrical properties [13]. These parameters were measured shown in table 2. In this work, we focused on the effect of different matrix membranes on the physical parameters and investigated the reasons for these differences. Nafion-IPMC and Aquivion-IPMC both have low surface resistance, Nafion-IPMC has lower elastic modulus than Aquivion-IPMC because of the different form membrane and number of particles penetrates into membrane. The water content of Nafion-IPMC higher than the Aquivion-IPMC due to equivalent mass of the two was different. Specific capacitance measuring charge discharge capacity. Obviously, the specific capacitance of Nafion-IPMC higher than the Aquivion-IPMC. These parameters affect the driving performance will be discussed in the following.

Table 2. Electro-mechanical parameters of Nafion-IPMC and Aquivion-IPMC (in wet state).

Sample type	Surface resistivity ($\Omega/\square$)	Elastic modulus/MPa	Water content	Specific capacitance/mF/cm ²
Nafion-IPMC	0.268	275	23%	0.1684
Aquivion-IPMC	0.190	365	21%	0.0518

3.3. Electrochemical properties of IPMCs

Electrochemical performances of the IPMC samples have been investigated employing CV and EIS measurements. Figure (5) shows the CV curves of the IPMC samples measured with potential range between -1 and $+1$ V and scan rate of 50mVs^{-1} . The results indicate that the charge/discharge proceeds capacitively for samples in this potential range. As can be seen, the current density of all the Nafion-IPMC was significantly higher than Aquivion-IPMC. The higher in current density also indicated

greater capacitive behavior and more efficient electrolyte ion transport of Nafion-IPMC, which would result in a better the electro-mechanical performances.

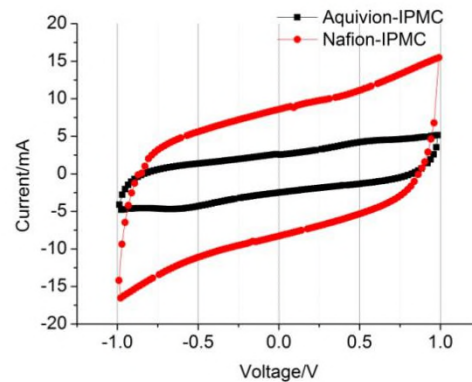


Figure 5. CV curves of Nafion-IPMC and Aquivion-IPMC.

The IPMC's equivalent circuit can be viewed as RC loop. The interlayer of IPMCs can be viewed as an ionconductive material and modeled by a capacitor (C) and a membrane resistor (R_m) in parallel [14]. The electrode can be modeled by two resistors ($R_{pd}/2$). The value of R_m , R_{pd} , C can be fitting out by (EC-Lab V9.24) calculated the Nyquist plots of the impedance spectra of the IPMC directly as shown in table 3. Form table 3, we known that the membrane resistance of Aquivion is larger than Nafion. Also the Surface resistance including interface resistance of Nafion-IPMC is lower than Aquivion-IPMC. Capacitance of the two type IPMCs show great difference consistent with the result was estimated by formula 2.

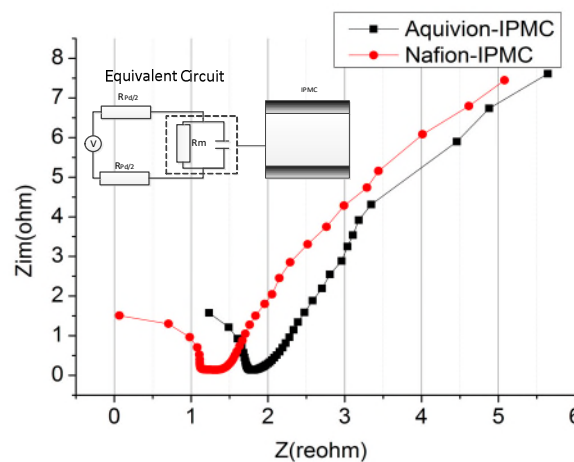


Figure 6. Nyquist plots of the impedance spectra of the IPMC samples.

Table 3. Equivalent electrical parameters corresponding to IPMCs.

Sample type	Membrane resistance/ R_m	Surface resistance / R_{pd}	Capacitance/ mF/cm^2
Nafion-IPMC	0.25	1.337	0.1835
Aquivion-IPMC	0.51	1.915	0.062

3.4. Mechano-electrical properties of IPMCs

IPMC's tip displacement with respect to time when working under 2V DC was shown in figure 7. Nafion-IPMC and Aquivion-IPMC's anode deformations were basically the same. While relaxation

amplitude of two sample were different. Nafion-IPMC's relaxation amplitude larger than Aquivion-IPMC's, even more than the initial equilibrium. The anode deformations is usually ascribe to fast cations distribution under the electric field, relaxation deformation was caused by the reverse diffusion of free water [16]. The different relaxation amplitude correlates with the water content which has been proven in ref [17].

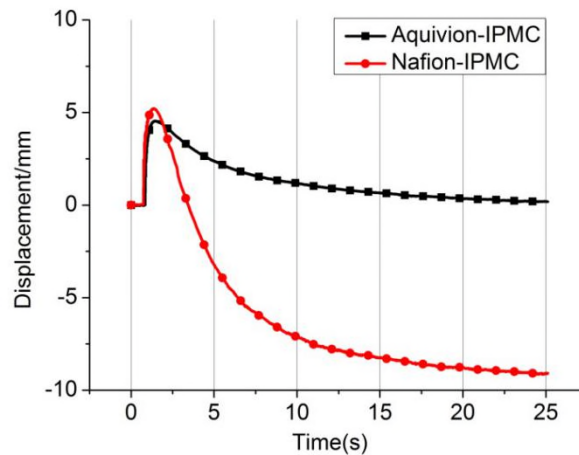


Figure 7. Displacement of IPMCs under DC 2 V.

IPMC's force responses of the two IPMC samples were plotted under 2V DC in figure 8. Obviously, Aquivion-IPMC generated a higher blocking force than Nafion-IPMC due to a higher elastic modulus.

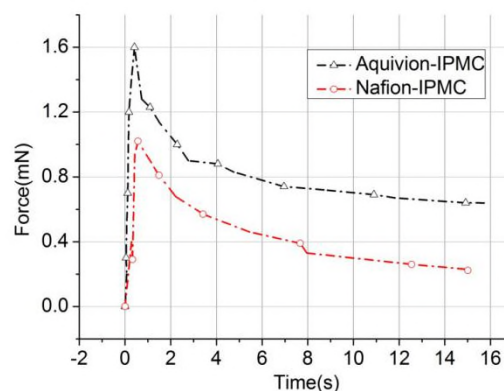


Figure 8. Blocking force of IPMCs under DC 2 V.

4. Conclusions and future work

In this paper, a series of experiments were performed with the aim of giving the comparison between the Nafion-IPMC and Aquivion-IPMC in mechano-electrical properties under the same condition. Firstly, the Nafion/Aquivion membranes and corresponding IPMCs were prepared and characterized. Then, electrochemical properties were measured. In view of the above results and discussions, the following conclusions can be drawn.

(1) Aquivion-IPMC's displacement deformation lower than Nafion-IPMC under 2V voltage because of Aquivion-IPMC own higher membrane resistance than Nafion and a lower capacitance compared to Nafion-IPMC

(2) Output force of Aquivion-IPMC larger than Nafion-IPMC's because of the Aquivion-IPMC's elastic modulus higher than Nafion-IPMC's.

As a result, The IPMC based on Aquivion can used as actuator identical with IPMC based on Nafion in aerospace, medical, robots, and so on.

5. References

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