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A novel method of manufacturing three-dimensional ionic polymer–metal composites (IPMCs) biomimetic sensors, actuators and artificial muscles

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Abstract

All commercially available (as-received) perfluorinated ion-exchange polymers are in the form of hydrolyzed polymers and are semi-crystalline and may contain ionic clusters. The membrane form of these polymers has a typical thickness in the range of approximately 100–300 μm. Such a thin thickness of commercially available membranes permits fast mass transfer for use in various chemical processes. Although ionic polymer–metal composite (IPMC) artificial muscles made with these ion-exchange membranes have shown a great potential to produce large bending displacements in cantilever form and high force densities (maximum force greater than 40 times of its own weight), achieving large forces to be utilized in many practical devices requires manufacturing and fabrication of three-dimensional IPMCs. Knowing that such as-received semi-crystalline membranes are not melt-processable, they are not suitable for the fabrication of three-dimensional electroactive materials or other composite forms. In this work, the authors report a newly developed fabrication method that can scale-up or down the IPMC artificial muscles in a strip size of micro-to-centimeter thickness. We have adopted a recently developed technique by Moor et al. [J Membr Sci 75 (1992) 7] for dissolving as-received ion-exchange membranes in appropriate solvents. By carefully evaporating solvents out of the solution, recasted ion-exchange membranes were obtained. The test results showed that a successfully fabricated IPMC strip in a size of 2 mm thickness, 5 mm width, and 15 mm length, produces generative forces (tip forces) more than 20 gmf up to approximately a half centimeter-displacement under a small voltage.

Keywords: Ionic polymer–metal composites (IPMC); Biomimetic sensors; Artificial muscles

1. Introduction

1.1. Nafion™

DuPont developed Nafion™, the first perfluoro-sulfonated ionomer membrane, in the early 1970s. They targeted the alkali industry. Typically, these membranes are manufactured from polytetrafluoroethylene (PTFE) as an effective backbone and sidechains ending with active ion-exchange sites such as sulfonate or carboxylate. The starting monomer is the perfluorinated alkenes with appropriate substituents (see Fig. 1 (left)). An important consideration is the length of the sidechain that determines the properties of the final product. In general, the overall process is non-trivial in the fact that sulfonylfluoride vinylether is copolymerized with tetrafluoroethylene and, then, base-hydrolyzed to become an active material (see Fig. 1 (right)). Various modifications can be made to a basic homogeneous membrane to meet specific characteristics. One example is to introduce weave fabric to improved mechanical strength (heterogeneous membrane). Also, the surface treatment can be done in order to improve permselectivity.

1.2. Liquid Nafion™

Generally speaking, the term *liquid Nafion™* refers to solutions of Nafion™ Perfluoro-Sulfonated Ionomers (NPSI). Commercially available NPSI membranes are (as-received membranes) are semicrystalline and have ionic aggregates. Therefore, they are not melt-processable since such supermolecular structures are resistive to flow. The well-adopted technique for obtaining liquid Nafion™ is to dissolve the as-received Nafion™ membrane at an elevated temperature (approximately 250°C) under pressure of a 50/50 mixture of aliphatic alcohols and water. The primary purpose of developing such liquid Nafion™ is to use

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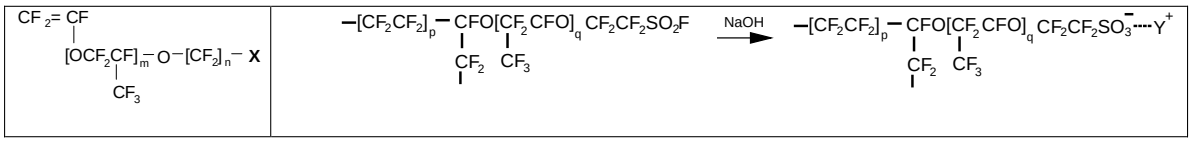

Fig. 1. The monomer (left) and the synthesis of Nafion™ (right). Note that $X = SO_3^-$ or COO^-, $m = 0–2$, $n = 1–4$, $p = 5–11$, and $q = 1$.

it in order to repair small holes in membranes or to coat electrodes. The drying induced the recasted film can be obtained but is mechanically poor (cracked and brittle) and is also easily dissolved in polar solvents including water and alcohol. A number of answers to this problem have been proposed [1–3]. Typically, the processes are to include additive solvents such as triethyl phosphate, dimethyl sulfoxide, dimethyl formamide (DMF) or ethylene glycol so as to obtain good insoluble recasted Nafion™ films. However, such recasted Nafion™ exhibit morphological differences relative to as-received Nafion™. Truly, there is little information about recasted Nafion™ membranes at the present time. An important issue to be discussed could be its micellar structure of the recasted Nafion™.

1.3. Melt-processable Nafion™ powders

Following the previous methods [1,3], the melt-processable Nafion™ powders can be made by dissolving the neutralized NPSI membranes in a mixed solvent of 50/50% water/alcohols, in a tetrabutylammonim cation (TBA^+) form. Due to the large and hydrophobic nature of TBA^+ form, steam stripping is effective in the fact that TBA^+ form of Nafion™ is easily separable floating to the surface of water. A definite advantage of this method is the complete recovery of amorphous NPSI in a powder form. After vacuum drying, a fine dry form of melt-processable NPSI can be obtained. The conversion to H^+ form is simple by boiling the sample in 2N HCl. Also, one should note that TBA^+ functions as a *pseudoplasticizer* due to its large size and hydrophobic nature. Therefore, it can reduce the extent of electrostatic cross-linkage and form relatively weak dipoles caused by the Coulombic force in aggregated ions. However, the method of producing such melt-processable Nafion™ powders is tedious and also has a low yield, compared to our proposed solution recasted techniques. The technique will be discussed in the next sections.

1.4. The concept of three-dimensional polymeric artificial muscle

Currently, we are developing three-dimensional components and bodies that can be used for artificial muscles and sensors (see the concept illustrated in Fig. 2) generate substantial conformational changes with a minimum input of electric potential. One excellent candidate is the IPMC. But, the current state-of-the-art IPMC is limited to the maximum thickness of approximately 200 μm due primarily to manufacturer's specification. A key engineering challenge is to fabricate thicker material. For many industrial applications of IPMCs, considerable force improvement is needed.

2. Experimental and results

2.1. Preparation of solution recasted Nafion™

The preparation of solution recasted Nafion™ film sample is described below. DuPon't liquid Nafion™ solution was purchased. According to manufactuer's specification, this solution contains 10% of Nafion™ and 90% of solvent approximately one-to-one mixture of 2-butanol and water. It was noted, initially, that during the solvent evaporation the solidified Nafion™ developed surface cracks. Therefore, an essential trick was to introduce an additive that makes the solvent mixture act like an azeotrope. The use of DMF was successful. Subsequently given a multiple layer of liquid Nafion™ dried, an approximately 2 mm thick sample was prepared successfully. First, a known quantity of liquid Nafion™ with an additive is placed in a Teflon-coated Pyrex glass. Second, knowing that this recasted Nafion™ is water soluble, an appropriate annealing was performed at an elevated temperature of 70°C so as to create crystallinity. Usually, the temperature is raised at 150°C for further curing. The annealing process can tailor mechanical and chemical stability of the solution recasted Nafion™ film.

The IPMC sample was prepared by using 2 mm thick recasted Nafion™ fabricated by following the process described earlier. Later, platinum electroding was done on both side of the sample with a particle penetration depth of ~20 mm. Fig. 3 shows photographs of the IPMC samples with the primary platinum electrode and secondary gold electrodes. Another fabrication method is also described in Fig. 4.

2.2. Mechanical testing

The mechanical tensile behavior of an as-received

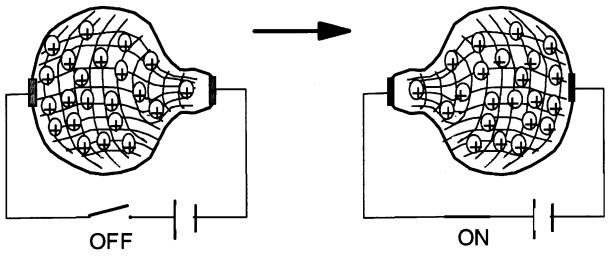

Fig. 2. The principle of electrically controllable three-dimensional polymeric artificial muscle.

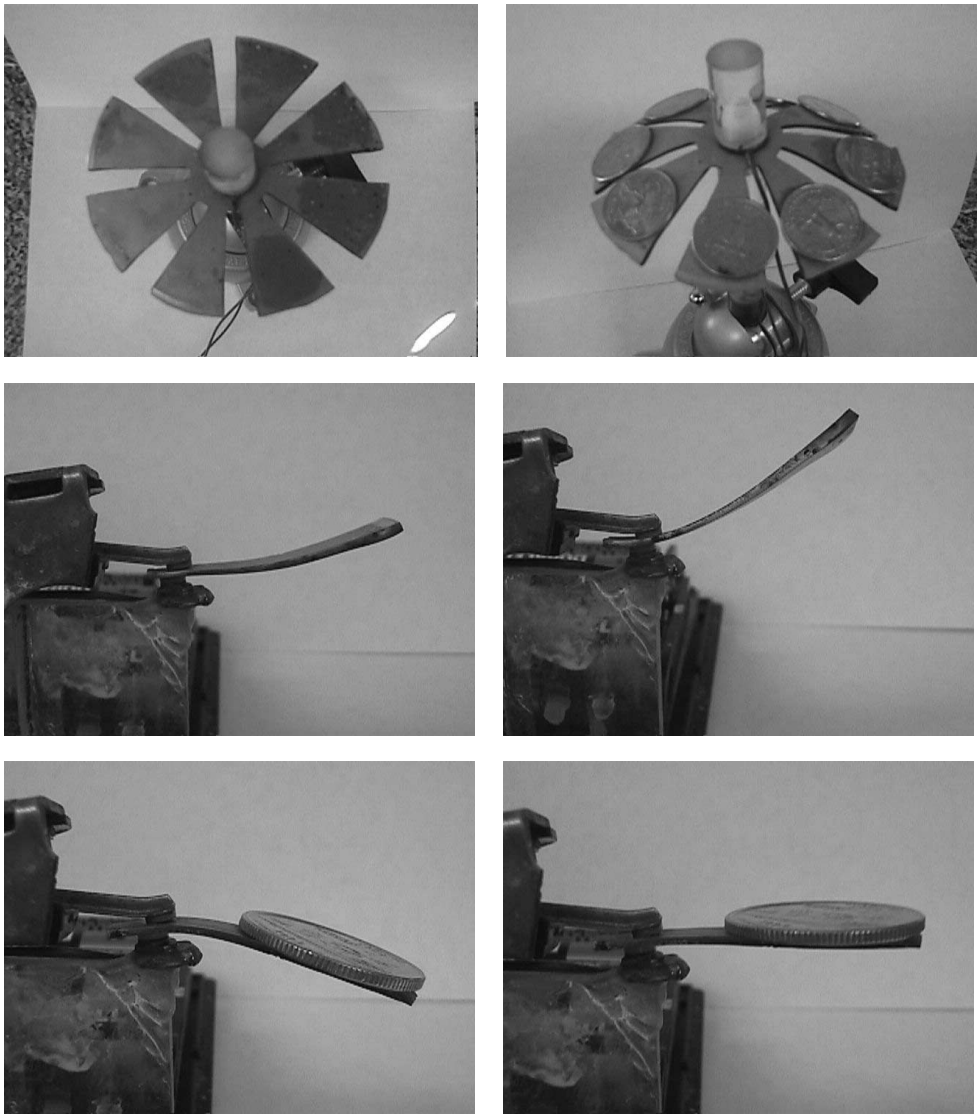

Fig. 3. The IPMCs made with solution recasted Nafion™. Top two photos show the fabricated eight-finger IPMC (*Octopus*-IPMC). It (2 mm thickness) can easily sustain the eight US quarters (note that a US quarter has a mass of 5.3 g). The diameter of this IPMC is approximately 10.5 cm. The electrode is centered. The middle and bottom photographs show the IPMC in action without applying load and with a load. As can be seen, a quarter is lifted. The time internal between the frames is approximately 1 s. A step voltage of 2.8 V was applied ($E = 1.4$ V/mm). These IPMCs were manufactured by typical metal reducing technique [4–13]. Platinum was composited initially and gold was plated later. The cation is Li^+.

Nafion™ (fully hydrated H^+ form, 16% H_20) was first measured and presented in Fig. 5. As can be seen, the as-received Nafion™ clearly shows the electrostatic cross-linking and crystallinity induced a tensile characteristics exhibiting an unclear yielding and strain induced further crystallinity — somewhat similar to cross-linked elastomeric behavior. Also, the normal stress/strain curve for the recasted membrane (fully hydrated H^+ form, 9% H_20) is superimposed. It clearly shows that a distinct plastically deformed behavior that is an indication of weakened (or eliminated) electrostatic cross-linking relative to dominating elastic forces. It appears that physical deformation seems to occur at yielding so as to be clearly distinguished.

2.3. Force/displacement measurement

The force/displace measurement was done separately in a cantilever beam configuration: The tip force (truly the maximum force) was measured by a load cell at the zero displacement condition (blocking force) and the tip displacement (truly the maximum displacement) was measured without a load applied. In Fig. 6 (left), the force responses of an IPMC sample (2 mm thickness, 15 mm effective length, and 5 mm width) are provided. Note that the applied step voltages across the sample (1/2 Hz) are 2, 4, and 6 V, respectively (1, 2, and 3 V/mm, respectively). Although these applied electric fields are very small, the responses of the sample are excellent in terms of useful

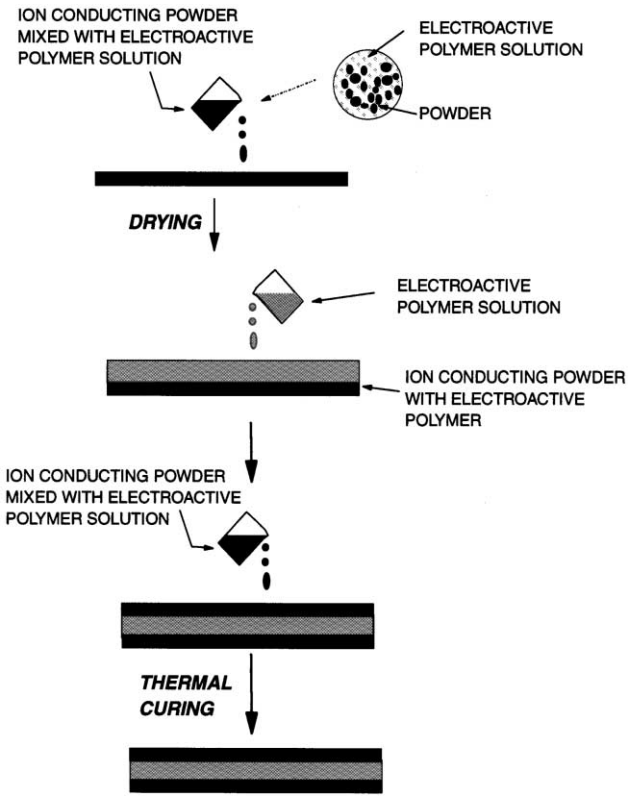

Fig. 4. An illustrative process diagram for the ion conducting powder-coated electrode made by the solution recasting method. First, the ion conducting powder (i.e. carbon, silver, platinum, palladium, gold, copper, and any other conducting powders) is mixed with the electroactive polymer solution (for an example, liquid Nafion™). The powder is fine and uniformly dispersed within the electroactive polymer solution. After formation of a thin layer, the electroactive polymer solution undergoes the drying process of solvents and, therefore, the residual consists of the ion conducting powder dispersed within the polymer. Second, the electroactive polymer solution (without the powder) is added on top of the layer of the ion conducting powder and dried. This is repeated until the desired thickness is obtained. Later, a layer of the ion conducting powder is formed by the same method described above. As a final step, the ion conducting powder-coated electrode is cured under the elevated temperature. If necessary, the surface conductivity can be enhanced by adding a thin layer of novel metal via electroplating or electrolessplating [10,14].

forces being generated. The detailed information regarding the experimental set up can be found elsewhere [10]. In Fig. 6 (right) the measured displacement is presented against the force (displacement vs. tip force = generative force). The useful meaning of this graph attributes the possible maximum work output (=mechanical energy stored in the IPMC beam, $U_m = \int_0^{\delta_{max}} F_T \delta \, ds \cong (1/2)\delta_{max}|F_T|$) of the IPMC although more elaborate interpretations may be needed (i.e. by simultaneous measurement of the tip velocity and displacement or curvature). In this configuration, internal stresses are usually built up when transverse generative strain is converted into bending motion, which lessens the mechanical output energy (note that flexural strength is generally lower than tensile or compressive strength since the thickness is small). Based upon these measurements, we can define the electromechanical coupling factor, k, (or

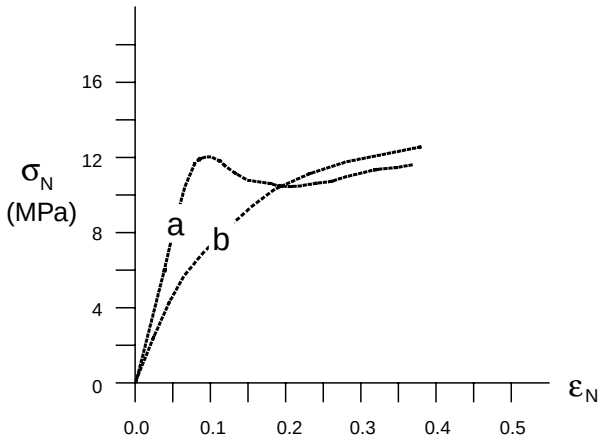

Fig. 5. Tensile testing results (normal stress, σ_N vs. normal strain, ε_N. Note that both samples were fully hydrated when they were tested. (a: solution recasted membrane; b: as-received membrane).

thermodynamic efficiency, E_{ff}) as

$$E_{ff} = k^2 = \frac{U_m(= \text{stored mechanical energy})}{U_e(= \text{electric input energy})}. \quad (1)$$

2.4. A scale-up consideration

In a cantilever configuration (see Fig. 7), the end deflection (=displacement), δ due to a distributed load $w(s, t)$, where s is the arc length of a beam of length L and t is the time, can be related approximately to the radius of the curvature ρ of the cantilever beam, i.e.

$$\rho \cong \frac{L^2 + \delta^2}{2\delta}. \quad (2)$$

Note that the radius of curvature ρ is in turn related to the maximum tensile (positive) or compressive (negative) strains in the beam as

$$\varepsilon \cong \frac{h}{2\rho}, \quad (3)$$

where h is the thickness of the beam at the built-in end. Herein, ones must realize that, for the actuation mode of the IPMC, the tensile strain can be simply realized, but difficult to isolate. The stress σ can be related to the strain ε by simply using Hooke's law, assuming linear elasticity (one can also consider other constitutive equations in which the stress σ can be related to the strain ε in a non-linear fashion, i.e. rubber elasticity). It leads to

$$\sigma = \frac{Mh}{2I}, \quad (4)$$

where σ is the stress tensor, M the maximum moment at the built-in end and I is the moment of inertia of the cross-section of the beam. Thus, the moment M can be calculated based on the distributed load on the beam or the applied electrical activation of the IPMC beam. Having also calculated the moment of inertia I, which for a rectangular

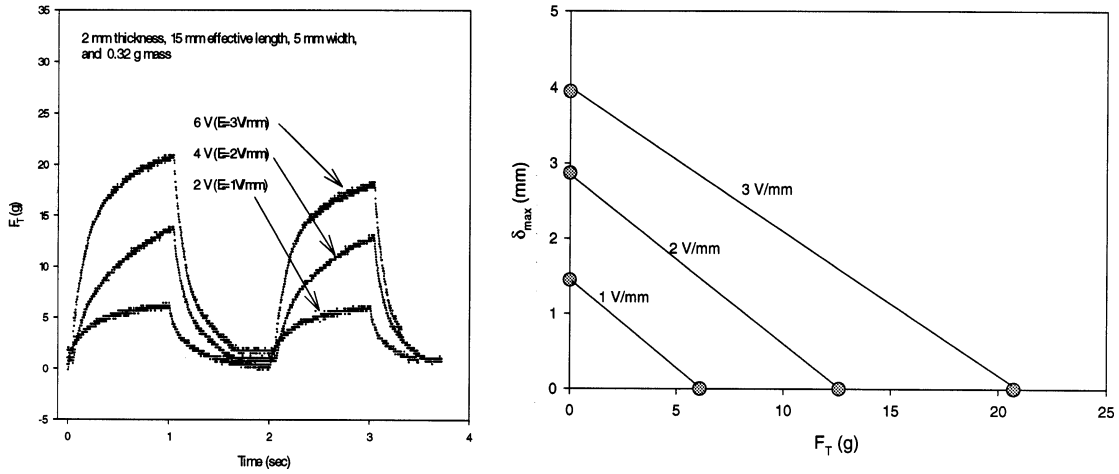

Fig. 6. Force responses of the solution recasted IPMC sample (left) and its conjugated graph showing tip displacement δ_T vs. blocking force, F_T. Note that the frequency is 1/2 Hz and step voltages of 2, 4, and 6 V were applied.

cross-section of width b will be

$$I = bh^3/12. \tag{5}$$

Then, the stress tensor becomes

$$\sigma = \frac{6F_T L}{bh^2}. \tag{6}$$

So, the stress σ can be related to the strain ε.

First, suppose we have two IPMCs having two different thickness of h and $2h$ (double the thickness) but width b and the beam length L are the same. If we want to maintain the same displacement δ (which means that the obtained curvature is the same) for both IPMCs, the necessary strain for the thick one is 2ε. Therefore, we can have the following:

$$\frac{\sigma_{2h}}{\sigma_h} \cong 2 = \frac{F_{T(2h)}}{2^2 F_{T(h)}} \Rightarrow F_{T(2h)} = 8F_{T(h)}. \tag{7}$$

This means, if we increase the thickness the IPMC by a factor of 2 and can maintain the same displacement, then the tip force (generative force [15]) can be increased by a factor of 8 ($= 2^3$).

The simple analysis presented above, clearly shows the importance of having a capability of fabricating the IPMCs in a three-dimensional format. Certainly, this study proves that the solution recasting process is an effective means to achieve the higher generative force and, further, allows us to deal with three-dimensional artificial muscles. The design values of F_T for a sample having a size of 2 mm thickness, 5 mm width, and 15 mm length, are simply calculated based upon Eqs. (3) and (6) in terms of an appropriate strain range up to 0.012 (1.2%). The results are provided in Fig. 8 for three different values of moduli. These results are well

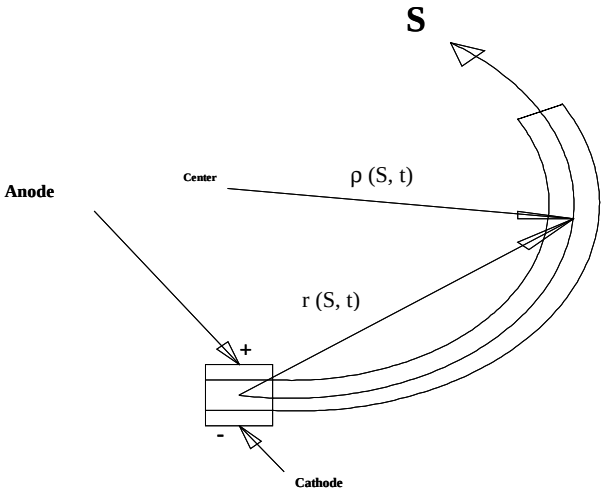

Fig. 7. A cantilever configuration of the IPMC in action.

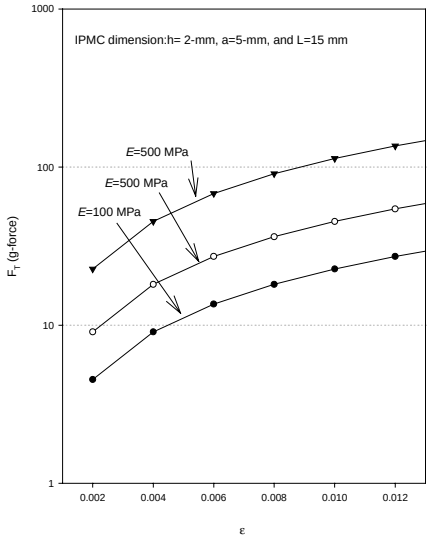

Fig. 8. The calculated tip force, F_T (= generative force), against the maximum strains up to 0.012 (= 1.2%) for an IPMC sample size of 2 mm thickness, 5 mm width, and 15 mm length. Note that the selected values of moduli are 100, 200, and 500 MPa, respectively.

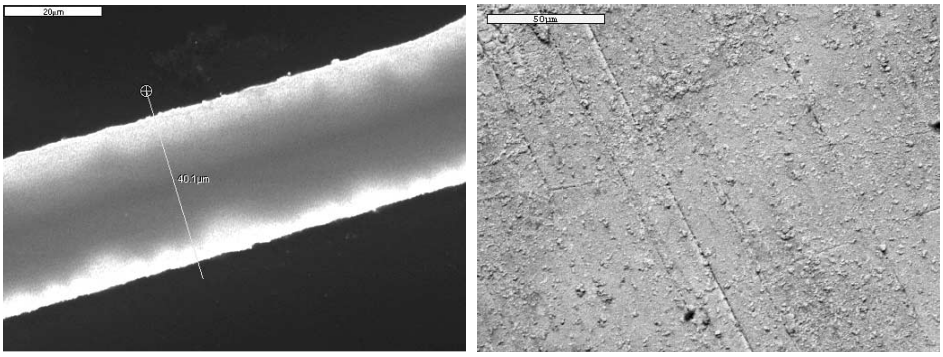

Fig. 9. Two SEM micrographs of the IPMC fabricated for microactuator applications (its cross-section-left and surface-right).

suited for the experimental data provided in Fig. 6. Such an IPMC sample shows a generative force capability much greater than 10 gmf.

The same principle can also be applied for designing thinner IPMCs that have applications in nano-to-micro actuators and sensors. As a result of our successful effort, we were able to fabricate an IPMC having a thickness of approximately 30 μm. Two SEM micrographs are included in Fig. 9 showing its cross-section and surface.

3. Closure

In this paper, our recent effort to develop three-dimensional IPMC artificial muscles is presented. An effective manufacturing technique, namely solution recasting technique, to fabricate three-dimensional sample was successfully developed and reported. A number of samples having a thickness greater than 2 mm was fabricated and tested. A test sample with a size of 2 mm thickness, 5 mm width, and 15 mm length has exhibited generative forces much greater than 20 gmf with a few mm displacement. It is obvious that the successful commercialization of the IPMC is highly dependent upon further improvement of its conceivable force generation for applications. In particular, the dimensional scale-up or scale-down of the IPMC is of a major factor enhancing its useful applications. The ultimate goal of using the IPMC as soft actuators can be clearly envisioned upon the successful development of three-dimensional sensors and actuators to be used as electrically controllable/deformable three-dimensional structures.

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