J Mater Sci (2007) 42:7031–7041
DOI 10.1007/s10853-006-0632-4

Direct assembly process: a novel fabrication technique for large strain ionic polymer transducers

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Received: 10 January 2006 / Accepted: 28 June 2006 / Published online: 26 April 2007

Abstract Ionic polymer transducers (IPT) consist of an ion-exchange membrane plated with flexible conductive electrodes on their outer surface. Compared to other types of electromechanical transducers, ionomeric transducers have the advantage of high-strain output (>9%), low-voltage operation (<5 V), and high sensitivity in the charge-sensing mode. A novel fabrication technique for ionic polymer transducers named the Direct Assembly Process (DAP) was developed in this paper. The DAP allows the use of any type of ionomer, diluent, and conducting powder in the transducer, and permits the exploration of any novel ionomeric design. In this paper the effect of diluent content of the IPT, electrode thickness, and composition were optimized in term of maximum peak strain and strain rate generated by an IPT. Decreasing viscosity and increasing polarity and content of the diluent were demonstrated to increase the strain rate of an IPT. The thickness of the electrode was varied and correlated with the maximum strain generated due to a 2 V step input. This study also demonstrated that RuO_2 composition has an optimal loading of 42 vol%, while SWNT electrodes have an optimal performance at around 30 vol%.

Introduction

Ionic polymer membranes are materials that exhibit ionic conductivity and ion selectivity. Several researchers have shown that these polymer membranes can function as electromechanical actuators and sensors [1–3]. An ionic polymer transducer is made of an ionomeric membrane (typically Nafion, a product of DuPont) sandwiched between two conductive electrodes. In this state the membrane will bend toward the anode when a voltage (typically less than 5 V) is applied across its thickness. Similarly, the polymer will generate charge when deformed. Ionic polymer transducers have the advantage of being able to generate large strains [1, 4] under small applied voltages, are compliant and thus compatible with conformal structures, and have a very high sensitivity to motion when used in charge-sensing mode.

In this paper, we present a method called the Direct Assembly Process (DAP) for fabricating transducers with controlled electrode dimensions and morphology. In this method large surface area electrodes are painted on an ionomer membrane. An alternative method that has been used by a number of researchers, the impregnation–reduction approach, is a method by which the metallic electrode is chemically deposited on the membrane [5]. Although this method is effective, the process does not enable direct control on the electrode morphology and limits the type of electrode particulate that can be placed on the membrane [6].

Recently it has been shown in both experiment and theory that the composition of the electrode layer strongly influences transducer performance. The depth and the uniformity of the electrodes has been shown to increase the performance of the transducer [7]. As discussed in Oguro et al. [8], increasing strain per unit voltage is observed with

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increasing number of platinum layers plated on the membrane until the mechanical stiffness of the electrode reduces the deflection. Experimental work by Akle et al. [6] has correlated the actuation properties of the transducer with the capacitance of the transducer. This result was consistent for ionomers with substantial differences in composition; therefore it strongly suggests that charge accumulation at the polymer–metal interface is a determining factor in the strain and strain rate generated during actuation. This experimental result is supported by physics-based modeling efforts [7, 9] that highlight the role played by the boundary layer that forms at the interface of the electrode and the polymer.

In this paper, the effect of diluent content, electrode thickness, and composition are optimized in term of maximum peak strain and strain rate generated by an IPT. Five organic solvents and ionic liquid diluent are studied and correlated to the strain rate, while the thickness and composition of the electrode are manipulated for RuO_2 and single walled carbon nanotubes (SWNT) conducting powders. Results are explained in terms of the electric double layer and percolation theories. Finally transducers fabricated using the impregnation/reduction process are compared to transducer fabricated using the DAP.

Traditional fabrication process for ionic polymer transducer

The most common fabrication process for ionic polymer transducers is the impregnation–reduction process. This method is an electroless chemical plating process which can be used on to any ion selective ionomer membrane. The impregnation–reduction consists of three main steps. The first step is to soak the polymer in a metal salt solution such as $PtNH_3Cl_2$ to populate it with a reducible metal [10]. The next step is to reduce the metal salt on the surface of the membrane by soaking it for 4–6 h in $NaBH_4$ or $LiBH_4$. The reduction occurs according to the following reactions,

$$NaBH_4 + 4[Pt(NH_3)_4]^{2+} + 8OH^- \longrightarrow 4Pt^0(s) + 16NH_3(g) + NaBO_2(sd) + 6H_2O \qquad (1)$$

and

$$NaBH_4 + 4H_2O \longrightarrow 4H_2(g) + NaOH(Na^+ + OH^-) + B(OH)_{3(sd)} \qquad (2)$$

Varying the concentration of the reducing agent controls the penetration depth of the electrodes inside the polymer. The third step is to electroplate the polymer composite with a thin (50–100 nm) of gold to increase the surface conductivity of the transducer. A fourth optional step is to perform ion exchange, such as exchanging Na^+ for the Li^+ ion. This is done by soaking the polymer in an NaOH or LiOH solution.

Several modifications to the basic method described above have been developed for the purpose of improving transducer performance. Shahinpoor and Kim [11] incorporated silver, graphite, and palladium particles in the membrane using a physically loading method. The metal powder is hot-pressed on membrane surfaces and impregnation–reduction is later performed. Physically loading the membrane reduces the number of impregnation-layers from an average of 5–1. Less expensive powders such as graphite are possible to incorporate using this method. Shahinpoor and Kim [12] also reported a fabrication path to make three-dimensionally shaped transducers. Nafion solution is casted in molds with the desired shape, and later an electrode is plated using any of the previously mentioned methods. The 3D technique is implemented to create thick transducers. In this same article Shahinpoor and Kim [12] suggests but does not implement, casting two conductor-ionomer mixed electrodes around the main casted membrane. The suggested path starts with casting a layer of the electrode mix, followed by a layer of pure ionomer and finally a layer of the mix is casted on the top to form the second electrode. Taegeun et al. [13] developed a replication method to manufacture a large surface-area ionic polymer actuator. High surface area etched aluminum foil was used as a template for replication using liquid Nafion solution, and finally Pt was plated on this high surface are surface to form a transducer with superior actuation properties, such as large strains and strain rate.

The impregnation–reduction process is a reliable method for making ionomeric polymer transducers, but it is limited in its ability to control critical parameters that have been shown to greatly affect performance. Control on electrode morphology in the impregnation/reduction process is limited to the change of chemical species and their concentrations, and manipulating the number plated layers. In this work, we show that control over electrode morphology and composition is critical to optimizing the transducer properties. For example, we will show that the thickness of the electrode layer correlates to the maximum generated strain. The impregnation–reduction method does not enable direct control over electrode thickness. In addition, the impregnation–reduction method does not allow for separate control over the electrode thickness for the purpose of developing electrodes with different thicknesses on opposing sides of the membrane. This is proved to be critical in extensional mode actuation of ionic polymer transducers [14, 15]. Finally, the impregnation–reduction process cannot incorporate non-metallic conducting powder such as carbon nanotubes in the electrode. Single walled carbon nanotubes are demonstrated to increase the strain and strain rate in ionic polymer transducers when used in the electrode layer [14, 16].

Direct assembly process (DAP)

In this paper, a fabrication method called the Direct Assembly Process is developed that will enable direct control over the electrode geometry and electrode composition. The Direct Assembly Process is inspired by fabrication techniques used in preparing supercapacitors and hydrogen fuel cells. There are two variations of the Direct Assembly Process studied in this work. The first variation is to apply the electrode on a dry membrane and the second variation is to solvate the membrane and then apply the electrode. In both variations the electrode can be either painted directly on the membrane or painted separately on a decal and later hot-pressed it on the membrane. The following sections describe these two methods.

Direct assembly process with dry membranes

The DAP consists of first dissolving the desired ionomer into an alcohol solution. In this study Nafion 1100 5% weight polymer solution is used. The Nafion dispersion is obtained from FuelCellStore and used without further modification. The next step in the process consists of mixing an electrically conductive powder with the polymer solution. For some conducting particulates additional solvents are added to the mixture to enhance dispersion. Isopropyl alcohol (IPA) is an inexpensive solvent that is easy to evaporate, while glycerol is added to increase viscosity. If the mix is to be applied using a brush, increasing its viscosity is found to enhance the uniformity of the electrode. The mix is sonicated and stirred for 1–4 h to ensure homogeneity and dispersion of the metal grains. The duration of mixing and sonication depends on the type of conducting powder and concentration of polymer solution and metal volume percent.

The conductor-polymer is applied to the polymer in one of two ways. The first method consists of directly painting several layers of the mix on each side of the membrane using a brush. The sample is placed in an oven at 130 °C for 15 min between each layer. The resulting composite is then hot-pressed at 210 °C and a pressure of 20 MPa. This step adheres the electrode to the membrane surface and decreases the interfacial resistance between the electrode and the membrane. The second DAP method is to paint several layers of the polymer–metal mix on a Teflon reinforced glass fabric named Furon, and then hot press these decals on the polymer using same pressure and temperature as in previous method. Once cooled down the membranes are hydrated, and the Teflon mesh is detached from the polymer. For dry actuators, the decal method provides better control over the loading and uniformity of the electrode. Loading is controlled by weighing the decals before and after painting the electrodes. Painting the electrode directly on the membrane causes the polymer to swell due to solvents from the electrode mix leading to wrinkles in the membrane. A vacuum plate is placed under the membrane during painting to decrease wrinkling.

At the conclusion of the painting process the surface conductivity of the electrode is not high enough to provide an equipotential surface for actuation. Two methods are developed to increase surface conductivity of water hydrated ionic polymer transducers. In the first method an additional platinum layer is applied to the surface using the impregnation–reduction method previously described. A gold overlayer is then electroplated on the outer surface of the platinum. The alternative method consists of depositing a Au layer by self-assembled monolayers. This method uses light etching lithography technique to apply a pattern to the surface. Such electrode enables distributed actuation/sensing on the submicron level. For more details on this method see Ref. [17].

As in the impregnation–reduction an optional ion exchange step could be made by boiling the membrane for 2 h in a 1 M chloride solution such as LiCL or NaCl. A schematic of the Direct Assembly Process is shown in Fig. 1.

A diluent other than water can also be incorporated into the dry membrane by following any of the previously discussed methods. In this study four diluents are incorporated in the membrane: water, formamide, Diethylene-Glycol (DEG), and 1-ethyl-3-methyimidazolium trifluoromethanesulfonate (EmI-Tf) ionic liquid. Several methods of adsorbing the diluent to the membranes are developed. Some diluents such as formamide require approximately 24 h to saturate the membrane at room temperature. This duration is decreased to 3 h if the membrane is sonicated inside the solution. This duration is shortened to less than 1 h by heating the membrane inside the solution at 100 °C. The diffusion of EmI-Tf ionic liquid in Nafion is slower compared to formamide. To date, our group achieved a maximum absorption of 58% w/w (weight of EmI-Tf to dry polymer weight). This uptake is achieved by heating the membrane at 150 °C for 4.5 h in the presence of EmI-Tf. A temperature of 150 °C degrades EmI-Tf after several heating cycles. Using a co-diluent such as ethanol or *N*-methylformamide proved to increase diluent uptake. The co-diluent is later evaporated by baking the sample at an elevated temperature under vacuum. Table 1 shows that an optimal composition of 40 vol% (volume of *N*-methylformamide to volume of EmI-Tf) and

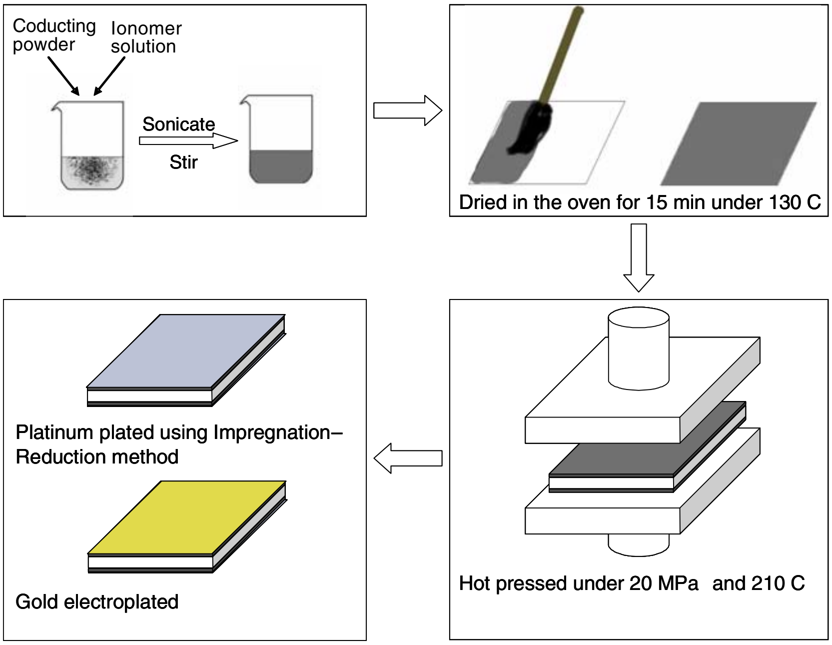


Fig. 1 Schematic showing the four steps Direct Assembly Process (DAP) for building dry transducers

temperature of 130 °C for 4 h had an uptake of 58.2% w/w. This is a more stable method due to a 20 °C decrease in temperature. Table 1 presents absorbtion of EmI-Tf corresponding to several temperatures, compositions, and durations.

One issue associated with the diluents formamide, DEG, and EmI-Tf, is that they excessively swell the membrane. For example formamide swells the membrane over 100% of its original volume, leading to cracks in the conductive surface electrode. Therefore the last step of increasing the surface conductivity is postponed until after the diluent is incorporated. The Pt/Au chemical deposition or solution-based assembly of Au previously described are implemented in aqueous environment and therfore limited to water swollen transducers. A third method of increasing surface conductivity is developed for non-hydrated transducers. The transducer is sandwiched between two 100-nm thick conductive gold foils and the entire composite is fused together by a hot-pressing process. For dry membranes this hot-pressing is carried out at 20 MPa and 210 °C for 2 min. However, the non-aqueous solvated ionomers will flow under this high pressure and long duration leading to the deformation of the transducer. In order to maintain the dimensional stability of the membrane during the hot-pressing process while still binding the three layers together, the pressure and pressing time are reduced. It is found for EmI-Tf ionic liquid that good results are obtained for hot-pressing carried out at 4 MPa and 160 °C for around 10–20 s depending on the metal loading and thickness of the electrode. As for volatile diluents such as formamide 140 °C and less than 5–10 s are sufficient and preserves the dimensional stability of the transducer better. The gold foils used are Falcon-Brand 24 carats gold leafs; they helped decreasing the surface resistance from greater than 100 kΩ/cm for the painted metal layers to less than 1 Ω/cm. Transducers with high metal loading in the electrode (> 25 vol%) a thin layer of diluted ionomer solution (50% w/w IPA/Nafion 5%) is painted over the high surface area electrodes. This step enhances the adhesion of the gold foils to the electrode.

Table 1 Diluent uptake as a function of diluent composition, temperature, and duration. The composition present the volume of *N*-methylformamide to the total volume of EmI-Tf and *N*-methylformamide. The last column presents the formamide vol% of the mixture in the membrane before evaporating the co-diluent

Percent *N*-methylformamide	Temp (C)	Time (h)	Total uptake (%w/w)	EmI-TF uptake (%w/w)	*N*-methylformamide uptake (%w/w)	Vol% *N*-methylformamide
20	70	3:30	36.7	30.2	6.6	23.2
20	130	4:30	70.4	56.1	14.2	26.0
40	130	4:30	83.5	41.7	41.8	58.2
40	130	1:30	91.3	51.2	40.1	52.1

Direct assembly process with solvated membranes

The Direct Assembly Process is also implemented when the polymer is in the solvated state (i.e., after the diluent has been added) due to the fact that dry assembly of the electrode might be inadequate for some diluents. As mentioned earlier, some diluents excessively swell the membrane leading to delamination of not only the gold overlayer but even the high surface area electrode. Moreover some diluents might dissolve the ionomer in the high surface area electrode. A solution of the Nafion ionomer requires complicated processes to cast into the semicrystalline structure of the membrane. In the amorphous state Nafion solution is unstable under the high temperature required for some diluents to be absorbed into the transducer. In this second DAP scheme, the membrane is solvated with the proper liquid after being exchanged with the desired cation. A proportional amount of diluent is added to the ionomer/conductor mix. Usually this amount corresponds to the weight of diluent absorbed in the membrane. The electrode is painted on the both surfaces of the membranes, then sandwiched between two gold leaves and melt pressed together under the appropriate temperature, pressure, and duration. These parameters are usually similar to the ones mentioned in the previous section. Challenges of this scheme are diluent loss and dimensional stability. Organic diluents evaporate at the elevated melt-press temperature though it is below their boiling point. A significant amount of diluent evaporates out of the membrane. This amount is around 30% depending on the boiling point of the diluent, melt press temperature, and diluent uptake. Some highly volatile diluents are impossible to incorporate using this method. The diluents with boiling point less than 10 °C smaller than the flow temperature of the solvated ionomer (T_g) are hard to incorporate using this scheme of DAP. The only possible path for such diluents is to build dry transducers and then incorporate the diluent. The platinum and electroplated gold layers are plated in solutions with the final diluent if possible. Otherwise, the impregnation–reduction reaction and the electroplating are done in a diluent (or a mixture of diluents) that have similar swelling properties to the low boiling point diluent to be incorporated. A schematic of the Direct Assembly Process with solvated membranes is shown in Fig. 2.

Electrode materials

Platinum and gold are traditionally used as electrode materials for ionic polymer transducers [10], although Bennett and Leo [18] have used low cost non-precious metals such as copper as electrode material. Tamagawa et al. [19] plated Nafion with combinations of silver, copper, and nickel metals using impregnation–reduction. Shahinpoor and Kim [11] reported loading the polymer membranes with metal particulates such as palladium. The metal powder is hot-pressed on membrane surfaces and palladium or platinum impregnation–reduction is later performed. This method enables less control and less penetration of the conducting powder to the electrode as compared to the DAP. Furthermore, the conducting particles might be damage during the process due to the high pressures and temperatures involved.

The ability to incorporate different electrode materials is enabled by our development of the Direct Assembly Process for fabricating the ionic polymer transducers. Hybrid ionomeric transducers consisting of several conducting powders are also manufactured and presented elsewhere [4, 16]. In this paper RuO_2 and SWNT conducting powders will be studied and their physical properties and activities are presented in Table 2. These two conducting particulates are studied due to their distinct.

Electromechanical characterization

Materials fabricated in this work are characterized for their performance as electromechanical transducers using a single test setup that measures two actuation properties; the strain (ε) and the electrical impedance (Z). The samples used for these tests are 3 mm × 30 mm rectangular transducers held in a cantilevered configuration in a clamp with fixed gold electrodes (see Fig. 3). The free length of the transducer is 19 mm. The thickness of the transducer varies between approximately 0.18 mm and 0.28 mm depending on the number of electrode layers. For the first test a random voltage with a RMS magnitude of 1 V is applied to the sample using a Fourier analyzer and amplifier. The displacement $\delta(t)$ at any point along the length is measured with a non-contact laser vibrometer. The current $i(t)$ induced in the polymer due to the applied voltage $v(t)$ is also measured by measuring the voltage drop across a small (0.1 Ω) resistor (see Fig. 3a). The frequency response function between the excitation voltage and the output displacement and between the input voltage and induced current are measured over the frequency range 0.2–200 Hz. This setup is also used to measure the time domain response of the transducer to a step or sine wave voltage input.

The free deflection $\delta(t)$ (in the time domain) or the free deflection frequency response ($\delta(\omega)/v(\omega)$) are used with equations to compute the bending strain as a function of time or frequency

Fig. 2 Schematic showing the four steps Direct Assembly Process (DAP) for building solvated transducers

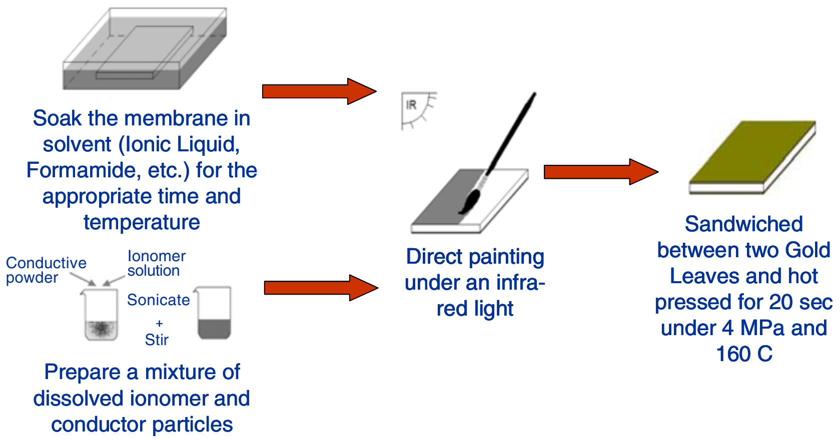


Table 2 Physical and electrochemical properties of electrode conducting materials

	σ (S/cm)	Density (kg/m^3)	Surface area (m^2/g)	Volumetric surface area 10^6 (m^2/m^3)	Percolation threshold	Actuation mechanism in electrolytes	Price ($/g)
SWNT	30,000	1,330	1,000	1,330	20 vol%	EDL/quantum	500
Anhydrous RuO_2	3,500	7,050	45–65	317–458	0.2 vol%	EDL/redox	50

EDL = Electrostatic double layer SWNT = Single walled carbon nanotubes

$$\epsilon(t) = \frac{\delta(t)T}{L_f^2} \tag{3}$$

$$\frac{\epsilon(\omega)}{v(\omega)} = \frac{\frac{\delta(\omega)}{v(\omega)}T}{L_f^2}, \tag{4}$$

where ε is strain, T is the thickness of the sample, and L_f is the free length of the sample. These equations assume that the transducer bends with a constant curvature; experimental results demonstrate that this is an appropriate assumption for the experiments performed in this paper [4].

The impedance $Z(\omega)$ and the capacitance C is computed using the expressions

$$Z(\omega) = \frac{v(\omega)}{i(\omega)} \tag{5}$$

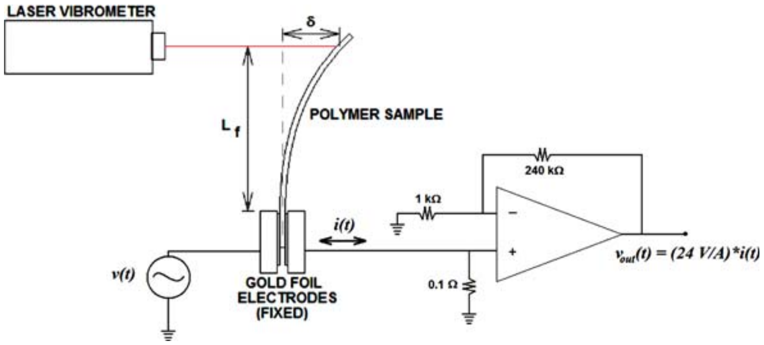
$$C = \frac{1}{Im(Z(\omega))\omega A} \tag{6}$$

where A is the area of the transducer and $Im(Z(\omega))$ is the imaginary component of the impedance. Equation (6) assumes that the polymer is a network consisting of a capacitor and resistor in series [6].

Optimization of the DAP

As mentioned earlier the DAP provided control on several variables in the transducer fabrication process. In this paper, we study three processing variables: the diluent content, electrode thickness, and electrode composition. Each variable is correlated with the speed of response and maximum strain generated by the actuator. Samples are

Fig. 3 Experimental setup used for the bending electromechanical measurements



fabricated using the Direct Assembly Process and are characterized according to the procedures presented in section ‘‘Electromechanical characterization.’’ Lithium is the cation for all of the ionomer membranes studied in this paper.

Ionic liquids and organic diluents

In this study, the ionic liquid EmI-Tf and organic diluents are used to solvate the transducers. EmI-Tf is a non-volatile molten salt which allows the transducer to operate in air without any significant loss of performance [20]. Earlier work by the authors [4, 21] indicated that it is possible to operate the transducers in air for over 250,000 cycles at ±2 V and 1 Hz without any degradation. Five organic diluents are also considered, PolyEthylene Glycols (PEG) with four different molecular weights (MW) and Formamide. PEGs are polar alcohols with relatively high boiling point. Ethylene Glycol (EG) is the basic unit, diethylene glycol (DEG) is a two repeating units, triethylene glycol (TEG) is three, and PEG 200 is an average of 4.2 repeating units. These diluents are linear polymers, and therefore increasing the molecular weight increases the boiling point and viscosity of the diluent. These organic diluents are chosen to study the effect of viscosity and dielectric constant on the strain rate of ionic polymer transducers. The relevant physical properties of these diluents are listed in Table 3.

In this experiment six samples are built using the Direct Assembly Process and characterized in bending according to procedures described in section ‘‘Electromechanical characterization.’’ Each of the samples utilizes a Nafion 117 membrane exchanged with Li^+ cation and solvated with one of the diluents. The diluent uptake is the maximum that can be achieved with current methods and are close to 100% of dry polymer weight for organic diluents and approximately 58% for Emi-Tf. Electrodes are composed of 45 vol% high surface area RuO_2 metal powder.

Table 3 Strain rate of ionic polymer transducers with different diluents. Physical properties of the diluents are provided as specified from supplier

	Strain rate (%/s)	Viscosity (10^{-3} Pa s or cP)	Dielectric constant	Normal boiling point (°C)
Ethylene glycol	0.073	16.1	37.7	197.3
Diethylene glycol	0.1331	35.7	31.7	245.3
Triethylene glycol	0.124	49.0	23.69	288.0
PEG 200	0.090	53.8	15.7	329.7[a]
Formamide	0.231	3.3	109.5	210.5
EmI-Tf	0.043	45.0	NA	NA

[a] Decompose

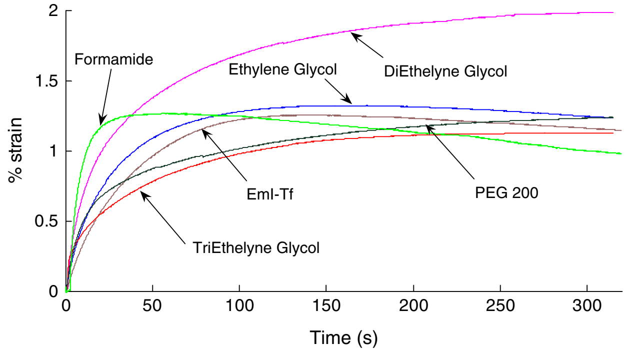


Fig. 4 (**a**) Measured response due to a 2 V step change in potential for actuators with RuO_2 electrodes and Formamide or EmI-Tf diluents. (**b**) Strain rate as a function volume uptake ionic liquid

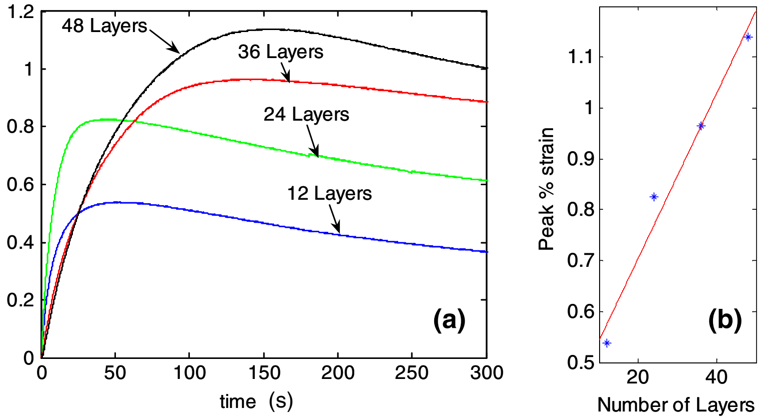
The transducers are characterized using the time domain response to a step potential of 2 V, as shown in Fig. 4. Previously published results [7] have shown that water-hydrated membranes exhibit response times on the order of 10–100 mS to a step change in potential. In our study, the high viscosity of the diluent leads to a slow response in the actuators (see Fig. 4 and Table 3). The diluents EG and DEG produce a response that is faster relative to the diluents with higher molecular weights. The diluent EG, with a low boiling point of 195 °C, evaporates fast compared to DEG which has a boiling point of 245 °C. DEG provided sufficient environmental stability to run step response experiments which are usually on the order of minutes to an hour. Moreover DEG transducers produced strains on the order of 2% for a +2 V step input. Relative to EG, formamide is an environmentally stable diluent that has a boiling point of approximately 211 °C and a low viscosity of 3.3 cP. Transducers solvated with organic diluents can operate in air only for few hours without a degradation in performance due to diluent evaporation. Transducers with Emi-Tf diluents response slower than actuators with formamide as shown in Fig. 4. The average strain rate during the first 2 s of the step is 430 μstrain/s and 2310 μstrain/s for EmI-Tf and formamide, respectively. Uptake varied from 58% (weight percent of dry polymer) for EmI-Tf to 100% for the formamide.

This study demonstrates that the strain rate response of transducers with an organic diluent is correlated with the viscosity and dielectric constant of the fluid. Ionic polymer transducers saturated with large dielectric constant and small viscosity organic fluids actuate at a faster rate.

Effect of electrode thickness on actuation response

In this experiment the thickness of the electrode is increased while keeping the composition of the electrode

Fig. 5 (**a**) Strain response of four samples with different electrode thickness due to a 2 V step input. (**b**) Peak strain as a function of electrode thickness



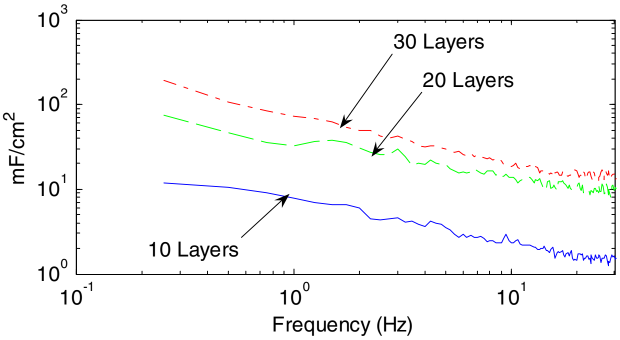


Fig. 6 (**a**) Capacitance per area FRF of three transducers with 10, 20, and 30 layers of 2.5:1 RuO_2 electrode

constant. Samples in this experiment are solvated with triethylene glycol. The amount of particles and the conductor/ionomer interfacial area increase proportional to the thickness of the electrode. Four samples are fabricated with 12, 24, 36, and 48 layers electrode ink painted on each side. Scanning electron microscopy (SEM) images indicates that each 12 layers corresponds to an electrode approximately 9.4 μm thickness.

The peak response of these samples is found to increase with the thickness of the electrode. Figure 5a is a plot of the step response of each transducer to an applied potential of 2 V and Fig. 5b is a plot of peak strain as a function of electrode layers. We attribute the increase in peak strain to an increase in the interfacial area of the electrode as the thickness is increased. This is consistent with the previous work by Akle et al. [6] in which the peak strain was correlated with charge accumulation at the electrode. Observing the shape of step response we see that the initial strain rate is a function of the electrode thickness. We believe that the variation in strain rate is due to the fact that ions diffuse from the bulk polymer towards the electrode to form an electric double layer. Figure 5a demonstrates that transducers with thicker electrodes tend to strain slower. This supports the concept that ions have to cross a thicker electrode to form the electric double layer, and as the resistivity of the electrode increases the speed of ion diffusion is reduced, thus resulting in a slower strain rate.

Figure 6 demonstrates that the capacitance in an ionic polymer transducer increases proportional to the electrode thickness. Our previous studies [6] demonstrates a linear relationship between capacitance and strain in ionic polymer transducer. This correlation between electrode thickness and peak strain further supports the fact that actuation performance in ionic polymer transducers is proportional to capacitance.

Optimization of conductor powder concentration in the electrode

In the third experiment the volume percentage of two different conductive powders (RuO_2 and SWNT) is controlled to assess the effect of particulate loading on the transducer performance. These materials are chosen due to the variety in conductivity, surface area, and percolation threshold. The properties of these conducting powders are found in Table 2. The total volume of conductor in the electrode was held constant while the concentration of conductor to polymer in the electrode was varied. RuO_2 samples with loadings of 12–67 vol% were tested for the diluents EmI-Tf and DEG. Transducers with SWNT particulates in the electrode (volume percentage between 5% and 40%) were also built and tested for ionic liquids diluent.

Experiments on the particulate composition and loading demonstrate that the rate of actuator response is strongly correlated with the volume percentage and percolation properties of the electrode. A plot of the strain rate versus volume percentage of particulate indicates that there is clear optimum value of the strain rate response (see Fig. 7a). Our results also demonstrate that this optimum value is a function of the particulate loading. Conductive powders consisting of RuO_2 shows an optimal loading

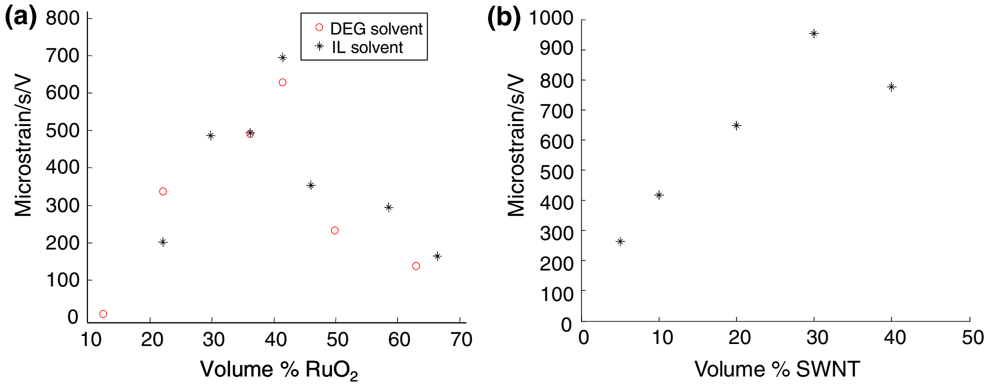


Fig. 7 (**a**) Strain rate as a function of RuO_2 volume % in the electrode. (**b**) Strain rate as a function of SWNT volume % in the electrode

around 42 vol% as shown in Fig. 7a. For the electrodes comprised of SWNT, the optimal strain rate is achieved for loadings of approximately 30% volume percentage as shown in Fig. 7b.

Six electrode samples were built using the DAP process. A Nafion/RuO_2 mix was prepared and painted on a thin gold leaf using a brush. Note there is no ionomer membrane in this design. The mix was solvated with 60 wt% of EmI-Tf ionic liquids. The composition of the electrode ranged from 10 vol% to 60 vol% RuO_2. The impedance of the six samples are measured using an HP 4195 impedance analyser. The conductivity of each electrode sample is plotted as a function of particulate loading which is shown in Fig. 8. Figure 8 demonstrates that a sharp increase in conductivity occurs around 19 vol% for RuO_2 electrodes.

Discussion

From the experimental studies presented in the previous section we propose a physical rationale for the relationship between electrode composition and transducer performance. The physical rationale for the composition to performance correlation is based upon three properties of the electrode: the percolation of conductive particulates, the volume percentage of the particulates, and the speed of ionic diffusion in the ionomer phase of the electrode. Two processes are occurring during the actuation of the ionic polymer transducer. The first is the motion of electrons in the conductor phase of the electrode, and the other is the diffusion of the ions from the ionomer toward the conductor particles in the electrode and form an electric double layer.

In the experiments discussed in section ''Optimization of conductor powder concentration in the electrode,'' it was clear that the volume percentage of the conductive particulate in the electrode was strongly correlated to the speed of response. As shown in Fig. 7a, the strain rate dropped sharply for volume percentages of RuO_2 of less than approximately 25%. Further experimentation with lower volume percentages demonstrated that this drop in strain rate was correlated with the percolation threshold of the electrode. Measurements of the electrode conductivity as a function of particulate loading (shown in Fig. 8) illustrate that the percolation threshold of the electrode is around 20 vol% of RuO_2. Thus, our results demonstrate that percolation of the conductive particulate network is critical to achieving high strain rate in the transducer. Classical percolation theory states that a continuous conducting network is formed by the coalescence of the grains. The percolation theory indicates that increasing the conductor phase decreases the resistivity of the electrode [22].

The decrease in strain rate at high loading illustrated in Fig. 7a and b is explained by the decreasing presence of ionomer leading to slow ionic diffusion in the electrode. Limiting ionic diffusion speed is also demonstrated from results in section ''Ionic liquid and organic diluents.'' Diluents with a large dielectric constant are more polar and dissociate better the ions in the actuator. Mobility of the ions increases by decreasing viscosity. Table 3 shows that formamide solvated transducers are the fastest, while the viscosity of formamide is lowest and has the highest dielectric constant. Comparing the performance of TEG to PEG 200 solvated transducers, it could be noticed that the former is 38% faster than the latter. The viscosity of PEG 200 is approximately 10% larger than that of TEG, while the dielectric constant of TEG is much larger by 51%. Ethylene Glycol is an outlier to the trend, and this is believed to be due to the low boiling point which leads to larger diluent evaporation during transducer fabrication. In this dissertation we studied a single ionic liquid (EmI-Tf) with an uptake of 58% by weight of dry ionomer. It has been also found that the content of ionic liquid within the membrane has an influence on the speed of response [23].

After the charging of the metal particles in the electrode, mobile ions will migrate within the ionomer to form an electric double layer around each of the conducting particles. These cations are mobile only in an electrolyte

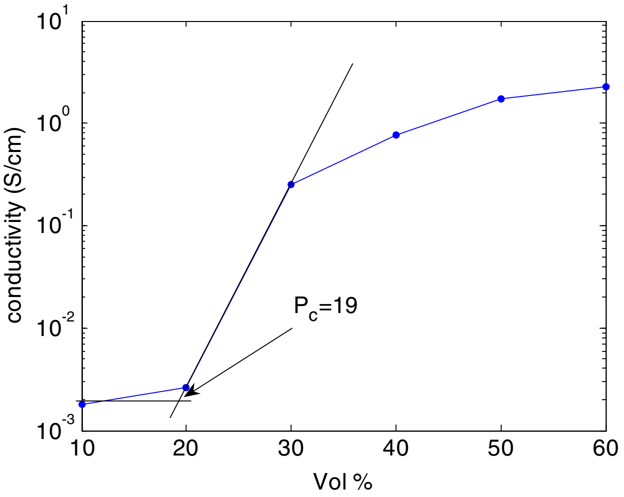


Fig. 8 Conductivity of the electrode as a function of RuO_2 volume % in the electrode

medium, which is the ionomer in ionomeric transducers. The thickness experiment presented in section ''Effect of electrode thickness on actuation response'' illustrates the electric double layer in ionic polymer transducers. As a whole the electric double layer (EDL) is an electrically neutral system that occurs at an interface or surface, in which a layer of positive charges opposes a layer of negative charges, surrounded by oriented polar molecules [24]. A larger conductor–polymer interface area accumulates more ions per unit volt and therefore increases the capacitance of an electric double layer. This increase in capacitance is presented in Fig. 6.

Conclusions

A new fabrication method for ionic polymer transducers is developed and characterized. The method, denoted the Direct Assembly Process, allows the fabrication of high strain and strain rate IPT with greater control of the fabrication parameters. Control of the processing parameters allows us control the diluent properties and the electrode morphology for the purpose of optimizing the actuator performance.

The results of this paper demonstrate the importance of diluent properties and electrode composition on the actuator performance. The EmI-Tf ionic liquid diluent produces an environmentally stable transducer with moderate velocity. Actuators based on formamide and ethylene glycols diluents exhibit a faster response time than ionic liquid transducers, but exhibit higher volatility. Increasing the uptake and decreasing the viscosity of the diluents leads to high speed transducers with excellent environmental stability. Our results also demonstrate that tailoring the electrode composition is an effective method for achieving high-strain transducers using ionomeric polymer materials. Transducers fabricated with thicker electrodes generate strains on the order of 2.3%. Each conducting powder in the electrode exhibited an optimal composition which proved to be a function of the conductivity and percolation threshold. Two conductive particulates were discussed in this work: RuO_2 and SWNT. RuO_2 electrodes are optimized around 42 vol% while SWNT demonstrates optimal loading around 30 vol%.

The processing methodology introduced in this paper allows us to develop general guidelines for optimizing the actuator performance. The conductivity and percolation threshold of the metal powders is crucial to controlling the speed of response, while the amount of ionomer–conductor interfacial area and of the conducting powder are correlated with the peak strain response of the transducer. Conducting powders with large aspect ratio (low percolation threshold), high electrical conductivity, and large surface area properties are good candidates for electrode materials in ionic polymer transducers. The electrical conductivity through the electrode is proved to be critical to the speed of response of the transducers, while displacing more ions by increasing capacitance improves the peak strain of the actuator.

Acknowledgement This work was partially supported by the U.S. Army Research Laboratory and U.S. Army Research Office under Contract/Grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI.

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