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Characterization of the Electromechanical Properties of Ionomeric Polymer-Metal Composite (IPMC)

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ABSTRACT

IPMC is an electroactive polymer (EAP) that has been the subject of research and development since 1992. The advantages of IPMC in requiring low activation voltage and the induced large bending strain led to its consideration for various potential applications. However, before the benefits of IPMC can be effectively exploited for practical use, the electromechanical behavior of this group of EAP materials must be properly understood and quantified. An experimental setup was developed for data acquisition from IPMC strips that are subjected to various tip mass load levels. This data acquisition setup was used to measure the displacement and curvature of IPMC as a function of the input signal. Sample strips were immersed in water to minimize the effect of moisture content. In order to avoid electrolysis, the samples were subjected to 1-V square wave with either positive or negative polarity. Experiments have shown that IPMC has history dependence and the characteristics response is dominated by the backbone (e.g., Nafion, Flemion, etc.) and ionic content (e.g., Na+, Li+, etc.).

Keywords: EAP, Characterization, Testing, Electromechanical Properties, Electroactive Polymers, Actuators

1. INTRODUCTION

Electroactive polymers (EAP), which are an emerging class of actuation materials [Bar-Cohen, 2001], have many attractive characteristics. Employing these materials as actuators in engineering devices and mechanisms requires the availability of properties database and scaling laws to allow designers to predict the response at various operation conditions. A metric for the comparison of these material properties with other electroactive materials and devices is needed to allow transducer/actuator designers to impartially compare the performance of the various materials [Sherrit and Bar-Cohen, 2001]. The general properties of EAP that need to be characterized and the significance of these properties are summarized in Table 1. In selecting characterization techniques it is instructive to look at the various Electroactive Polymers and the source of their strain-field response. EAP can be divided into two major categories, including ionic and electronic, based on their activation mechanism. Coulomb forces drive the electronic EAP, which include electrostrictive, electrostatic, piezoelectric and ferroelectric. This type of EAP materials can be made to hold the induced displacement while activated under a DC voltage, allowing them to be considered for robotic applications. Generally, these EAP materials exhibit a greater mechanical energy density than the ionic EAP and they can be operated in air with no major constraints. However, the electronic EAP require high activation fields (50-150-V/µm) that may be close to the breakdown level. In contrast to the electronic EAP, ionic EAPs are materials that involve mobility or diffusion of ions and they consist of two electrodes and electrolyte. The activation of the ionic EAP can be made by as low as 1-2 Volts and generally induce a bending displacement. Examples of ionic EAP include gels, ionomeric polymer-metal composites, conductive polymers, and carbon nanotubes. Their disadvantages include a need to maintain wetness and difficulties to sustain a constant displacement under activation of a DC voltage (except for conductive polymers). Generally, the properties that are expected to be of most significance to design engineers in assessing the capability of EAP as potential actuators include: Electrically induced stress (MPa) and strain (%), operation bandwidth (Hz) or response time and relaxation; required driving Voltage (V); power density (W/cm^3); efficiency (%); lifetime (cycle); material density (g/cm^3) as well as environmental constraints and behavior.

Ionomeric Polymer-Metal Composites (IPMC) are ionic EAP [Nemat-Nasser and Thomas, 2001] and they are involved with challenging requirements for the characterization of their electromechanical behavior. Developing methodologies for the material characterization of IPMC requires new approaches and the results are expected to benefit the field of EAP in enabling effective testing of other EAP materials. This topic has been the subject of research at JPL and is reported in this manuscript. A series of issues were investigated ranging from the characterization of the input signal to the determination of the mechanical response to the effect of various drive signals and the spectral electrical and mechanical response.

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TABLE 1: The properties that need to be characterized for EAP materials and the assumed metric.

Measurement		Properties	Significance
Mechanical		Tensile strength [Pa]	Mechanical strength of the actuator material
		Stiffness [Pa]	Required to calculate blocking stress, mechanical energy density, and mechanical loss factor/bandwidth
		Thermal expansion coefficient [ppm/C]	Affects the thermal compatibility and residual stress
Electrical		Maximum voltage [V]	Necessary to determine limits of safe operation
		Impedance spectra [ohms and phase angle]	Provides both resistance and capacitance data. Used to calculate the electrical energy density; electrical relaxation/dissipation and equivalent circuit.
		Nonlinear Current [A]	Used in the calculation of electrical energy density; quantify nonlinear responses/driving limitations
		Sheet Resistance [ohms per square]	Used for quality assurance
Microstructure		Thickness (electrode & EAP), internal structure, uniformity, anisotropy and hosted defects.	These are features that will require establishing standards to assure the quality of the material.
Electro-active Properties	Strain	Electrically induced strain [%] or displacement [cm]	Used in calculation of 'blocking stress' and mechanical energy density
	Stress	Electrically Induced Force [N], or mechanically induced charge [C]	Electrically induced force/torque or Stress induced charge
	Stiffness	Stress/strain curve	Voltage controlled stiffness
Environmental Behavior		Operation at various temperatures, humidity and pressure conditions	Determine material limitations at various conditions

2. CHARACTERIZATION OF IONIC EAP WITH DIFFUSION DEPENDENT STRAIN

Characterization of the properties of the ionic EAP materials, which involve diffusion dependent strain, poses a unique challenge to the development of test methods [Sherrit and Bar-Cohen, 2001]. The emphasis of this reported study is on ionomeric-polymer metal composite (IPMC) consisting of Nafion® [Tant, et al, 1997; and Shahinpoor, et al, 1998] and Flemion® [Oguro, et al, 1999] as membranes made of fluorocarbon backbones and mobile cations (counter-ions). The exact mechanism that is responsible for the electro-activation is still a subject of a series of studies. However, recently significant progress has been made towards understanding the related phenomena [Nemat-Nasser and Thomas, 2001]. When a voltage (<5V) is applied to a hydrated IPMC sample, the large ionic conductivity may promote electro-osmosis and/or electrolysis. The former response manifests itself as a bending of the film towards the positive electrode (anode) and can be exploited in actuation applications [Sewa, et al 1998]. The induction of electrolysis is an undesired electrochemical reaction that consumes power and may damage the electrodes. Kanno, et al, [1994] have shown that the bending response of Pt - electroded Nafion (Na+ counter-ion) is complicated and it involves relaxation processes. If a DC voltage is applied for sufficient time, the primary deflection will change to a new steady state, which would depend on the backbone and counter-ion content. This phenomenon is thought to be due to the excess concentration of water near the cathode and its subsequent back-flux [Okada, et al, 1998]. It is interesting to note that this behavior is not evident in Au–electroded Flemion (tetra-n-butylammonium counter-ion) [Oguro, et al, 1999]. The large size of the cation and its sluggish mobility may provide an explanation. The large bending deflections, the required hydration, and the relaxation processes that are involved with IPMC electroactivation make the task of electromechanically characterizing such materials difficult. The focus of the authors' effort was on testing the response of gold-electroded Flemion (tetra-n-butylammonium counter-ion) and Nafion (with Li+ cation). Similar tests can be applied to other ionic EAP materials, such as polypyrrole [Otero and Sasinena, 1997] and also electronic EAP materials.

3. EXPERIMENTAL SYSTEM

Since IPMC is soft, in order to minimize measurement errors, any characterization method that is being considered needs to be a non-contact type or the effects of mechanical impedance of the probe must be known. A data acquisition system was developed to allow measurements from IPMC strips that are subjected to various signal amplitude and voltage levels and tip mass loads. Using a 30Hz frame/sec video setup and an image-processing algorithm the deformation of Flemion/tetra-n-butylammonium+ strips (Made by AIST, Japan) was tracked while the samples are subjected to various electrical signals. Test conducted using Nafion/Li+ IPMC (made by ERI) have shown a very fast reaction followed by a slow relaxation. The speed of bending of the strips was determined to be too fast for the video setup and the data acquisition. A new system was constructed having a rate of up to 125 frames of 640x480 pixels per second with up to 350 frame/sec (Figure 1). The new video system consists of a digital CCD camera MegaPlus model ES-310 (Redlake MASD, Inc.) with an image acquisition board model NI PCI-1422 (National Instruments Corp.).

4. DATA ACQUISITION OF RAPIDLY RESPONDING IPMC

A general view of the data acquisition system is shown on the left in Figure 1, whereas a photographic view is given on the right. This system is set to acquire and digitize the deformation in side views of bending IPMC strips that are subjected to an electric signal (Figure 2(left)). Modifications that were made to the algorithm that acquires the deformation of the tracked sample allows capturing 2D images of large IPMC deformations with minimal error. Using electrical signals with controlled shape and a real time captured data, the curvature of the tested IPMC strips under the input voltages, currents and/or tip force is extracted as a function of time.

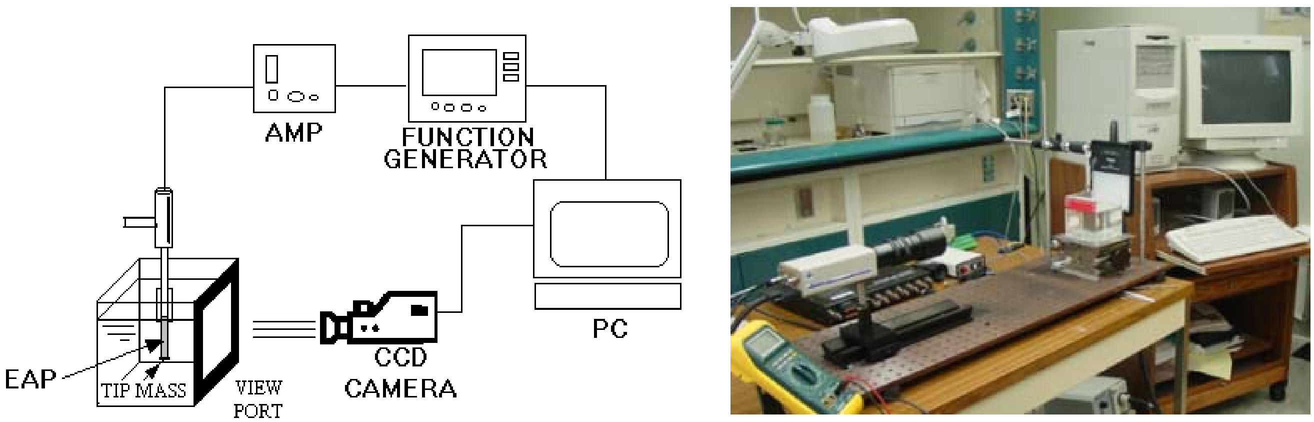
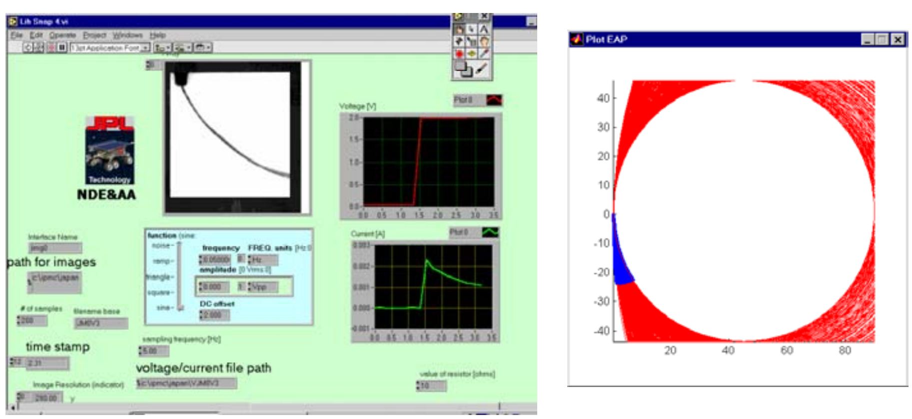
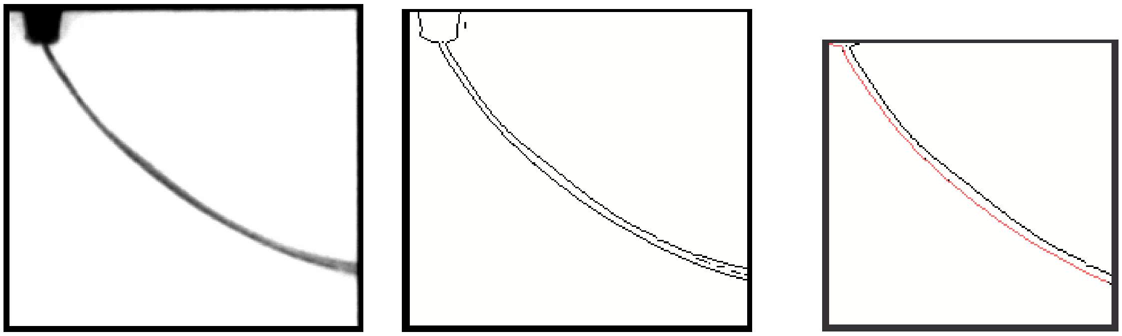


FIGURE 1: Setup for data acquisition of the curvature as a function of various parameters for IPMC.

A best-fit algorithm was used initially used with the assumption that the IPMC curvature deformations fit circular curves as shown on Figure 2(right). This algorithm was based on the use of a Normal least square method. Later, the methodology was modified in conjunction with the use of the new video capture capability, where the images are reduced through the process of clipping, edge-detecting and surface-tracing as shown in Figures 3(a)-(c). In the image tracing process, a best-fit edge detection algorithm enabled more accurate curve description. For this purpose, the displacement of a Flemion sample (made by AIST, Japan) is represented by one of the sample's surfaces as shown in Figure 3(c). This digitized image represents a significant improvement to the data acquisition process where the top and bottom surfaces of the sample are clearly defined and distinguished by the computer software. In Figure 4, the curvature vs. time is shown on the left and the standard deviation of the acquired radius on the right. As shown in Figure 4(top), the standard best-fit method was found to be insufficiently robust for this particular application and errors were observed in the acquired data. To eliminate the noise that is introduced, an initial parameter optimization routine was used to zero-in on the global minimum for best-fit and significant improvement in the smoothness of the acquired curves was observed as shown in Figure 4(bottom).

FIGURE 2: A view of the computer display of the data acquisition system.





(a) (b) (c)

FIGURE 3: The developed image-processing algorithm used to acquire the IPMC curvature as a function of loading parameters through (a) clipping, (b) edge-detecting and (c) surface-tracing.

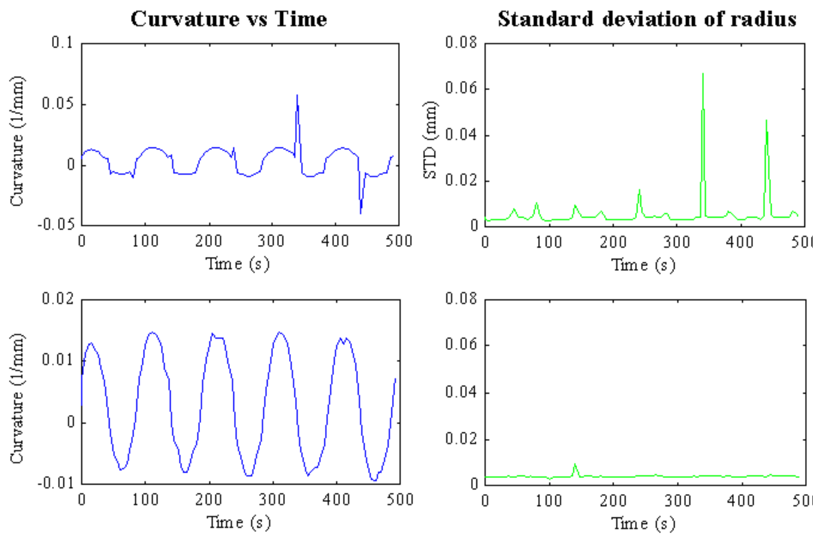


FIGURE 4: Curvature data acquisition using best-fit methodologies.
Top: using normal least square.
Bottom: Using parameter optimization routine.

As pointed earlier, our recent studies comparing the behavior of Nafion/Li+ and Flemion/TBA+ revealed that the time response of these materials is significantly different. Using a 27.8x3.3x0.2-mm gold electroded Nafion/Li+ IPMC sample that was activated using 0 to +1V square wave over 200-sec have shown time response characteristics as shown in Figure 5 (left). Nafion/Li+ reacts quickly in one direction and then relaxes back. The Flemion/tetra-n-butylammonium samples are not showing a relaxation. A 32.7x3.4x0.17 mm sample was subjected to a 1-V DC and the result is shown in Figure 5(right). This result shows that IPMC behavior is highly dependent on the backbone/cation. It is interesting to point out that the Nafion based sample exhibited remnant deformation that led to a drift with the increase in the number of cycles. The Flemion based sample continued to deform. The process may over thousands of seconds of activation to the DC voltage.

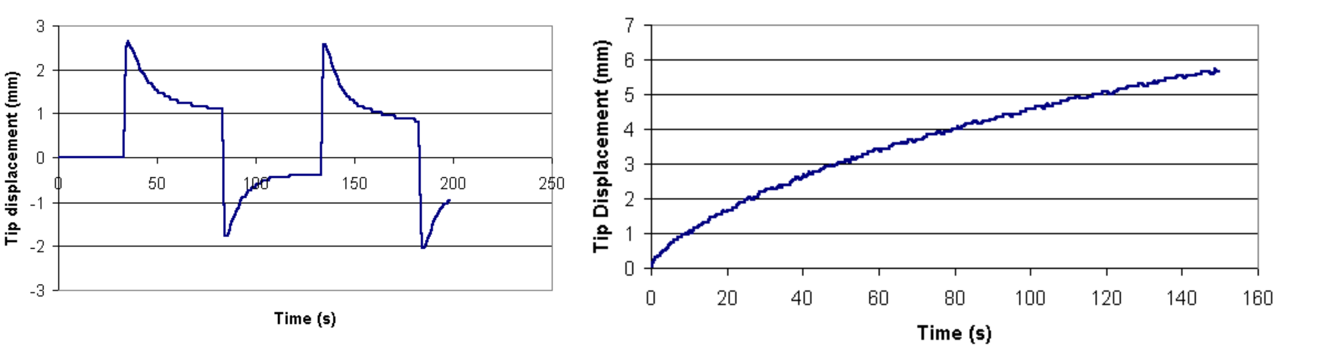


FIGURE 5: Displacement as a function of time for Nafion/Li+ (left) and Flemion/tetra-n-butylammonium (right) samples.

5. MEASURING EFFECT OF LOAD AND REMOVAL OF HYSTERESIS

To enhance the capability to load and change tip mass a miniature mounting fixture was developed in the form of a clip where loads are introduced in the form of copper wires that are inserted into the compartment within the clip. A schematic view of the sample-mounting fixture is shown in Figure 6. The clip is made of a none-conductive material to avoid affecting the induced electric field.

The Flemion/TBA+ samples were observed to remain deformed a long time after the voltage was brought to zero. This remnant deformation was observed to be common to IPMC materials after being subject to electrical activation. The remnant deformation poses difficulties when attempting to examine the repeatability of the measurements. A series of experiments were conducted to develop a methodology of removing this deformation. Two key approaches were used: (a) application of an electric field with an opposite polarity and (b) application of pressure to mechanically flatten the sample (equivalent of ironing). The procedure that was used has been as follows:

1. Sample starting condition: used sample pressed on flat surface in DI water for 5 days.
2. 1st run: applied 1V step voltage for 200 seconds
3. Electrically re-position: after 16 hours in water, applied negative voltage until the sample appeared to be straight.
4. 2nd run: applied 1V step voltage for 200 seconds
5. Mechanically re-position: pressed on flat surface for 5.5 hours
6. 3rd run: applied 1V step voltage for 200 seconds

The time responses in these three runs are shown in Figure 7 as the curvature changes versus time. The bending effect after the 3rd run is significantly smaller than the 1st run while the 2nd run is reasonably close to the 1st run. It has been observed that the use of electric removal of the remnant deformation returns the samples much closer to its original condition than the mechanical treatment. This result may indicate that the cause of remnant deformation is mainly electrical in nature rather than mechanical, i.e. plastic deformation.

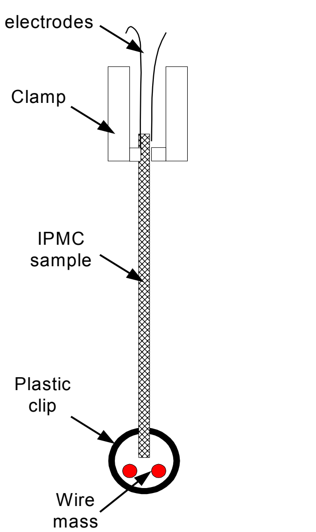


FIGURE 6: A schematic view of the tip mass loading-fixture

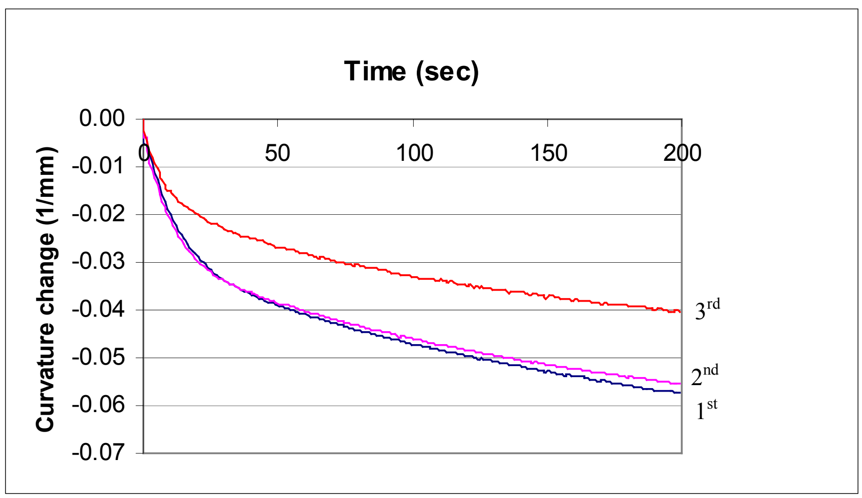


FIGURE 7: Curvature change under 1V step voltage in three sequence runs. The remnant deformation after the 1st run was removed electrically and that after 2nd run removed mechanically.

6. SPECTRAL RESPONSE OF IPMC

To determine the spectral response of IPMC a system was designed using a photometer setup (Fotonics probe) that can respond at vibration frequencies of up to 20KHz with microns resolution and allows testing small samples. Measurements of the electromechanical response were made up to 500Hz. The test setup is shown in Figure 8 where the short samples were subjected to electrical stimulations at various frequencies and the tests were made with the sample in air and in water. The low frequency response in the Hz range was recorded as well as a resonance frequency at higher frequencies. A low peak of vibration amplitude is observed around 1 Hz and the amplitude decreased at the <1-Hz range due to relaxation, whereas the decrease at >1-Hz is attributed to insufficient time to charge the sample. The resonance frequency is attributed to the sample length and mechanical properties of the medium. As expected the resonance frequency was found to be higher in air compared to when immersed in water. In addition, a higher amplitude response was observed when the sample was activated in air for the same applied voltage. Cantilever beam samples with dimensions of 7.75 x 3.3 x 0.196-mm were tested at 6.5 mm away from sample mount. A typical response in water is shown in Figure 9, where a resonance was observed at 113 Hz in water and 272Hz in air. The water loading has the characteristics of an added mass and therefore reducing the resonance frequency. The drying of the sample may be also a cause to have higher resonance frequency in air. Using this setup the time response of Flemion with both Li+ and TBA+ were compared as show in Figure 10. The sample dimensions are 7.7 x 3.3 x 0.196-mm shaped as a cantilever beam and the measurements are made 6.5-mm from sample tip.

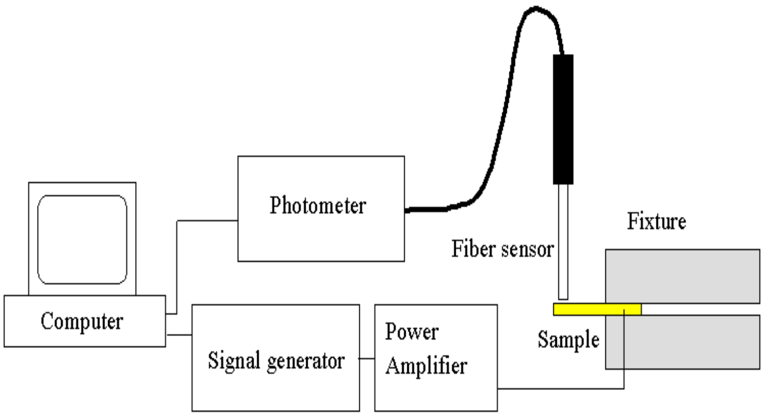


FIGURE 8: Schematic view of the photometer setup

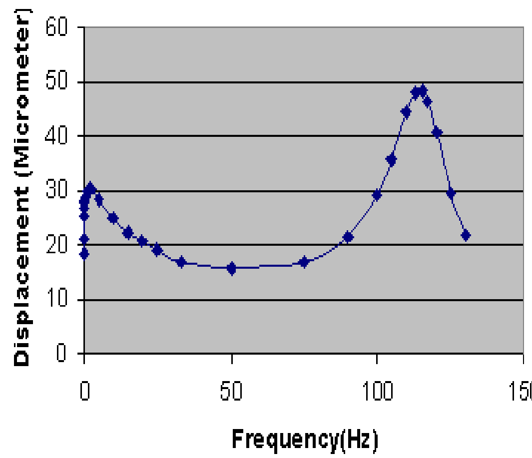


FIGURE 9: A typical spectral response of IPMC immersed in water

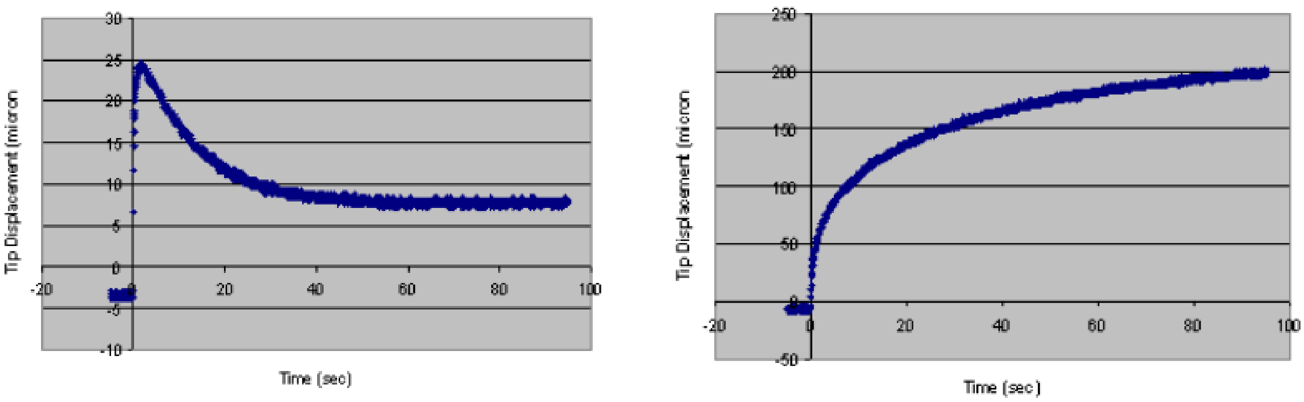


FIGURE 10: Time displacement measurements as a function of time for Flemion samples both Li+ (left) and TBA+ (right).

7. SENSING TEST

One of the questions that needed an ability to address is the capability to determine if IPMC provides an inverse effect, namely operate as a sensor. Also, if there is sensing characteristics the question that needed to be answered – what is the spectral response. Efforts were made to assure that no Radio Frequency (RF) transmission is picked up inductively (electromagnetic transmission). An ultrasonic test setup with a broadband pulser/receiver ranging from 0.1- 20-MHz and a set of broad band transducers with a center frequency that is rated at 0.5, 1, 2.25, 5, and 10-MHz were used (see Figure 11). The transducers were aimed towards an IPMC strip (27.8x3.3x0.2-mm with gold electrodes, and Li+ cations made by ERI) and the strip was connected via a broadband amplifier to oscilloscope to detect any significant received signal. Also, using tuned music-forks with resonance frequencies of 329.6 Hz (tone E) and 440 Hz (tone A). In all these tests no significantly signal was detected by the tested IPMC strips to indicate that this EAP has a sensing capability.

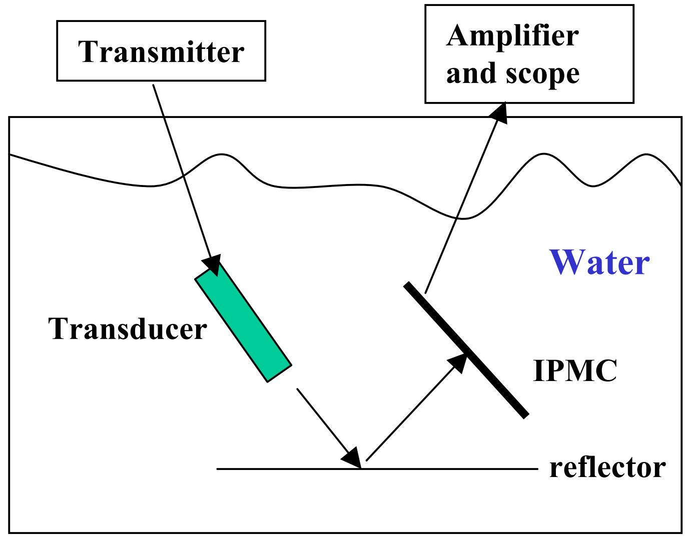


FIGURE 11: A schematic view of the ultrasonic setup that was used to examine the possibility of sensing capability at the spectral range from 0.5 MHz and above.

8. GAUGING EAP MECHANICAL PROPERTIES VIA ACOUSTIC WAVE RESONATORS

In another set of experiments that are currently being designed to independently measure the elastic modulus of IPMC samples composite resonators are being investigate. This method is based on non-linear curve fitting of impedance data for a thin piezoelectric and an acoustic layer [See Sherrit et al. 2002 for details]. An example of this technique is shown in Figure 12 where the results for the impedance spectra of PZT and Kapton are shown in comparison with the impedance spectra of PZT alone. Nonlinear Regression of data using Mason's Model was used to determine the acoustic velocities and stiffness of the Kapton layer. This technique is currently being investigated for Nafion and potentially it would allow monitoring changes such as dehydration of the material at various temperatures in real time.

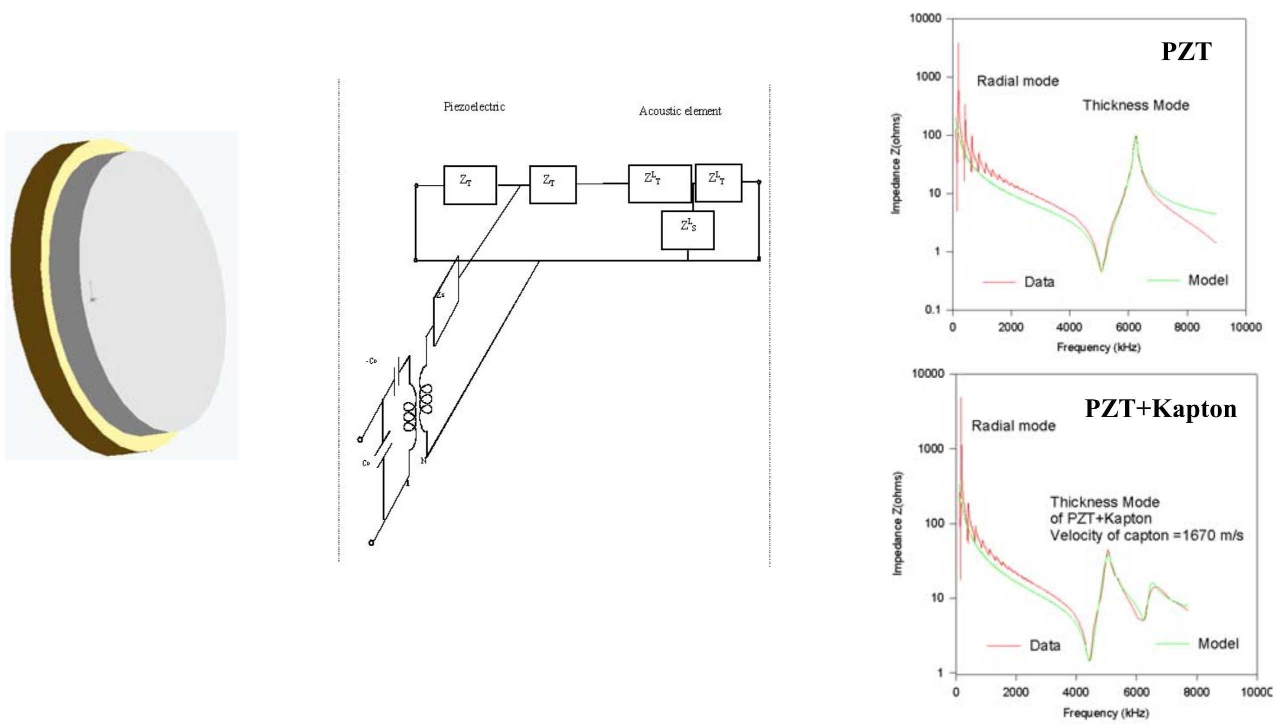


FIGURE 12:. A schematic of the composite resonator and Mason's equivalent circuit for the experiment along with example data for a free piezoelectric disk resonator and a composite resonator of PZT and Kapton.

10. CONCLUSION

Accurate information about the properties of EAP materials is critical to designers who are considering the construction of mechanisms or devices using these materials. In order to assess the competitiveness of EAP for specific applications there is a need for a properties matrix. This matrix needs to provide performance data that is presented in such a way that designers can scale the properties for incorporation into their models of the device under design. In addition, such a matrix needs to show the EAP material properties in such a form that allows the users to assess the usefulness of the material for specific application. This data needs to include properties and information that can be compare with the properties of other classes of actuators, including piezoelectric ceramic, shape memory alloys, hydraulic actuators, and conventional motors. The range of actuation and stress generation of the various types of EAP is quite large and the excitation field that is required for these materials can vary by 5 orders of magnitude.

Some of the macroscopic properties that can be included in the matrix are maximum strain, maximum blocking stress, response time, maximum electric and mechanical energy density as well as maximum energy efficiency. In addition, due to the mechanical interaction that is associated with the electro-reaction there is a need to characterize both the passive and electroactive properties. The properties that may be of significance when characterizing EAP are described in Table 2. While some of the properties (particularly those that are driven by polarization mechanisms) have relatively well-established methods of characterization, the ionic materials and particularly IPMC still require new techniques. These materials pose the greatest challenge to characterization methods developers due to their complex behavior. This complex response is associated with the mobility of the cations on the microscopic level, the strong dependence on the moisture content, as well as the nonlinear and the hysteresis behavior of the material. The technology related to the characterization of EAP is expected to evolve as the field is advanced and standards methods will need to be established in the coming years.

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