Proceedings of SPIE's 6th Annual International Symposium on Smart Structures and Materials, 1-5 March, 1999, Newport Beach, CA. Paper No. 3669-09

Electrical Impedance of Ionic Polymeric Metal Composites

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ABSTRACT

In recent years the use of ionic polymer metal composites such as Nafion-based platinum ionomers have emerged as electroactive polymer materials with great potential for robotics and other applications. An effective activation of these materials requires understanding of their mechanism of operation. Generally, the material needs to be maintained hydrated to assure its electromechanical activity. To allow the control of the response of the material, a study is underway to investigate the electrical response. Particular emphasis is placed on possible electrochemical reactions and deviations from linear dielectric behavior. Currently, efforts are made to determine the necessary drive characteristics of the source to allow low power operation (≤ 1.0 W) of the material as an actuator.

Keywords: IPMC, Electroactive Polymers (EAP), bending EAP, miniature actuators

1. INTRODUCTION

Ionic polymer metal composites (IPMC) are emerging electroactive polymers that respond with a large bending displacement when exposed to relatively low voltage levels. The widely used family of these materials is composed of perfluorinated IPMC with metallic electrodes are deposited. Specifically the base polymer material is Nafion. In this study, the authors used platinum as the metallic electrodes however other researchers reported success using metals such as gold [Yoshiko, et al, 1998]. In this study the counter-ion was Na^+, but the authors are well aware of the greater efficiency of using lithium as ions to induce a higher displacement per given volt [Yoshiko, et al, 1998].

Generally, hydrated Nafion exhibits a mechanical bending response when excited by a relatively small electrical voltage at amplitudes at levels below 5 V [Abe, et al, 1998]. This coupling of energies is thought to be due to electro-osmotic drag, in which water is transported by mobile cations (counter-ions) via solvation shells and hydrodynamic drag forces [Helfferic, 1995]. The cathode side expands with respect to the anode causing an overall bending deformation of the membrane. If a DC voltage is applied for sufficient time duration, the induced concentration gradient of water induces back-diffusion that is accompanied by relaxation back to the original position [Asaka and Oguro, 1995]. The electric field is also likely to cause electrochemical reactions. Nafion has been used in fuel cells and as water electrolyzers [Holze and Ahn, 1992]. The standard potential for the hydrolysis reaction is:

$$H_2O_{(l)} = H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \qquad (1)$$

which occurs at 1.23 V. Unfortunately, many of the actuation applications of IPMC require large bending amplitudes [Bar-Cohen, et al 1998] and therefore large applied voltages that exceed this potential level. The electrical conductivity depends strongly on the degree of hydration. Losing the water content degrades the performance of this material as an electroactive polymer. In order to operate in dry environment, the authors were assisted by researchers from NASA-Langley Research Center, who developed a protective coating for the Nafion membranes [Bar-Cohen, et al 1998]. Since the impedance characteristics of IPMC changes with the degree of hydration, impedance analysis can be used as a quality check for the operability of these materials as actuators. Moreover, impedance data provides insight into the diffusion and chemical processes that occur in the material. Previous research has investigated the displacement and dielectric response to various waveforms with amplitudes ≤1.0 V [Asaka et al, 1995]. However, no work has been done regarding the application of larger voltages where electrochemical reactions and deviations from linear behavior are likely to occur.

2. EXPERIMENTAL PROCEDURE

In order to determine the electrical behavior of IPMC the impedance characteristics were analyzed. The active material was Nafion #117 (Dupont) with platinum electrodes and mobile Na^+ counter-ions. A Schlumberger SI 1260 impedance analyzer was used to obtain the magnitude and phase of the impedance as a function of frequency. Time-domain current measurements were made using a voltage across the sample and simultaneously across a small resistor in series with a DAQ AT-MIO card (National Instruments). The voltage was applied with a Stanford Research Systems DS335 wave form synthesizer and amplified using a Hewlett Packard HP 467A power amplifier. All measurements were computer controlled using LabView (National Instruments) and an IEEE 488 bus. Discrete Fourier analysis of the time-domain data was accomplished using Matlab software. The dimensions of the samples was 30 mm x 5.0 mm x 0.2 mm. Electrical contact to samples was provided by aluminum clips.

3. RESULTS AND DISCUSSION

Figure 1 displays the current response to DC step voltages of 1.0 V and 4.0 V. The sampling frequency was 10 Hz. The Nafion sample was submerged in distilled water. The initial transient response is due to the charging of the capacitor via ionic diffusion.

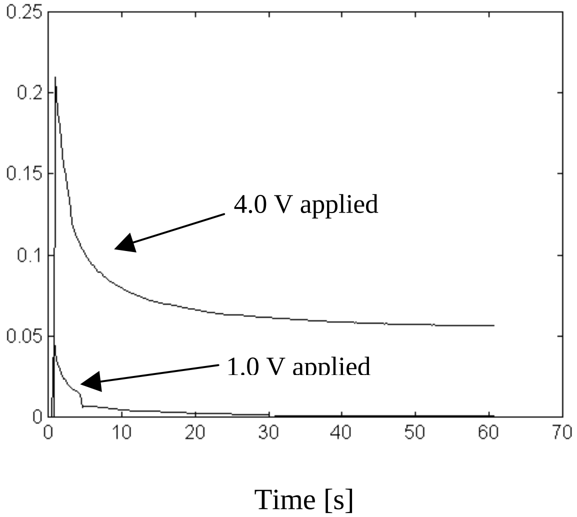


Figure 1: Current response to applied step voltages of 1.0 V and 4.0 *V*

The steady-state condition of the current when applying 4.0 V corresponds to nearly 0.6 A. At this level, gas evolution (bubbling) occurs, which suggests the presence of an electrochemical (electron transfer) reaction. Water electrolysis, Eq. (1), is likely to be taking place with oxygen produced at the anode and hydrogen gas at the cathode. At constant temperature and pressure and assuming ideal gas, the hydrogen is twice the volume of the oxygen. Although this reaction is not the main cause of bending (since deformation is observed even at voltages less than 1.0 V), it may influence the mechanical response. A coating procedure has been developed at NASA Langley [Bar-Cohen, et al 1998] to prevent dehydration and maintain good ionic conductivity in dry environments. Gas evolution can cause “blistering” of the coating as well as de-bonding. Additional chemical processes (i.e. corrosion) at the aluminum contacts may occur and introduce errors in the measurements.

The impedance spectra for the same Nafion membranes that were immersed in distilled water is shown in Figure 2. The applied voltage was 0.05 V. The response at low frequencies are probably governed by space charge effects at the electrodes [Wintersgill, et al 1998], and no typical Debye relaxation is observed below 200 kHz. Large bending occurs only at frequencies below 0.1 Hz. The phase angle is small and considerable power is lost as heat. At higher frequencies (>5.0 Hz) ion migration is effectively clamped and the material behaves as a resistor with no mechanical deformation.

For some applications [Bar-Cohen, et al 1998] it is necessary to generate large bending deformations, which requires voltages in excess of 5 V. Nonlinear dielectric responses are possible at this level. The current as a function of electric field is plotted in Fig. 3. The applied signal was a pure cosine wave of amplitude 7.0 V at 0.03 Hz. The sampling frequency was 10 Hz. The slope represents electrical impedance. Significant deviation from linear behavior is observed, as well as hysteresis. The area of the loop corresponds to energy dissipated as heat. Fourier analysis is well suited to quantify both nonlinearity and hysteresis [Leary, et al 1998].

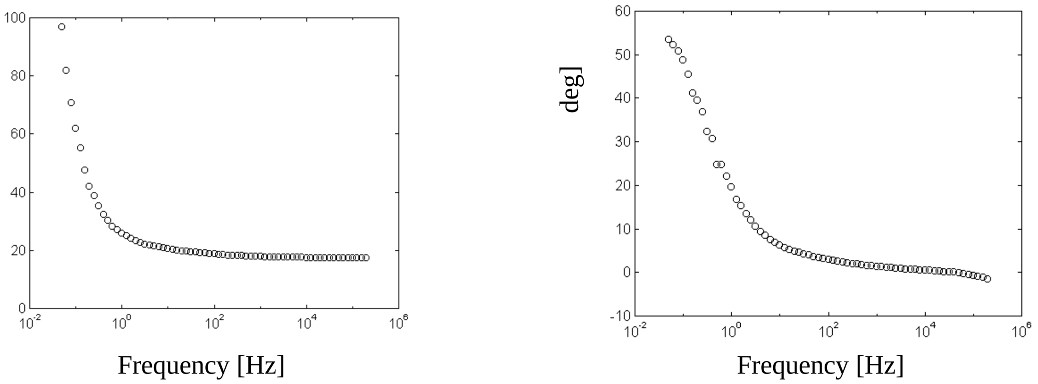


Figure 2: Impedance spectra; magnitude and phase angle

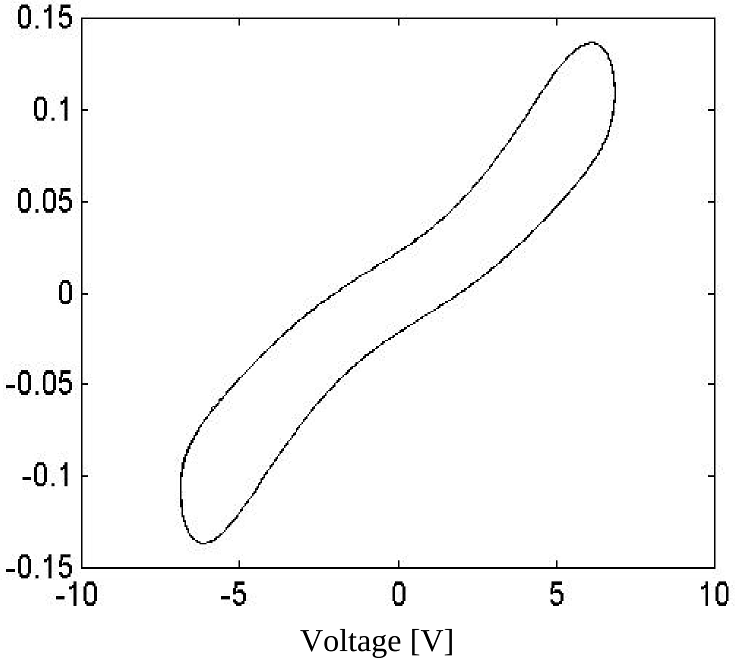


Figure 3: A nonlinear hysteretic behaviur occurs when a cosine wave of cosine wave of 7.0 V and 0.03 Hz is applied to Nafion sample.

A nonlinear response will produce harmonics of the frequencies at its input. A discrete Fourier transform (DFT) of the applied voltage and induced current signals are shown in Fig. 4. At an amplitude of 1.0 V, no significant nonlinearity can be seen; the only frequency component in the current signal was at the fundamental (i.e. 0.03Hz). However as the applied voltage amplitude is raised to 7.0 V nonlinear distortion is noticeable (Fig. 5) and 3rd and 5th harmonics have appreciable magnitudes. The corresponding polynomial to describe the plot in Fig. 3 should therefore be of the form:

$$I = aV + bV^3 + cV^5 + \text{higher odd terms} \qquad (2)$$

Where I is the current, V is voltage and a, b, c are constants.

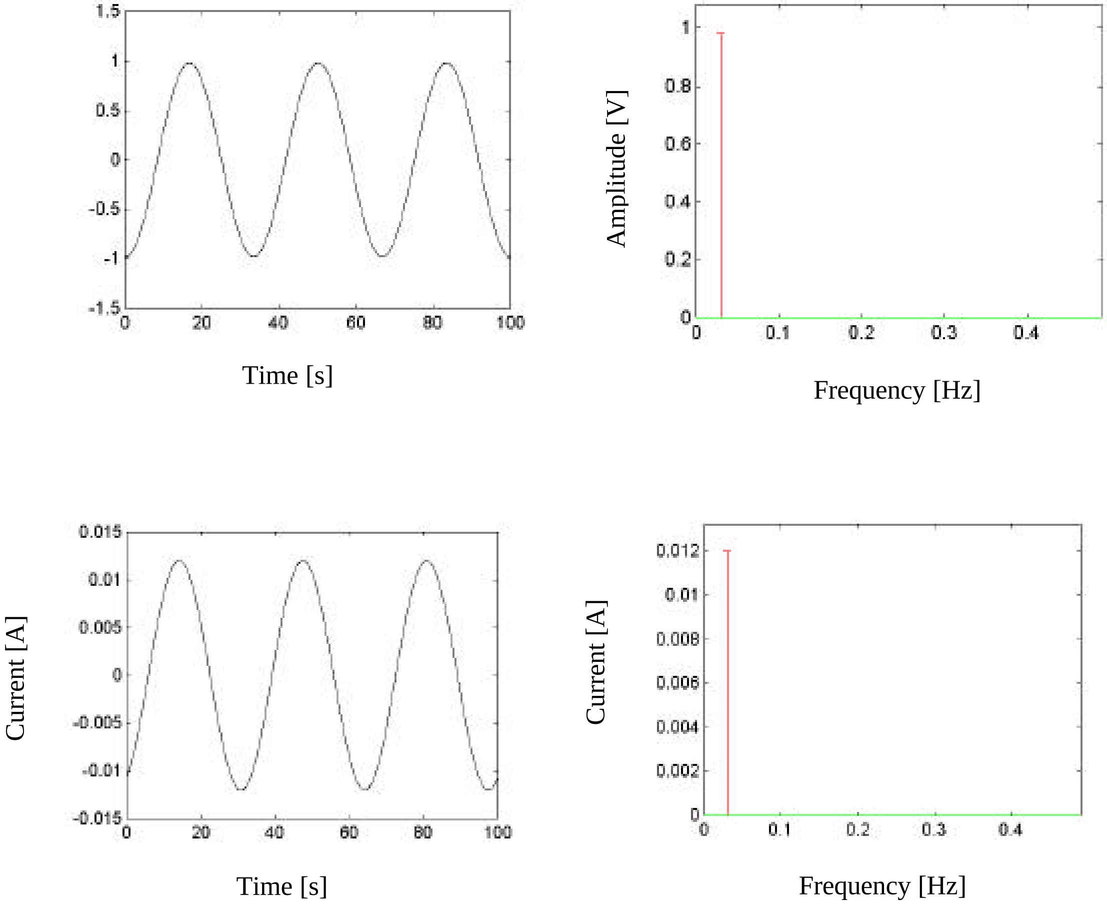


Figure 4: Harmonic analysis of the applied voltage and induced current signals. No significant nonlinear distortion was observed at 1.0 V.

In general the DFT of a real time signal will be complex and therefore phase information can also be obtained. The phase difference between the applied cosine wave and the fundamental component in the current signal corresponds to a power dissipated. This is shown as rectification of the power signal in Fig. 6. When a cosine wave of 7.0 V at 0.03 Hz was applied, the average power was .38 W. This corresponds to 12.5 J of heat generated per cycle, which is equal to the area of Figure 3.

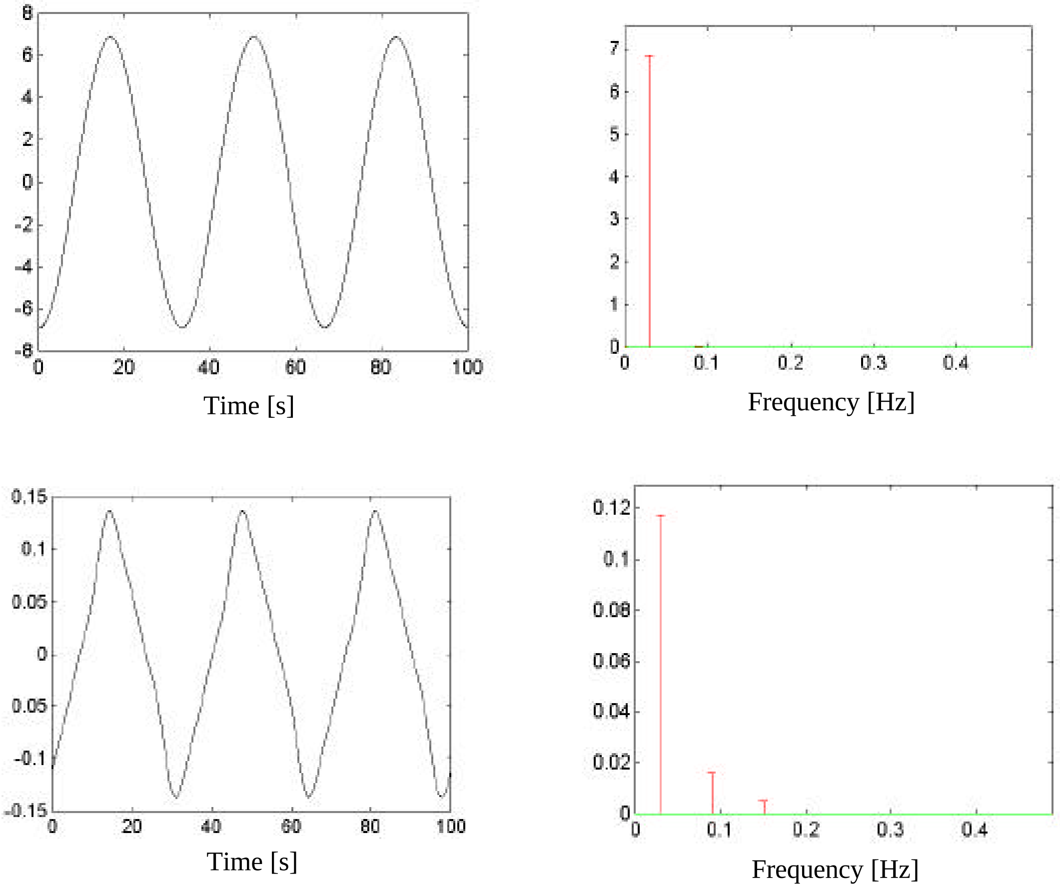
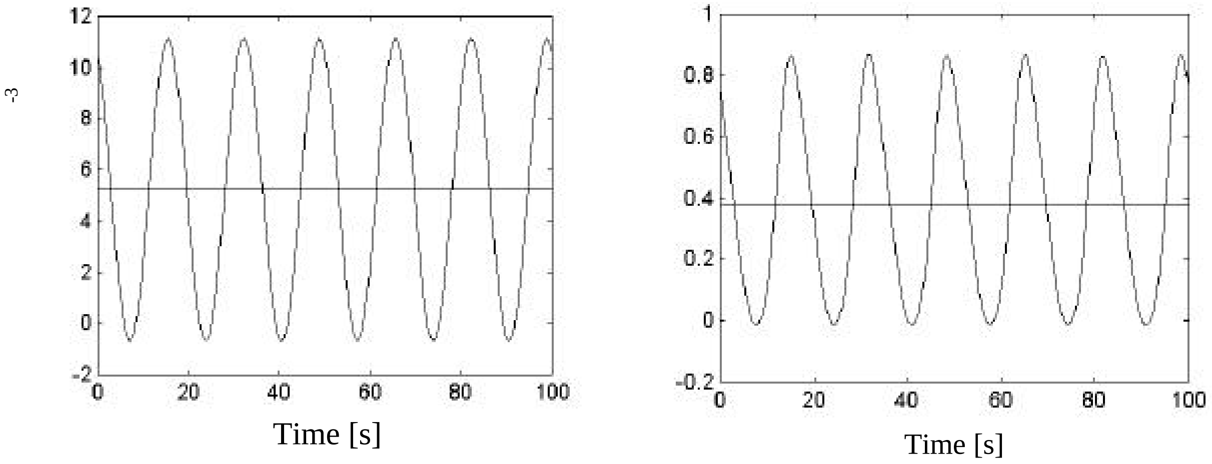


Figure 5: Fourier analysis shows that odd harmonics are present in the current signal when 7.0 V cosine wave is applied.



(a)

(b)

Figure. **6 (a)** Power signal corresponding to 1.0 V cosine wave applied. The horizontal line represents 5.2 mW dissipated as heat; **(b)** Power signal corresponding to 7.0V cosine wave. The horizontal line represents 0.38 W dissipated as heat.

4. CONCLUSIONS

Nafion ionomers offer large bending actuation at small applied voltages. To employ these materials in robotic and other mechanisms it is necessary to understand their electrical behavior in order to developed effective control algorithms. The presence of electrochemical reactions and nonlinear dielectric behavior have been observed at operational voltage levels. Consideration of these effects is necessary when developing control algorithms. Further works needs to correlate mechanical bending with electrical characteristics.

5. ACKNOWLEDGEMENT

The research at Jet Propulsion Laboratory (JPL), California Institute of Technology, was carried out under a contract with National Aeronautics Space Agency (NASA) as part of the telerobotic program, funded by Code S. and Dr. Chuck Weisbin is the Program Manager at JPL.

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