

ION-CONDUCTING POLYMER FILMS AS CHEMICAL SENSORS

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ABSTRACT

Solid Polymer Electrolytes (SPE) are widely used in batteries and fuel cells because of the high ionic conductivity that can be achieved at room temperature. The ions are usually Li or protons, although other ions can be shown to conduct in these polymer films. There has been very little work on using these films as chemical sensors. We have found that thin films of polymers like polyethyleneoxide (PEO) are very sensitive to low concentrations of volatile organic compounds (VOCs) like common solvents. We will present impedance spectroscopy of PEO films in the frequency range 0.01 Hz to 1 MHz for different concentrations of VOCs. We find that the measurement frequency is important for distinguishing ionic conductivity from the double layer capacitance and parasitic capacitances.

INTRODUCTION

There is a rich literature on the electrical properties of polyethyleneoxide (PEO) because of its importance as an electrolyte in lithium batteries [1]. However, there have been relatively few reports of its use as a sensor material [2]. Much of the reported work on PEO as an electrolyte involves attempts to increase the ionic mobility without the use of water because of the incompatibility with lithium. Plasticizing agents and non-aqueous electrolytes like propylene carbonate are often used to increase the room temperature ionic conductivity [1]. In this paper we report on the chemical sensing characteristics of thin films of PEO doped with LiClO₄ deposited on planar arrays of interdigitated electrodes. The planar configuration allows easy integration with sensing electronics and fast response to vapor phase analytes.

EXPERIMENTAL

The PEO was purchased from Polysciences and had MW 4,000,000. The LiClO₄ was purchased from Aldrich Chemical and both components were dissolved in acetonitrile, mixed and spun-cast on to planar interdigitated electrode (IDE) arrays. The 50 pair arrays had 5 micron gold lines separated by 10 micron gaps on quartz substrates. Samples with PEO to LiClO₄ ratios from 7:1 to 15:1 were fabricated. Impedance spectra were taken with a Solartron SI 1260 Impedance/Gain-Phase Analyzer coupled to the 1296 Dielectric Interface. The samples were temperature controlled in an oven and the different vapors were provided by a vapor generation system described elsewhere [3].

RESULTS AND CONCLUSIONS

The impedance spectra from polyelectrolytes containing no redox species have the same general characteristics, shown in Fig. 1. We prefer to show the data in the form of log impedance vs. log frequency and the phase in a separate graph rather than the

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common Nyquist plot because we are often trying to identify the best frequency range for sensor operation. The simulated spectra from a simple lumped circuit is shown for two cases: the film in dry N₂ at 22°C and in 20% relative humidity. The parasitic capacitance comes from the quartz substrate and the gas phase above the electrodes and dominates the high frequency impedance. The region showing the ionic conductivity is relatively frequency independent in the mid-frequency range and has a phase corresponding to almost pure resistance. The value of R_{ionic} gives the strongest dependence on the concentration of different volatile organic compounds (VOCs). The lowest frequencies show the double layer capacitance (C₂) on the electrodes; the phase moves towards pure capacitance as the frequency goes lower. Figure 2 shows the impedance spectra for various concentrations of two VOCs, acetonitrile and water vapor. The phase angle data are similar to Fig. 1 and the responses are reversible on the one minute time scale. The responses to acetonitrile are much larger than reported in Ref. 4, provided that the correct measurement frequency (minimum phase angle) is used to obtain R_{ionic} . It can be seen that if a single frequency, such as 10 Hz, is used, the response appears to saturate at the higher concentrations because the double layer capacitance is relatively insensitive to the concentration of analyte. Response data for 11 different VOCs with widely varying solubility parameters [5] was obtained, with the peak response found for dimethylmethylphosphonate (DMMP), a simulant for nerve agent. Our hypothesis is that the response depends on the solubility of the VOC and its ability to plasticize the PEO chains, thereby aiding ionic transport. In conclusion, we have found that the impedance of polyelectrolytes is a sensitive detector for VOCs when operated in the correct frequency range.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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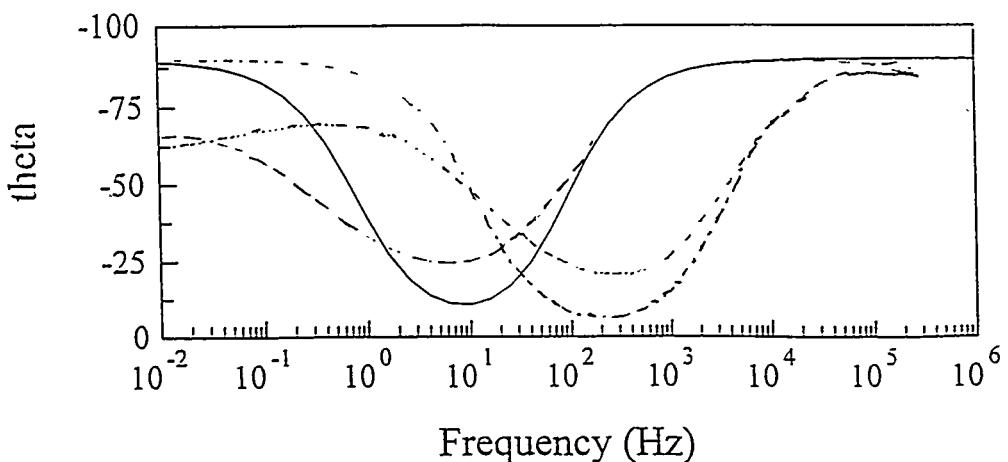
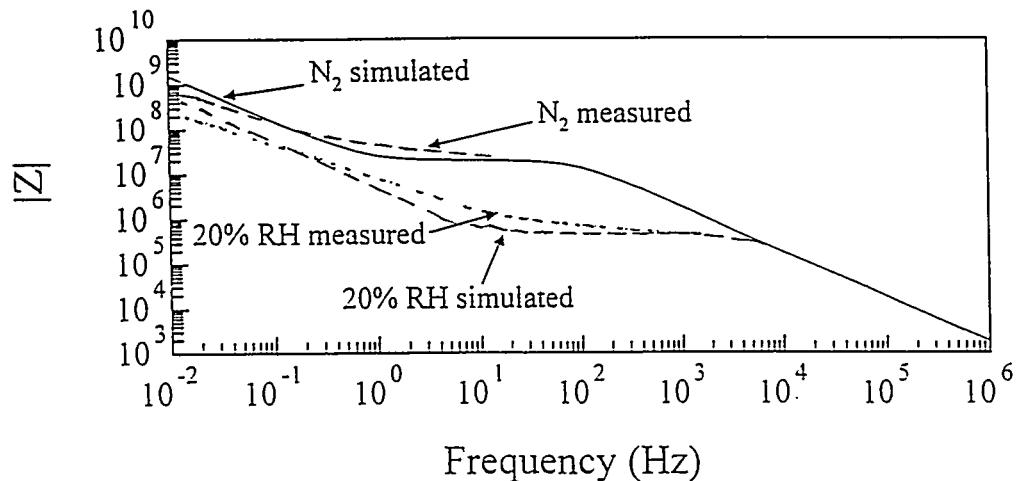
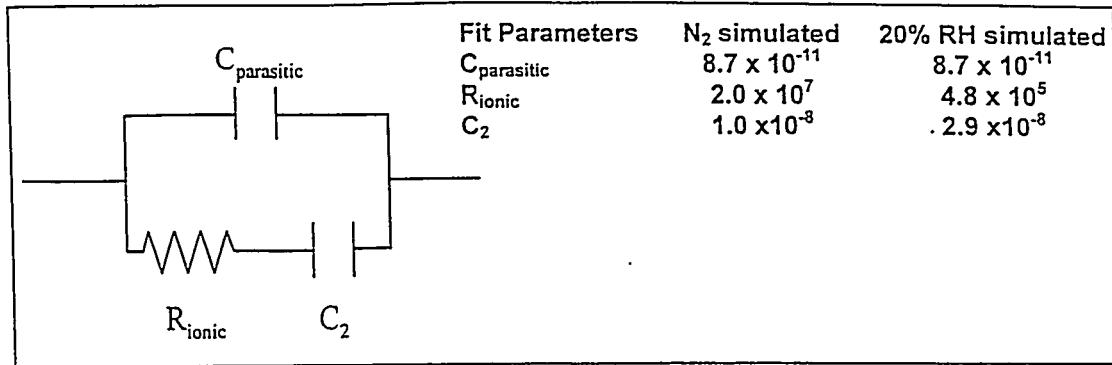


Figure 1. Impedance spectrum of a PEO film doped 7:1 with LiClO₄. The labeled lines are for experiments in dry N₂ (several hours of drying), and a controlled level of 20% RH at 21°C. Also shown are simulations of the spectrum using the lumped circuit with parameters shown in the box. The phase shift, theta, for the same runs is shown in the lower figure. The general fit is good, particularly for the high frequency parasitic capacitance and the region showing the ionic conductance, where the phase angle approaches zero. The largest discrepancies are in the region where the double layer capacitance is dominating the impedance spectra at low frequency. A detailed discussion of the double layer region will appear in a future publication.

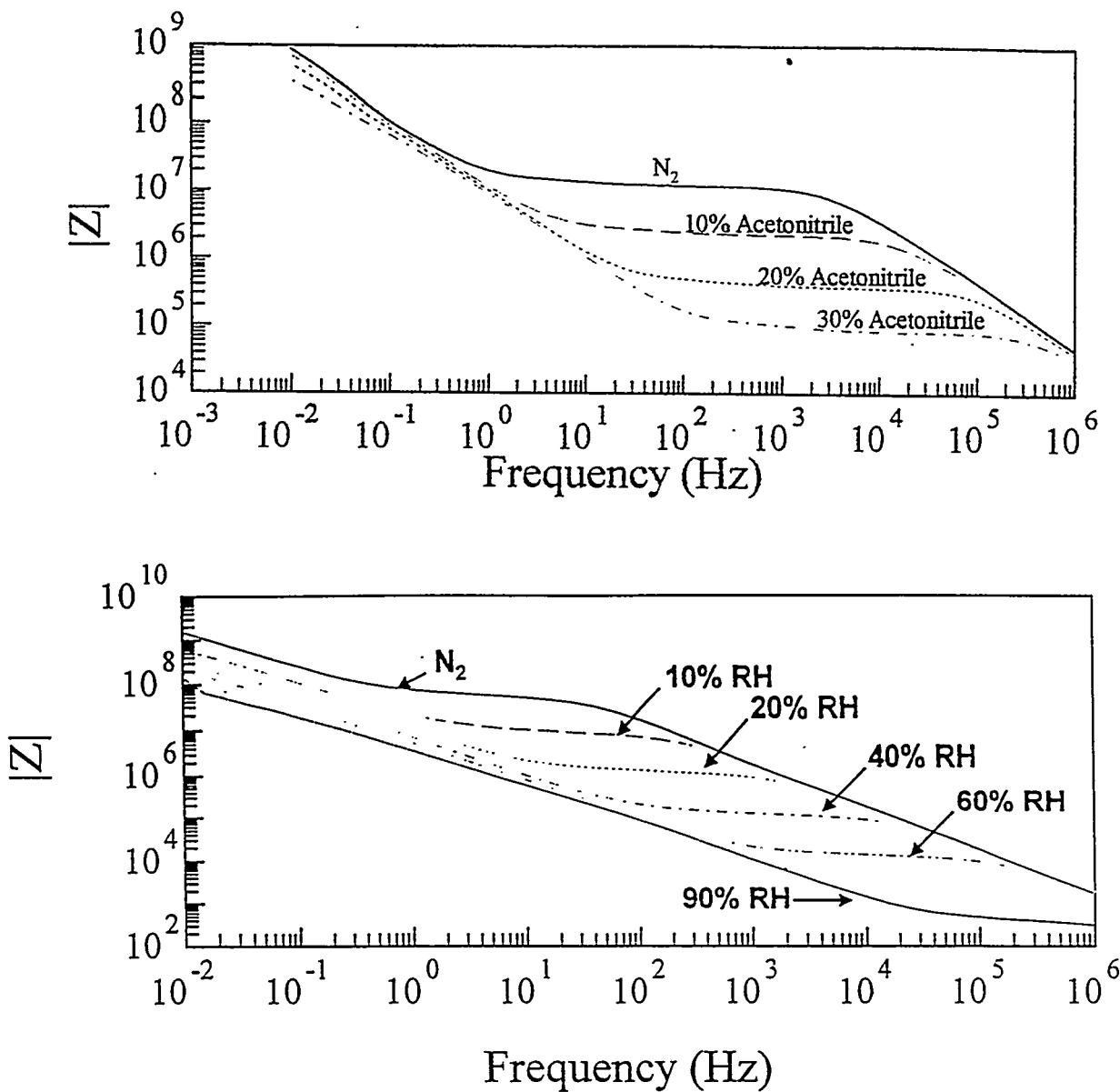


Figure 2. Impedance spectra for two analytes: acetonitrile and water vapor. The vapor generation system and the sensors are both at 21°C. The phase angle spectra are similar to the ones shown in Fig. 1, with the minimum in phase angle occurring at a frequency roughly half way between the line for the parasitic capacitance and C_2 , the double layer capacitance. The ionic conductance is a very strong function of the analyte partial pressure in both cases, roughly exponential. It can be seen that picking one frequency for the sensor read-out has the difficulty of becoming insensitive to the analyte partial pressure at one extreme or the other due to the two capacitances. The double layer capacitance in the acetonitrile case is roughly 6 microfarads/cm², using the electrode area of 0.004 cm² for each side of the capacitor. This capacitance was calculated at 0.1 Hz; it can be seen in Fig. 1 that the double layer capacitance is somewhat frequency dependant and is higher at lower frequencies. The difference between the double layer capacitance for acetonitrile and water vapor is partly due to the fact that the film for the acetonitrile data is 10:1 PEO to LiClO₄ and the film for the water vapor is 7:1 ratio. Different analytes often show different double layer behavior, but it is not clear yet whether these differences are consistent enough to use as a method of identifying the analyte molecule.