Studying an Ion-Conducting Polymer in the Presence of FeCl3

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Introduction

Thermoelectric materials have the advantage of converting heat into electricity and can be used for heat flux and temperature sensing. These technologies are based on the Seebeck effect, which is a creation of a voltage from a temperature gradient. The voltage is generated as a result of of the diffusion of mobile charge carriers transported by the heat flux. Thermoelectric behavior can exhibit two behaviors: n-type (-) or p-type (+). P-type describes a higher concentration of charge carriers on the hot side when a thermal gradient is applied while n-type describes a higher concentration of charge carriers on the cold side as a result of thermal gradient. Another important quantity is the conductivity which describes the movement of charge carriers across a material as a result of an electric field. Both the conductivity and the Seebeck effect are both inversely related and the design of a thermoelectric material often results in the sacrifice of one property.

Ionic Seebeck coefficients in traditional p-type polymer blends demonstrate unstable, short-lasting ionic conductivities. Many of these polymer blends are polar and can be dissolved in water to increase ion conductivity. Although these ion-conducting polymers can exhibit an increased ionic conductivity and ionic Seebeck effect with the addition of water, tracking and determining the contributions of ionic conductivity, as well as the Seebeck effect, is often unclear and difficult. It is currently unclear the microscopic changes that occur when a thermal gradient is applied to these ion-conducting polymers. Also, ionic contributions from thermal gradients usually fade exponentially so there is no control over how long the ionic contributions can last in these polymers.

Poly(2-(dimethylamino) ethyl methacrylate)methyl chloride quanternary salt, a highly amorphous polymer that consists of a charged side group and a counterion whereby the latter is the only charge carrier in the polymer matrix, is studied to evaluate the ionic conductivity and ionic Seebeck effect. In addition, we intend to change the behavior of the Seebeck effect and ionic conductivity with the addition of FeCl3 instead of water to the polymer matrix.
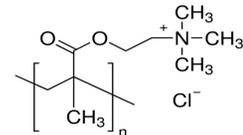
Figure 1: Chemical structure of poly(2-(dimethylamino) ethyl methacrylate)methyl chloride quaternary salt (QS)

Materials and Methods

Materials
- Poly(2-dimethylamino)ethyl methacrylate)methyl chloride quanternary salt
- Methanol
- Ferric(III) trichloride
- ITO/glass substrate
- SpinCoater Machine
- Acetone
- Isopropyl
- Seebeck Instrument
- Four-point Probe
- Ultrasonic Cleaner
- Ozone Cleaner

Methods
The polymer solutions were made in a glovebox. Concentrations of 20 mg/mL and 35.5 mg/mL were made and were heated at 40-45℃ for 30 min. and in the ultrasonic cleaner for about 15-20 min. for solvation to occur. Glass-ITO substrates were cleaned in the ultrasonic cleaner using water, acetone, and isopropyl for 15 min separately and ozone cleaned for 15 minutes. The solutions was filtered and spin coated at 200 rpm for one minute. Afterwards, the solutions were annealed at 67-68℃ for one hour and stored in the glovebox. The ionic conductivity and Seebeck coefficients of the samples were measured using a Seebeck machine.

ITO electrodes
Polymer Solution
ITO electrodes
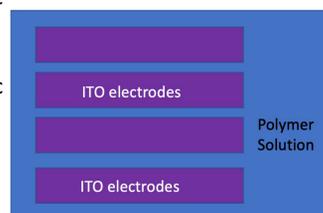
Results

Conductivity and Resistance

Composition	Conc (mg/mL)	Resistance
QS	20	-800 Mohm-1 Gohm
QS+3%wt FeCl3	20	>1 Gohm
QS+10wt%	20	->1 Gohm
QS	35.5	-2.5-2.7 MOhm
QS+3%wt FeCl3	35.5	-2.0-2-6 MOhm
QS+10wt%	35.5	N/A
QS	35.5	-470 MOhm
QS+3%wt FeCl3	35.5	-296 MOhm
QS+10wt%	35.5	246 - 255 MOhm

Conductivity vs Weight Percentage of FeCl3
35.5 mg/mL Quantenary Salt
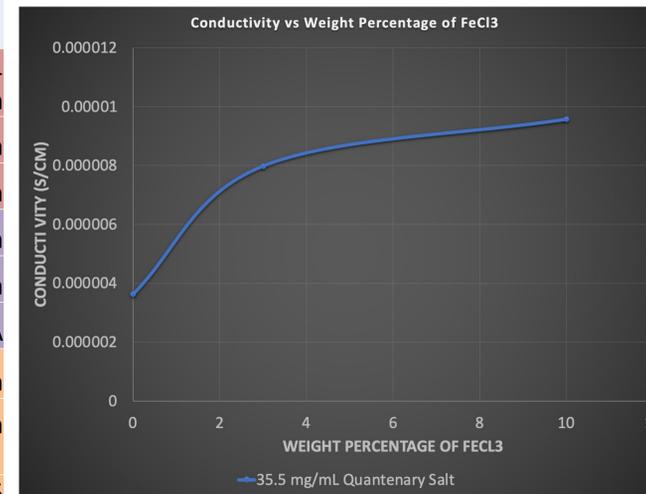
Seebeck Effect

Composition	Conc (mg/mL)	Seebeck (uV/K)	
QS	20	-25887	N/A
QS+3%wt FeCl3	20	38485	N/A
QS+10wt%	20	-184469	-7076
QS	35.5	-52800	-75300
QS+3%wt FeCl3	35.5	-571	+2351
QS + 10wt%	35.5	N/A	N/A
QS	35.5	-11028	-7168
QS+3%wt FeCl3	35.5	-6879	-10001
QS+10wt%	35.5	+13298	+43425

Seebeck vs Weight Percentage of FeCl3
35.5 mg/mL Quantenary Salt
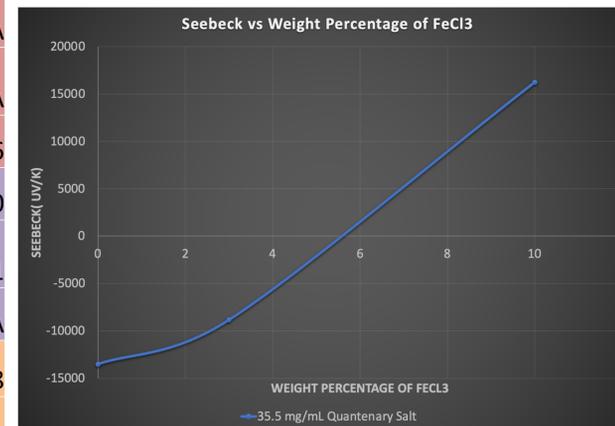
Conclusions

- The amount of the FeCl3 dopant can change the Seebeck behavior of the polymer from n-type to p-type due to the FeCl3 reacting with the chloride ion in the polymer matrix and forming FeCl4 complex.
- Exposure to the environment can lead to the polymer reacting with the water vapor or other molecules in the atmosphere that can lead to a decrease in the overall magnitude of Seebeck coefficient and lead to purely n-type behavior.

Future Work

The actual mechanism by which the FeCl4 complex changes the Seebeck coefficient is unclear. It its possible that local reorganization is occurring locally to allow movement of ions across the polymer matrix. Further research could be focused on trying to take scanning electron microscopic images of the samples to detect any aggregations when a thermal gradient is applied and the the time dependence of this local reorganization.. In addition, the formation of polymer blends that contain a copolymer blend and the dopant FeCl3 could be added to determine the how the See beck coefficient and ionic conductivity is affected by the local reorganization in these amorphous polymer. In addition it would worth studying the effects that FeCl3 causes in more complex polymer structures that are miscible in water. This work could help us design a better anion echange membrane or thermoelectric medium for incorporation in heat-harvesting technology electronics

References

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