

Measuring the Conductivities of Ionic and Metal Ligand Coordinated Polymers

CNF Project Number: 2952-21

Principal Investigator(s): Meredith Silberstein

User(s): Max Tepermeister

Affiliation(s): Sibley School of Mechanical and Aerospace Engineering, Cornell University

Primary Source(s) of Research Funding: Defense Advanced Research Projects Agency

Contact: meredith.silberstein@cornell.edu, mt845@cornell.edu

Website: silbersteinlab.com

Primary CNF Tools Used: SC4500 Evaporator, ABM Contact Aligner, Heidelberg Mask Writer

Abstract:

Ionic polymers are a new class of material that promise to enable deformable computers and bio-compatible electronics. We developed a gold on glass experimental electrode setup with built-in spacers using photolithographic tools. We then used this setup to characterize a wide range of ionic polymers and discovered some unexpected trends in their behavior, including an increase in conductivity with ion size.

Summary of Research:

The primary goal of this research project is to discover circuit elements describing synthetic soft materials that utilize ionic transport. This work is funded through a Defense Advanced Research Projects Agency Young Faculty Award.

Circuit design to date has been primarily based upon metal and semiconductor substrates—inherently hard materials with features that have minimal similarity to or compatibility with biosystems. Biosystems have a diverse set of highly nonlinear and environmentally responsive features within underlying circuitry (e.g., neurons, membrane ion channels) that operate via ion transport and storage. While these systems have been extensively studied within biomechanical contexts, few reduced-order circuit models have been developed. Moreover, soft ionic conducting material development has primarily been focused on maximizing conductivity for use as electrochemical conversion and storage device membranes. As a result of the foregoing prevailing conditions, progress in wetware has been limited: hampered by the disparate knowledge bases.

As part of this broader effort, we are experimentally characterizing the ionic conductivity of a wide range of polymers. These electrochemical impedance spectroscopy and cyclic voltammetry experiments are conducted on a Gamry 3000AE in the Silberstein lab with either a 2-wire standard or 4-wire Kelvin measurement.

It is critical for the accuracy and repeatability of these experiments that the electrodes be non-reactive and that the distance between electrodes and electrode area be set at a constant value.

Utilizing CNF tools, we built a gold on glass electrode using a liftoff process that meets all our requirements. We patterned S1800 series photoresist onto fused quartz 100 mm wafers, then deposited a 10 nm titanium adhesion layer followed by a 100 nm gold layer via electron-beam thermal evaporation. The photoresist and excess gold was then removed using the water-jet liftoff machine. We then photo-patterned 5 μm and 10 μm thick SU-8 spacers on the periphery of the electrodes.

Some of the materials we test are viscous liquids, so we designed the spacers in a sparse grid to allow for the test materials to flow out of the test cell. A diagram and image of these devices are shown in Figure 1 and 2 respectively. The SU-8 spacer can be seen in Figure 2 as the small lighter rectangles in a square around the central gold square.

In order to perform impedance spectroscopy measurements, sample material is dropped on one of these electrodes and a second electrode is clamped on top, rotated by 180°. The central 1 cm^2 squares of gold overlap and create a parallel plate capacitor. By applying

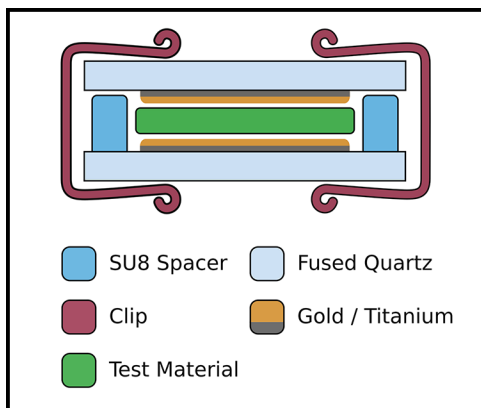


Figure 1: Diagram of experimental setup.

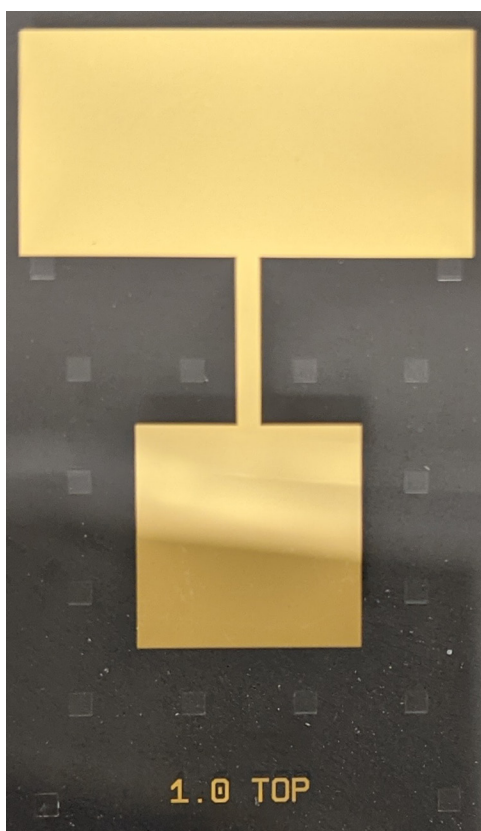


Figure 2: One electrode out of four on a wafer.

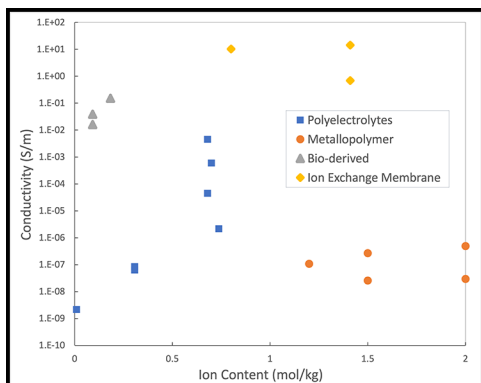


Figure 3: Conductivity vs. ion content for four material classes.

oscillating electric fields at various frequencies, we can precisely characterize the electrical response of our test material. This electrochemical testing fixture has been applied to testing metal ligand coordinated polymers, polyionic hydrogels, and ionomers swollen with ionic liquids. Figure 3 shows the ionic conductivity of a wide range of materials that we have characterized, mainly with this device.

With PDMS, we have found that the ionic conductivity of ligand functionalized PDMS with metal salts incorporated far exceeds the conductivity of unfunctionalized PDMS. Further, the conductivity of metallo-PDMS depends on both the type of anion and cation within the added salt and on the concentration of the salt. Interestingly, larger anions lead to higher conductivity despite expected size effects on their diffusivity because they associate less strongly with the metal cation. Advantageously, these larger anions are also able to be incorporated into the polymer at larger concentrations without precipitating into crystallites. We also found that by using more than one cation type, we could partially de-couple viscosity and conductivity. With the polyionic hydrogels and ionomers, we have used the test setup to characterize their basic electrical response, and are in the process of characterizing the properties of various material junctions. These junctions promise to give current rectifying behavior in a way similar to semiconductor diodes.

Conclusions and Future Steps:

The tools at the CNF were instrumental in creating a precise and repeatable experimental setup for our material characterization, leading us to surprising conclusions about the behavior of some ionic systems. In the coming year, we are interested in moving beyond single material characterization and towards device/junction characterization. Many proposed devices require length scales on the order of microns in order to function effectively. As such, one possible way to make these devices is by patterning positive and negative ionomers themselves using photolithographic techniques, which we hope to explore in the near future.