Measuring the Mechanical and Electrical Properties of Ionically Conductive Polymers

CNF Project Number: 3058-23 Principal Investigator(s): Meredith Silberstein User(s): Max Tepermeister, Ellen van Wijngaarden

Affiliation(s): Sibley School of Mechanical and Aerospace Engineering, Cornell University Primary Source(s) of Research Funding: DARPA Contact: meredith.silberstein@cornell.edu, mt845@cornell.edu Website(s): silbersteinlab.com Primary CNF Tools Used: DISCO Dicing Saw, Harrick Plasma Generator, Malvern Nano ZS Zetasizer

Abstract:

The mechanical and electrical properties of polymers enable their use in biosensors, biohybrid robotics and energy conversion devices. This research focused on how the mechanical and electrical properties of ionically conductive properties can be tuned for different applications. We used photolithography to fabricate an electrode setup to characterize a range of ionic polymers, revealing unexpected trends including increase in conductivity with ion size. Recent work has focused on the properties of biopolymers, specifically extracellular polymeric substances from bacteria including *Sphingomonas* and *Pseudomonas Aeruginosa*. Preliminary results demonstrate our ability to tune properties based on the blend of polymers present.

Summary of Research:

The primary goal of this research project is to characterize mechanical and electrical properties of ionically conductive polymers. This includes describing synthetic soft materials that use ionic transport as well as characterizing soft biopolymers with potential applications in ionic circuits. Traditional materials for circuit design are metal and semiconductor substrates; hard materials that are typically incompatible with biosystems. Biosystems utilize circuits to achieve environmental responses as seen in neurons and membrane ion channels. These systems have been previously studied from a biomechanical perspective, however, few reduced order circuit models have been developed. Research into soft ionic conducting materials has focused primarily on maximizing conductivity for use in electrochemical conversion and storage device membranes, with limited progress in the development of experimental wetware.

As part of this broader effort, we have experimentally characterized the ionic conductivity of a wide range of polymers. Impedance spectroscopy experiments were conducted on a Gamry 3000AE in the Silberstein lab. CNF tools were used to fabricate a gold-on-glass electrode using S1800 series photoresist patterned onto fused quartz wafers as shown in Figure 1. Electronbeam thermal evaporation was used to deposit a titanium adhesion layer followed by a gold layer. The water-jet liftoff machine was used to remove any excess gold before photopatterning spacers on the periphery of the electrodes. The SU-8 spacer can be seen in Figure 1 as the small lighter rectangles in a square around the central gold square. Impedance spectroscopy measurements were performed by adding the sample between the electrodes to create a parallel plate capacity. An oscillating electric field at various frequencies was applied to determine the electrical response of the test material. The system was used to test metal ligand coordinated polymers, polyionic hydrogels, and ionomers swollen with ionic liquids. Figure 3 depicts the ionic conductivity of a broad range of materials that have been characterized using this device.

Results showed that the ionic conductivity of ligand functionalized polydimethylsiloxane (PDMS) with metal salts incorporated was far greater than the conductivity of unfunctionalized PDMS. Additionally, the conductivity of metallo-PDMS depended on both the type of anion and cation within the salt and the salt concentration. Notably, the larger anions led to higher conductivity values despite having a lower diffusivity due to their size. This trend resulted from the larger anions dissolving into the polymer and dissociating better than smaller anions. Further details can be found in the recently published manuscript [1].

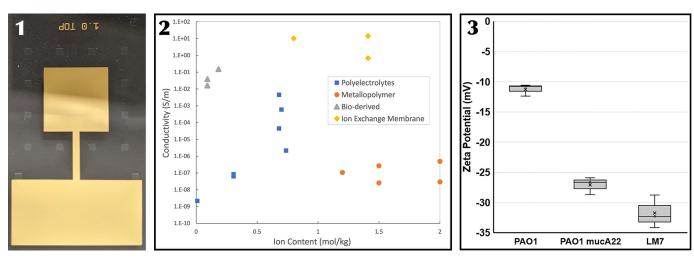


Figure 1, left: Experimental setup showing one electrode out of four on a wafer. Figure 2, middle: Conductivity vs ion content for four material classes. Figure 3, right: Zeta Potential results comparing ionic polymers from wild type Pseudomonas Aeruginosa, (PAO1), an alginate overexpression strain (PAO1 mucA22), and Sphingomonas LM7.

Initial tests completed for the characterization of biofilms have focused on a recently isolated strain of Sphingomonas bacteria, LM7. Sphingomonas bacteria are known for the production of high molecular weight polymers, primarily made of polysaccharides, that are widely used in applications in oil and gas as well as food processing. The work aimed to identify the initial properties for comparison to materials from other species, such as *Pseudomonas Aeruginosa*, and various material characterization methods were used to establish the properties of the Sphingomonas biofilms. The malvern nano-s zetasizer was used to measure molecular weight, size and zeta potential, as shown in Figure 3, to compare the biofilm from Sphingomonas LM7 to strains of P. Aeruginosa and biopolymers from literature, such as gellan gum. Biofilms were grown over a period of four days before cultures were centrifuged to remove cells and the polysaccharide was removed from the supernatant using cold ethanol precipitation. Enzymes and phenol extraction were used to break down and remove DNA, RNA and proteins. The final material was dialyzed, lyophilized and then rehydrated as per zetasizer specifications for the desired measurements.

The zeta potential results from *Sphingomonas LM7* were compared to material from the well-known biofilm producer *P. Aeruginosa* wild type (PAO1) and PAO1mucA22, a strain of *P. Aeruginosa* modified to overexpress alginate, a negatively charged polymer. The zeta potential values indicate a negative charge for the *LM7* polymer similar to the PAO1mucA22 strain and significantly lower than the wild type biofilm. The value

for *LM7* is similar to the values for zeta potential reported in literature for a similar biopolymer, gellan gum from another *Sphingomonas* strain [2]. Next steps will include additional materials characterization tests to better understand the ionic and mechanical properties of these biopolymers and testing a wider variety of biopolymer blends.

Conclusions and Future Steps:

The tools and technical expertise provided at the CNF was essential to the rapid design and fabrication of the experimental setup for material characterization providing novel insight into the behavior of ionic polymers. In the coming months, we will investigate device/junction through the design of additional microscale devices. We will also expand on our preliminary material tests of extracellular polymeric substances to include material from bacteria genetically modified to produce specific polymer blends.

References:

- Xinyue Zhang, Jinyue Dai, Max Tepermeister, Yue Deng, Jingjie Yeo, and Meredith N. Silberstein. Macromolecules 2023 56 (8), 3119-3131 DOI: 10.1021/acs.macromol.2c02519.
- [2] Duarte LGR, Alencar WMP, Iacuzio R, Silva NCC, Picone CSF. Synthesis, characterization and application of antibacterial lactoferrin nanoparticles. Curr Res Food Sci. 2022 Mar 26;5:642-652. doi: 10.1016/j.crfs.2022.03.009. PMID: 35373146; PMCID: PMC8971344.