

57204-ND7:

Elucidating the Local Kinetics of Triboelectric Effects in Polymers by Scanning Probe Microscopy

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Project overview

For this New Direction project, we aim to study the triboelectric charge generation and dissipation in polymers, which are useful in energy harvesting systems and in eliminating uncontrolled, hazardous electrostatic charge in industrial processes to prevent dust and pipeline explosions. Triboelectric charging is a phenomenon where insulating materials become electrically charged after they are brought into frictional contact. Next to the insulators, conductive materials are needed to carry away the charge accumulated on the insulating surfaces, in order to manipulate triboelectric effects.

Conductive polymers are promising alternatives to thermally evaporated metallic thin films to carry away triboelectric charges, because conductive polymers offer numerous advantages including large-area conformal coverage and ambient solution deposition that does not require energy-intensive vacuum equipment. Common conductive polymers such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) show good conductivity of 0.2 S/cm as pristine films, and depending on the processing conditions the conductivity can be increased further by two orders of magnitude. However, most conductive polymers become unstable when the redox potential exceeds the potential window of 1 V with respect to Ag/AgCl. Materials that can tolerate a wide potential window in both positive and negative voltage range will be more robust against degradation with triboelectric cycles. Thus in this reporting period we investigated two conjugated polymers that possess a wide potential window, to understand the material properties and stability under repeated voltage sweeps.

Results and Discussions

The conjugated polymers here are selected because they showed good conductivity and reversible redox capacity in the negative potential range between 0 to -2 V with respect to the Ag/AgCl reference electrode. The chemical structures and cyclic voltammetry characteristics are shown in Figure 1. The polymers were synthesized by Prof. Azoulay's lab in the University of Southern Mississippi. These materials are narrow bandgap conjugated systems that show a conductivity of 0.4 S/cm for the structure with methyl units (QxMe) and 1.4 S/cm for the one with thiophene units (QxTh). The materials are novel because they are reversibly active in the negative potential window and can serve as n-type electrodes, which are the bottlenecks in various energy generation/storage devices. N-type conjugated polymers are typically less stable than the p-type counterparts, which for instance PEDOT:PSS can be cycled for thousands of cycles with less than 10% loss in conductivity and capacitance. Thus we proceed to characterize and understand the effects of repeated voltage cycles on electronic and morphological properties of the polymers.

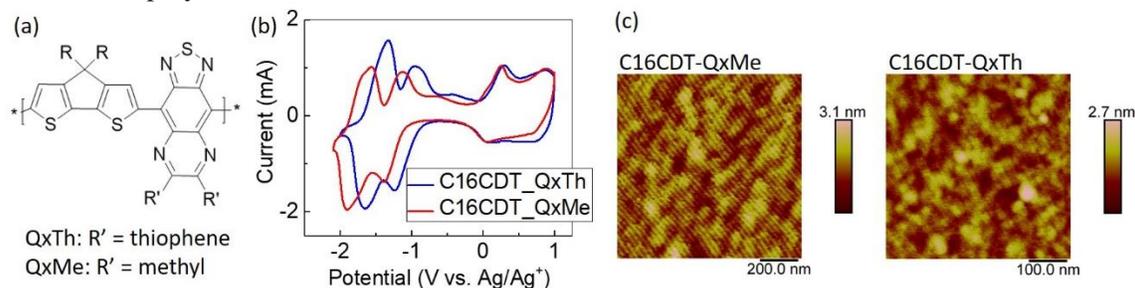


Figure 1. (a) Chemical structures and (b) cyclic voltammetry of the conjugated narrow bandgap polymers. The side chain is $R = C_{16}H_{33}$, and the R' is either a methyl or a thiophene unit. (c) Atomic force microscopy images of the conjugated polymers.

The atomic force microscopy (AFM) images in Figure 2 shows that the two polymers are amorphous with film roughness of 0.6 nm. In addition to AFM, we initially wanted to measure local electric

field emanating from triboelectric charges on different surfaces by Kelvin force microscopy (KFM). Unfortunately we were not successful in modifying the equipment to gain precise control over measurement conditions in the KFM. We changed our approach from KFM to electrochemical analyses in order to infer electronic properties.

The thin films were cycled by either cyclic voltammetry or galvanostatic charge discharge as shown in Figure 2. The cycling condition here is at a lower voltage range than typical triboelectric charge/discharge cycles that can reach high voltages up to tens of volts, but we choose to limit the range for now to measure subtle changes rather than catastrophic breakdowns. Moreover, as the materials are integrated into devices and systems, the voltage limits can be tuned depending on application requirements. While the C16CDT-QxMe film retains only 20% of its initial capacitance after 1000 cycles, the C16CDT-QxTh shows up to 60% capacitance retention in Figure 2. The two polymers differ in structure only by the side unit, and this drastic difference is very interesting and deserves further study. Our next step for this project is to understand this difference in cycling behaviors; we will carry out x-ray structural measurements such as GIWAX studies and more electronic characterization to determine the origin of cycling stability in the C16CDT-QxTh polymer. Through this understanding, this project will impact on future material designs to obtain the desired charge retention and conductivity in conducting polymers.

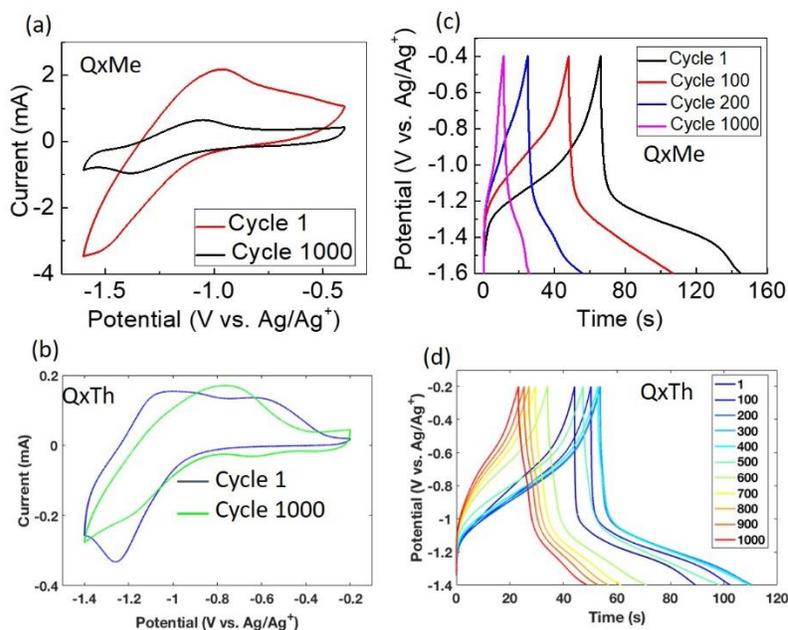


Figure 2. Comparison of the (a, b) cyclic voltammetry and (c, d) galvanostatic charge discharge characteristics of the conjugated polymers before and after repeated voltage cycles.

Education and Outreach

This project supported the partial stipends of two PhD students and involved two undergraduates from the UCSD summer research program for under-represented students. One of the undergraduate researchers will be presenting her results in the upcoming Society of Hispanic Professional Engineers Conference in Cleveland, OH. The principal investigator presented at the 2018 ACS March Meeting in New Orleans, LA and would like to thank the PRF for travel support.