

57204-ND7:

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

Tse Nga Ng, University of California San Diego

### Project overview

For this New Direction project, we initially aimed 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. During the course of this research, we uncovered remarkable redox stability in the novel n-type conductive polymers that we used. We shifted our focus onto understanding the origin for the redox stability in these n-type polymers, important for applications involving charge transfer like in triboelectric processes and in energy storage.

Conductive polymers are promising alternatives to thermally evaporated metallic thin films to transport 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. N-type conjugated polymers are typically less stable than the p-type counterparts and degraded rapidly with redox cycling, exhibiting a low capacitance retention of < 80% at 1000 cycles. In the first reporting period we investigated two conjugated polymers that possess a wide potential window, to understand the material properties and stability under repeated voltage sweeps. In this final report, we explain the charge delocalization attributes that lead to good redox stability in an exemplar n-type polymer, with a coulombic efficiency of 99.6% and that retains 92% of the initial capacitance after 1000 full charge-discharge cycles, which exceeds other n-dopable organic materials.

### Results and Discussions

The conjugated polymers here were 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  $\sim 10^{-3}$  S/cm. 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. We proceeded to characterize and understand the effects of repeated voltage cycles on electronic properties of the polymers.

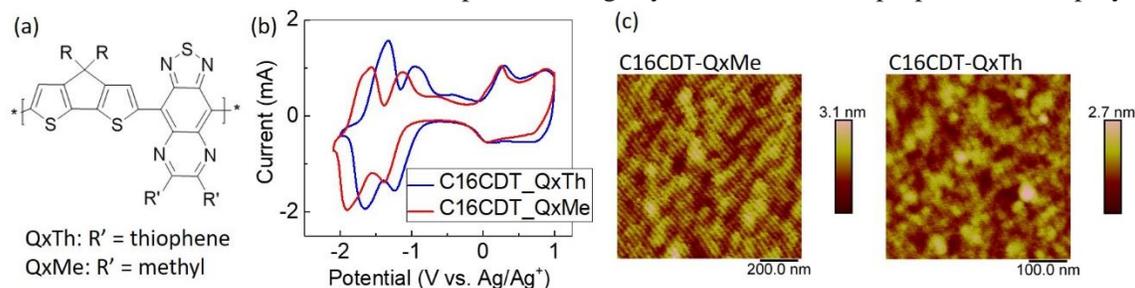


Figure 1. (a) Chemical structures and (b) cyclic voltammetry of the conjugated narrow bandgap polymers. The side chain is  $R = C_{16}H_{33}$ , and the  $R'$  is either a methyl or a thiophene unit. (c) Atomic force microscopy images of the conjugated polymers.

The atomic force microscopy (AFM) images in Figure 1c showed that the two polymers were 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.

Since we have compared the characteristics of the two polymer variants in the last report, this report focused on understanding the more stable one with the thiophene side unit QxTh. This polymer was cycled by galvanostatic charge discharge as shown in Figure 2. The material retained 92% of its initial capacitance and showed excellent cycling stability with coulombic efficiency to be above 99.6% over 1000 redox cycles. The coulombic efficiency is the ratio of the output charge to the input charge in a charge-discharge cycle, and the high value here indicates excellent redox reversibility and is unique among n-type materials.

To explain the redox stability, molecular orbital calculations of spin densities was carried out by my collaborator Prof. Neeraj Rai. We found there is significant internal charge-transfer character between electron-rich and electron-deficient components throughout the  $\pi$ -framework and extensive delocalization of the spin density in this exemplar polymer. When the polymer is oxidized or reduced, there were no distinct redox sites, and only a slight increase of positive charge density on the donor and negative charge density on the acceptor unit. Overall, extensive  $\pi$ -conjugation is maintained as seen in the molecular electrostatic maps of the neutral, oxidized, and reduced states. Through this understanding, this project has impacts on future material designs to improve the redox stability and the conductivity in n-type polymers.

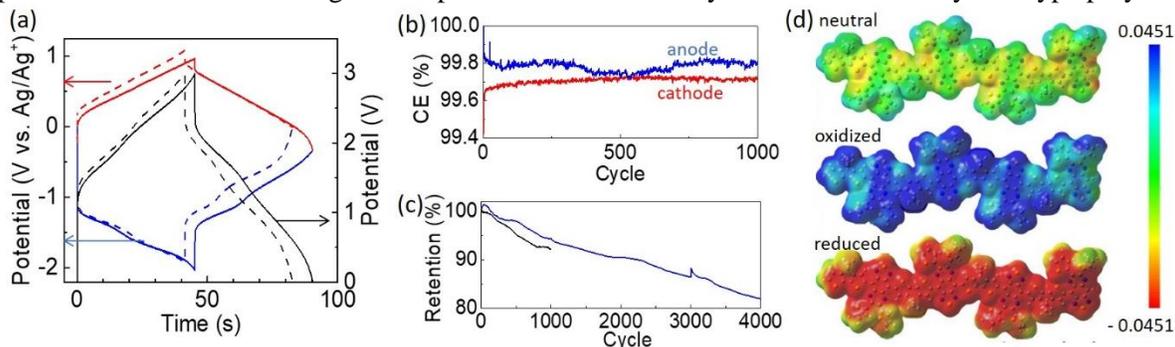


Figure 2. (a) Galvanostatic charge–discharge measurements of the QxTh film as an anode (blue) or a cathode (red) at a current density of 1 A/g. The solid lines are measured in cycle 1 and dashed lines in cycle 1000. The black curves represent potential differences between the two electrodes. (b) Coulombic efficiency and (c) capacitance retention versus redox cycles. (d) Molecular electrostatic potential map, as an isosurface for the total electron density. The blue and red surface represents the highest (fewer electrons) and lowest (more electrons) electrostatic potential, respectively. The color scale is in units of  $e/\text{bohr}^3$ .

The results here have been submitted for peer review to a journal, and upon publication, the article will be deposited into the PRF program archive.

### Education and Outreach

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