Oxidative Molecular Layer Deposition of Conjugated Amine Polymer Thin-Films

Quinton K. Wyatt,[1] Mitchel Vaninger,[2] Thomas W. Heitmann,[2,3] Helmut Kaiser,[3] Matthias J. Young,[1,4,*]

[1]Department of Chemistry, University of Missouri, Columbia, MO, USA

[2]Department of Physics and Astronomy, University of Missouri, Columbia, MO, USA

[3]Missouri Research Reactor, University of Missouri, Columbia, MO, USA

[4]Department of Biomedical, Biological and Chemical Engineering, University of Missouri, Columbia, MO, USA

Electrically-conductive and redox-active polymers such as polyethylenedioxythiophene (PEDOT), polypyrrole (PPy), and polyaniline (PANI) have applications in flexible electronics, energy storage, electrochemical desalination, and chemical sensors. In each of these applications, delivering conformal, thin-film polymer coatings is attractive to provide lower weight, faster charging, and higher sensitivity. Unfortunately, traditional approaches for polymer synthesis struggle to deliver uniform thin film coatings onto 3D substrates. In general, molecular layer deposition (MLD) is an attractive route for the formation of these polymer coatings because MLD growth involves alternating self-limiting surface reactions and inherently provides uniform coatings on 3D substrates. Previous work reported a scheme for MLD of conductive and redox-active polymers employing sequential doses of monomers and a chemical oxidant ($MoCl_5$), termed *oxidative* MLD or "oMLD," and demonstrated the formation of PEDOT films using this approach. In this report, we expand on this prior work and study oMLD of amine-containing conductive and redox-active polymers including PPy, PANI, and their derivatives using alternating exposures of monomers and $MoCl_5$ oxidant. We perform both in-situ and ex-situ experimental measurements to study the growth behavior of these polymers, and identify unexpected monomer-dependent growth. We also measure the conformality and the electrical and electrochemical properties of the resulting films. We find that pyrrole and substituted-aniline both undergo self-limiting surface reactions to form conformal, electrically-conductive and redox-active polymer films. We also identify that copolymer alloys of PPy and substituted-PANI growth chemistries yield improved electrochemical properties over isolated monomer chemistries. Our results provide new insights into the oMLD growth mechanism in general, and offer the prospect for molecular-level control of conjugated polymer structures delivered in a conformal, thin-film geometry.