DESIGN AND APPLICATION OF POLYMERIC MIXED CONDUCTORS

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Organic electronics has been a highly researched field owing to the low cost, biocompatibility, mechanical flexibility, and superior performance relative to their inorganic counterparts in some applications. Significant advancement has been achieved across various device platforms including organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), and organic solar cells, for instance. Recently, soft materials that can conduct both charge and ions simultaneously (i.e., organic mixed conductors) have been a major catalyst in the fields of biosensors and energy storage. Extensive research efforts in the organic electronics field are being invested to establish the relevant structure-property relationships to design and develop higher performing organic mixed conductors. Simultaneously, these materials are utilized in developing prototype biosensors with the aim of superior performance, lower cost, and better patient comfort and outcomes than currently available technologies. Following suit, this dissertation is dedicated to furthering organic electronics on both fundamental and applied fronts. Specifically, this work examines a novel class of redox-active macromolecules, radical polymers, as the organic electrochemical transistor (OECT) active layer. In addition, wearable ocular biosensors utilizing soft materials to realize design innovation are presented.

For the first part of the present dissertation, radical polymer-based blends are evaluated for mixed electron and ion conduction in OECTs. Traditional macromolecular design motifs for OECT active layer materials have been a closed-shell macromolecular backbone for electron conduction with charge-neutral hydrophilic side chains (e.g., triethylene glycol) for ion conduction. When poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) is blended with poly(3-hexylthiophene) (P3HT), 2,2,6,6-tetramethylpiperidin-N-oxy (TEMPO) radicals in PTEO act as an independent voltage regulator that modulates the ionic and hence electronic transport of the OECT devices. Electrochemical analysis of the blend films reveals that the ionic transport and hence electrochemical doping of the P3HT phase occur when the applied bias matches the onset oxidation potential of TEMPO radicals in PTEO even though that of P3HT is lower than that of TEMPO oxidation. By optimizing the blend ratio, figure-of-merit (i.e., μC^*) values over 150 F V^{-}

^{1} cm^{-1} s^{-1} at loadings as low as 5% PTEO (by weight) are achieved, placing the performance on the same order as top-performing conjugated polymers despite the mediocre performance of pristine P3HT (<10 F V^{-1} cm^{-1} s^{-1}). These findings suggest that introduction of open-shell moieties in the OECT active layer as a secondary redox-active species may significantly improve OECT performance metrics and offer a new paradigm for future macromolecular designs.

In the second part of the dissertation, novel design strategies for wearable ocular electroretinography (ERG) sensors are presented. Typically, wearable sensors are custom-made contact lenses fabricated in a bottom-up fashion where the pre-fabricated sensor component is either embedded in the contact lens body or sandwiched between two. The present work instead utilizes commercially available contact lenses, and the corneal electrode is integrated via electropolymerization of poly(3,4-ethylenedioxythiophene):iron(III) p-toluenesulfonate (PEDOT:Tos) on the lens surface. Electrochemical analysis of the PEDOT:Tos reveals that the measured impedance is several orders of magnitude lower than that of noble metals (e.g., Au) used as the working electrode in commercial electrodes. The mechanical and chemical stability along with the soft form factor of the present design strategy enables high-fidelity recording of ERG signals in human subjects without the need for topical anesthesia.

Following the similar strategy, a new seamless wearable ocular sensor integration strategy utilizing polydopamine (PDA) conformal coating is demonstrated. In this work, we utilize its strong adhesive property originating from the van der Waals interactions between catechol moieties of PDA and various hydrophilic functional groups (e.g., hydroxy, ether, etc.) already present in commercial contact lens materials. The facile integration demonstrates high peeling strength (> 55 J m^{-2}), chemical and mechanical stability. A series of *in vivo* assessments demonstrates high accuracy, reliability, and user comfort of the fabricated wearable sensor in both animal and human subjects. The findings suggest that the PDA-assisted integration strategy may be applied in designing various future-generation wearable ocular electrophysiological sensors.