論 文 の 内 容 の 要 旨

論文題目　Development and biosensing application of organic electrochemical transistors with highly conductive PEDOT:PSS:Poly(acrylamide)-based hydrogel channels
（高導電性PEDOT:PSS:Poly(acrylamide)ハイドロゲルをチャネルとした有機電気化学トランジスタの開発およびバイオセンシング応用）

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Sensors built on smart, functional materials pave the way for democratized health care by providing high quality personal health data at the point-of-care. In the aftermath of the novel coronavirus pandemic, the need to advance such technologies is salient. The required materials must be mediators of electronic and ionic transport, mechanically compliant and flexible, and crucially, chemically stable and biocompatible. Hydrogels of semiconducting conjugated polymers (CPs) fit this profile exceptionally well.

PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polymerized with poly(styrene sulfonate)) is one of the most widely studied CPs for technological applications, and it can be formed into hydrogels by a variety of processing methods. In this regard, the formation of composite hydrogels by interpenetrating a second polymer network is highly promising for biosensing, because of the capability for orthogonal design of electrical, electrochemical, and mechanical properties.

In this thesis, we successfully prepared double-network composite hydrogels by facile one-pot free radical polymerization of neutral and anionic acrylamide monomers dispersed into commercial-grade PEDOT:PSS. The resulting free-standing hydrogel sheets are highly conductive in the dry state and remain so when re-swelled (ca. 15 S/cm) in analogues of physiological media (i.e., phosphate buffered saline). These outstanding properties allowed

organic electrochemical transistors (OECTs) and typical electrochemical electrodes to be readily fashioned by manual forming, with low resistance ohmic contacts to Au electrodes formed by simple thermo-mechanical annealing.

Electrical transport and electrochemical characterization revealed that, while volumetric capacitances were reduced by the non-conductive second network, carrier mobilities were essentially unimpeded from that of neat PEDOT:PSS (cf. 1 cm^2/Vs) indicating good compatibility between the two phases. Reliable contacts also allowed us to investigate the kinetics of electrocatalyzed reduction of dissolved O_2 on PEDOT and informed an optimal potential sweep rate to balance Faradaic and capacitive currents in the cathodic regime of operation.

Accordingly, we applied these highly conductive hydrogels towards the detection of glucose, by extracting an electrochemical signal based on the coupling of PEDOT electro-catalytic action to the boronic-boronate acid equilibrium in the presence of diol molecules. These signals could be directly amplified by using the hydrogel as the channel of an OECT—a departure from the traditional embodiment of OECT biosensors.

Finally, we observed novel redox-mediated resistance switching effects in these CP hydrogels, due to the coupling of electro-mechanical swelling of the interpenetrating second network and the formation of electronic band structure in PEDOT. This effect could be induced by surface modification of the current collecting electrodes, suggesting that the accumulation of space charge when the channel resistance is of similar magnitude to the contact resistance. Redox-mediated, reversible box-shaped hysteresis loops in various device configurations suggest the application of this phenomena in new bioelectronic devices.