生理的 p H 環境で動作する PEDOT: lignosulfonate 薄膜における キノンジアニオン電荷移動錯体形成の検討

Investigation of quinone dianion charge-transfer complex formation in PEDOT:lignosulfonate thin-films operating at physiological pH 東京大学¹, ポズナン技術大学² ^O(P)Alex C. Tseng¹, Tomasz Rębiś², 坂田 利弥¹ Univ. of Tokyo¹, Poznań Univ. of Tech. ^{2°}(P)Alex C. Tseng¹, Tomasz Rębiś², Toshiya Sakata¹ E-mail: sakata@biofet.t.u-tokyo.ac.jp

1. Introduction

Lignosulfonates (LS), produced as by-products of paper pulp processing, are a naturally abundant and lowcost source of electro-active polymers containing quinone and sulfonic acid functional groups. To improve electron transfer with quinones, LS may be blended with conducting polymers such as PEDOT (poly(3,4ethylenedioxythiophene), whereby sulfonic acids act as anionic dopants for PEDOT and quinones impart catalytic activity thanks to a reversible $2H^+/2e^-$ redox reaction. This property makes PEDOT:LS appealing for sustainable development of electrochemical devices including supercapacitors and biosensors.

In the case of charge storage application, PEDOT:LS electrodes are operated at low pH to optimize the kinetics of $2H^+/2e^-$ redox, thus demonstrating large pseudocapacitance and cycle stability [1]. However, to apply the catalytic activity of quinones in biosensors, it is necessary to characterize the pH dependent behaviour of quinone redox in PEDOT:LS, which is increasingly kinetically limited as H⁺ becomes scarce.

2. Experimental Methods

Electrochemical electrodes and organic electrochemical transistors (OECTs) based on PEDOT:LS thinfilms were prepared via galvanostatic electro-polymerization following the optimized conditions previously reported [2]. Briefly, 1.0 mg/mL each of 3,4-ethylenedioxythiophene (Sigma-Aldrich) and lignosulfonate sodium salt (DP841, Borregaard Lignotech) were prepared together in 0.1 M HClO₄ electrolyte (Fujifilm Wako Pure Chem. Corp.) and simultaneously oxidized at a constant current density of 0.25 mA/cm² using a Solartron 1470E potentiostat. Depending on intended device structure, Au rod-type electrodes (BAS Inc.) or sputtered Au/Cr on glass substrates were used as working electrode. Pt wire counter electrodes were referenced to Ag/AgCl to monitor the oxidation potential, which was typically \geq 0.9 V throughout electropolymerization. Cyclic voltammetry (CV) and transport characterization were performed using an ALS 618E electrochemical analyzer and Keysight B1500A semiconductor parameter analyzer, respectively.

3. Results

OECT channels of ca. 20 µm length and 1 µm thickness were formed by bridging split working electrodes following electro-polymerization for 30 min. Such channels exhibit pH dependent CV expected of quinone redox in PEDOT:LS while demonstrating gating behaviour ($I_{on}/I_{off} \sim 4$) sufficient for simultaneous characterization of hole transport in PEDOT. Fig. 1 shows the family of voltammograms and transfer curves with increasing pH (3 cycles/pH step). Based on oxidation peak potentials, a Nernstian shift of 61 mV/pH is extracted, in agreement with previous studies. However, significant hysteresis in drain current (I_D) is observed, with anodic going half-sweeps resembling preceding cathodic going half-sweeps. Importantly, I_D is continually suppressed at pH > ~3 even as voltammetric currents (I_G) stabilize. Together these results suggest that rather than diffusive loss of quinone species, the formation of a charge transfer complex between oxidized PEDOT and reduced quinone dianions may account for the decrease in quinone redox peak heights. **References:**

