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論 文 要 約

THESIS OUTLINE

論文題目

Study on the Fabrication of Conducting Polymer Materials by AC and Pulsed Bipolar Electropolymerization

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論文概要

In a bipolar electrolytic system (Figure 1a), driving electrodes (DEs) generate a uniform electric field across the solution with the low ionic concentration electrolyte. Bipolar electrodes (BPEs) are available as wireless electrodes involving anodic and cathodic reactions simultaneously at their terminals. When the alternating current (AC) bipolar electropolymerization of aromatic monomers was conducted on a BPE under the specific condition (Figure 1b), site-selective formation of conducting polymer fiber was observed from both ends of the BPE in a wireless manner.

In this thesis, the first objective is to extend the AC-bipolar electrosynthesis of conducting polymer fibers to high ionic concentration systems. The robustness of the growth models was verified under high viscosity and high ionic concentration conditions. The former condition can weaken the diffusion and electrophoresis effect that facilitate the formation of the fiber shape. The latter can elevate the doping rate of the generated poly(3,4-ethylenedioxythiophene) (PEDOT). The enhanced conductivity of PEDOT can affect the fiber generation process because the generated PEDOT acts as a BPE in the step-by-step growth. Furthermore, the enhanced conductivity of PEDOT is useful in applications.

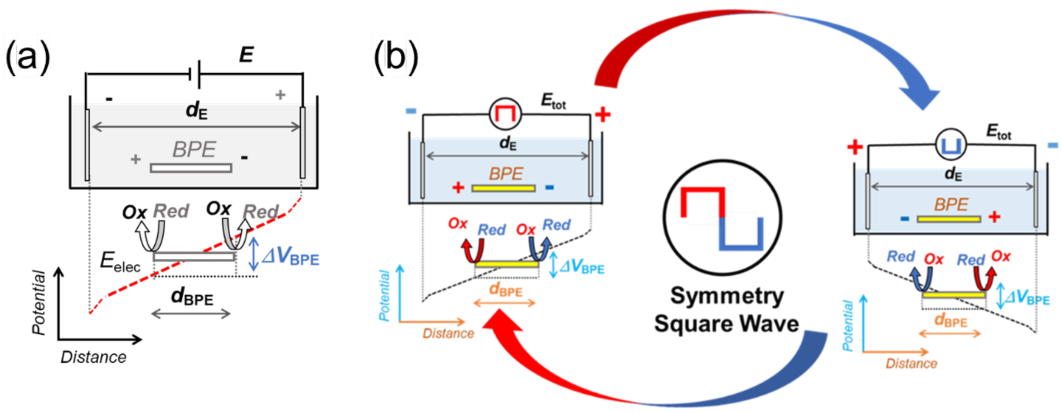

Figure 1. Potential distributions between the driving electrodes in (a) DC bipolar electrolytic system and (b) AC bipolar electrolytic system with square waveform (SQU).

In Chapter 1, the background and the purpose of the thesis were described.

In Chapter 2, the author successfully demonstrated the AC-bipolar electropolymerization of EDOT in three ionic liquids (ILs): [DEME][BF_4], [EMIM][BF_4], and [DEME][TFSI]. The resulting morphologies of PEDOT included clusters, films, and fibers, respectively. The differences in the deposited PEDOT morphologies were also discussed in terms of the physicochemical properties of the three ILs, such as electric field transmission efficiency (EFTE) and diffusion coefficient. Notably, [DEME][TFSI], with intermediate EFTE and diffusion coefficient values among the three ILs, yielded linear PEDOT fibers (Figure 2), similar to the morphology observed in a previous report using a dilute electrolyte solution. The use of ILs is an ideal approach for environmentally friendly electrosynthesis of conductive polymers.

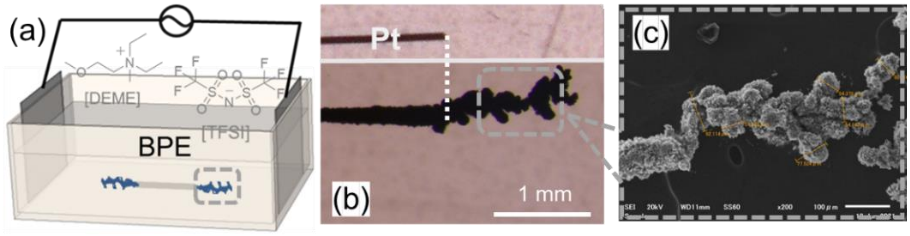

Figure 2. (a) Schematic illustration of AC-bipolar electropolymerization of EDOT in [DEME][TFSI]. (b) Optical microscope and (c) SEM images of the obtained linear PEDOT fiber (fiber-like structure).

In Chapter 3, the author designed a bipolar electrolytic system with highly concentrated electrolytes that provides the ability to adjust viscosity by changing the concentration of the supporting electrolyte. This system offers greater flexibility than ionic liquids in enhancing or weakening the electrophoresis and diffusion of $(EDOT)_n^+$. PEDOT fibers were successfully obtained in a highly concentrated electrolyte of 2000 mM Bu_4NClO_4/acetonitrile (MeCN), as shown in Figure 3b. Comparing the concentrated electrolyte bipolar electrochemical system to the IL bipolar electrochemical system, the viscosity of the former system is relatively lower. As shown in Figure 3a, concentrated electrolyte systems exhibited a higher diffusion coefficient to allow the effective electrophoresis. The fiber propagation in the concentrated electrolyte system was faster than that in ILs, the fiber diameter was slightly thinner than that in ILs.

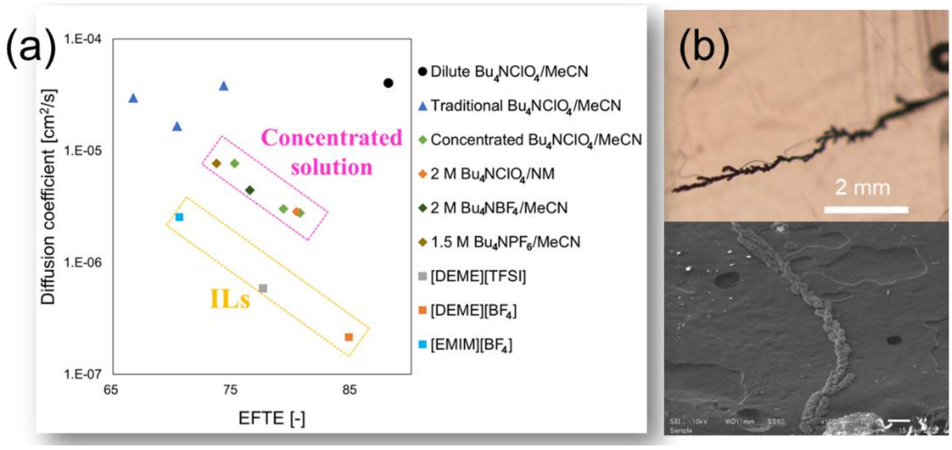

Figure 3. (a) Diffusion coefficient vs. EFTE of electrolyte solutions. (b) Optical microscope and SEM image of the PEDOT fiber obtained in 2 M Bu_4NClO_4/MeCN.

In Chapter 4, the author aimed to develop a bipolar electropolymerization method that can keep PEDOT deposits in the oxidized state. In order to achieve this goal, it is necessary to ensure that the direction of the electric field for fiber growth remains unchanged, i.e., unidirectional electric field electrolysis. Therefore, a pulsed direct current (PDC) bipolar electrochemical system (Figure 4) was investigated, and the PEDOT fibers, films, and other complex depositions were achieved by adjusting the PDC electrical signals, including pulse width (PW), duty cycle factor (DF), and waveform shape. Electrophoresis of charged oligomers $(EDOT)_n^+$ played an important role in the formation of PEDOT fibers under AC electric field. In contrast to AC-bipolar electrolysis, the deposition process of cationic EDOT oligomers in PDC was completely controlled by free diffusion during electric field turn-off time (Figure 4b). The resulting PEDOT fibers (films) exhibited a tendency for fractal growth, classified as diffusion-limited aggregate (DLA)-like (Figure 4c), while 2D or 3D depositions with relatively smooth boundaries were classified as Dense Branching Morphology (DBM)-like (Figure 4d). These studies are expected to contribute to a better understanding of the fine tuning of the bipolar electropolymerization process.

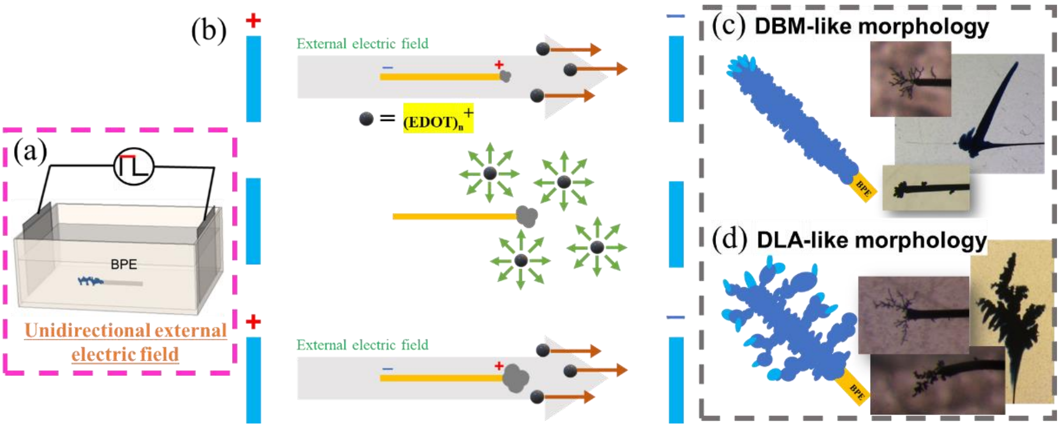

Figure 4. (a) Schematic illustration of the PDC bipolar electrochemical setup. (b) The contemplated free diffusion of $(EDOT)_n^+$ in OFF-time of PDC (No external electric field). (c) DBM-like morphology, the boundary of the deposits is relatively smooth, and the end (sky blue) of the deposits is active in the direction of the electric field. (d) DLA-like morphology, the deposits have many branches with multiple active sites (sky blue).

In Chapter 5, the general conclusions of this thesis were summarized.