

論文 / 著書情報  
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| 題目(和文)            |  |
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## 論文要旨

THESIS SUMMARY

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|--|---------------|----------|---|-----------------|------|
| 系・コース：<br>Department of, Graduate major in | 応用化学<br>エネルギー | 系<br>コース | 申請学位 (専攻分野)：<br>Academic Degree Requested | 博士<br>Doctor of | (工学) |
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

This dissertation entitled “Study on the Fabrication of Conducting Polymer Materials by AC and Pulsed Bipolar Electropolymerization” focuses on the conducting polymer fiber from the ends of the BPE in a wireless manner, especially in high viscosity and high ion concentration conditions. The former condition can weaken the diffusion and electrophoresis effect that facilitates the formation of the fiber shape. The latter can elevate the doping rate of the generated poly(3,4-ethylenedioxythiophene) (PEDOT). In addition, the pulsed electrolysis can keep the PEDOT deposits in an oxidized state by applying the unidirectional electric field, and the conducting polymer deposited on only one side of BPE also shows its fine reaction site selectivity. The bipolar electrosynthesized conducting polymer fiber, film and other deposits are also thoroughly analyzed.

Chapter 1, “General introduction,” introduces the principle of bipolar electrochemistry. The electrolytic setup consisting of a pair of driving electrodes (DEs) can generate a uniform electric field across the solution in the low ionic concentration electrolyte, then the bipolar electrodes (BPEs) are available as wireless electrodes involving anodic and cathodic reactions simultaneously at their terminals. Based on the AC-bipolar electropolymerization system in dilute electrolyte developed so far, the possibility of controlling the morphology of product polymer fibers by using concentrated electrolyte or pulsed electropolymerization is described.

Chapter 2, “Bipolar Electropolymerization in Ionic Liquids,” demonstrates the AC-bipolar electropolymerization of EDOT in three ionic liquids (ILs): [DEME][BF<sub>4</sub>], [EMIM][BF<sub>4</sub>], and [DEME][TFSI]. The resulting PEDOT deposits included cluster, film, and fiber morphologies. 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, similarly to the morphology observed in the previous report using a dilute electrolyte solution. The use of ILs is an ideal approach for environmentally friendly electrosynthesis of conductive polymers.

Chapter 3, “Bipolar Electrosynthesis in Concentrated Electrolyte,” describes 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 effect and diffusion of (EDOT)<sub>n</sub><sup>+</sup>. PEDOT fibers were successfully obtained in a highly concentrated electrolyte of 2000 mM Bu<sub>4</sub>NClO<sub>4</sub>/acetonitrile. Comparing

the concentrated solution bipolar electrochemical system with the IL bipolar electrochemical system, the viscosity of the former system is relatively lower. This allows a higher diffusion limit, weakening the effect of electrophoresis. The fiber propagation in the concentrated electrolyte system was faster than that in ILs, and the fiber diameter was slightly thinner than that in ILs. The one-dimensional (1D) PEDOT fiber was obtained in the highly concentrated electrolyte, but the diameter of the fibers was larger than that obtained in the dilute electrolyte. The nanomorphology of the PEDOT fibers was observed as the 3D PEDOT networks. The conductivity test for the PEDOT fibers obtained by the AC-bipolar electropolymerization, which was performed for the first time, showed that the PEDOT fibers prepared in the dilute and concentrated electrolytes had similar conductivity. The thicker shape of the PEDOT fiber obtained in the concentrated electrolyte compared to the fibers obtained in the dilute electrolyte can be expected to be an electrode material for electrochemiluminescence (ECL) in a low-cost light-emitting device.

Chapter 4, “Pulsed Bipolar Electropolymerization,” aims to find a bipolar electrochemical deposition paradigm that can maintain 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 was investigated, and the PEDOT fibers, films, and other complex depositions were achieved by adjusting the PDC electrical signals, including pulse width, duty cycle factor, and waveform shape. The resulting PEDOT fibers (films) exhibited a fractal growth tendency, classified as a diffusion-limited aggregate (DLA)-like growth, while 2D or 3D depositions with relatively smooth boundaries were classified as a dense branching morphology (DBM)-like growth. These studies are expected to contribute to a better understanding of the fine tuning of the bipolar electrochemical deposition process.

Chapter 5, “General Conclusion,” summarizes the PEDOT fiber formation strategy in the BPE systems, which has been successfully applied to different electrolyte systems with low and high viscosities. The characterization suggests that the physical properties of the electrolyte play a crucial role in shaping the conducting polymer fibers. The findings in this research contribute to the future development of both conductive polymer chemistry and bipolar electrochemistry.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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