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Diffusion-limited characteristics of mechanically induced currents in polypyrrole/Au-membrane composites

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ABSTRACT

A mechanically induced current (MIC) in a polypyrrole/Au-coated membrane (PPy/Au-membrane) composite with various surface morphologies was investigated, and the electrolyte conditions were determined in an electrochemical cell. A MIC was induced on porous PPy/Au-membranes with a thin layer of PPy. Conversely, relatively small MICs were observed in non-highly porous films such as free-standing films and PPy/Au-membranes with thick PPy deposits. A MIC smaller by one order of magnitude was also observed in a Au-membrane without PPy. These results indicated that the MICs was due to a charging phenomenon in both the redox and the double layer capacitances. The MIC also varied with supporting electrolyte and their concentration. The MIC was strongly reduced in solutions with diluted electrolytes and with bulky cationic electrolytes, indicating that the number and the penetration speed of mobile ions limited the magnitude of the MIC. These characteristics indicated that the MIC was essentially a diffusion limited current. A two-electrode MIC cell was also configured to investigate a power generation film in a normal saline solution, which can possibly be utilized for biomedical applications.

1. Introduction

A mechanically induced current (MIC) in an electrochemical soft actuator is an interesting function that provides a strain sensor [1] and a power generation film. This functionality, combined with other features on soft actuators, such as light weight nature, flexibility and biocompatibility [2] can provide the possibility of fabrication novel-type sensors and related devices. Recently, both the MIC and the electrochemo-mechanical deformation (ECMD) have been frequently reported by many researchers [3,4]. These facts have suggested that redox active materials can convert between the energy states (i.e., electrochemical and mechanical states). Thus, a MIC is a type of counter-phenomenon of ECMD for redox active film [5]. Further investigations of MICs have provided structural optimization and modeling of coupling parameters between electrochemical and mechanical energies, and have been recently reported by several groups [6,7].

Charging an electronic double layer could be another route utilized for generating a MIC. A blank measurement would be required to investigate the individual contribution of the electronic double layer or the redox components. The mixing characteristics of both the electronic double layer and the redox components have already been reported by analyzing the cyclic voltammetry (CV) data for conducting polymers [8–10]. The physical charging values caused by a change in area, as in the electronic double layer, can be identified by the current level involved in the MIC. Similarities between the dependence of the MIC on the size of the ion or its concentration in the electrolyte should be investigated and compared to the redox contribution of the electrochemical actuator previously reported [11,12]. These characteristics could lead to the mechanism and a way to enhance the MIC effect.

The fabrication of these sensitive devices has provided a detailed insight of the generation mechanism for MICs and possible applications for practical use. Surface porosity has been determined to be a key factor for improving the redox current. A similar concept has also been incorporated to increase the actuation performance [13]. Incorporating a membrane filter into the device can be another route to fabricate the porous actuation films for supporting its free-standing characteristics, even with a thin active film deposition. Au possesses high ductility; therefore placing a Au coating on the filter surface before depositing the polymer can be an effective method to provide metallic high-conductance, even under expansion, by which the whole film surface can be held at the same redox potential. Thus the device can become sensitive to the redox equilibrium because of the highly conducting network by the Au.

A two-electrode structure has been determined to be an important configuration for the practical use of an electrochemical device. A two-electrode type MIC film can be fabricated even with a single type PPy or complemented ion exchange PPy films. A two-electrode

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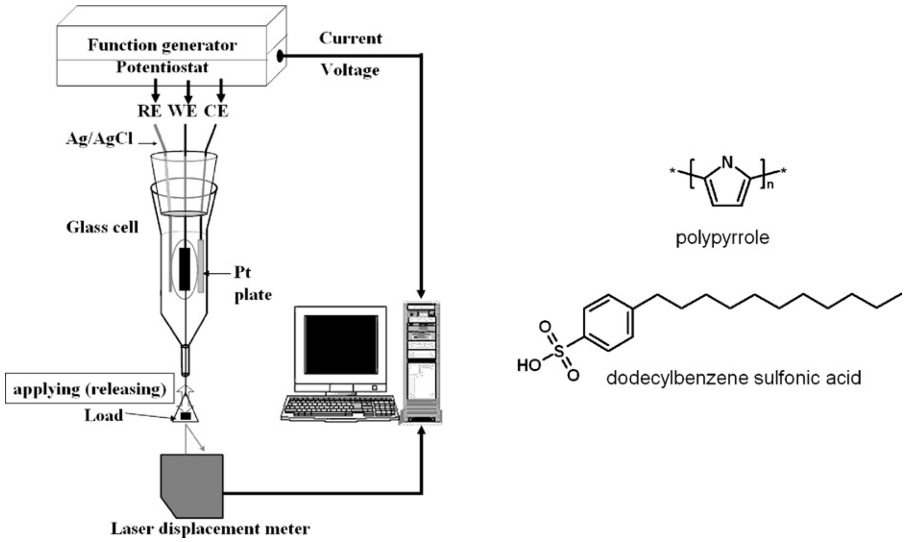

Fig. 1. Electrochemical cell configuration exhibiting the system set up and the chemicals utilized.

MIC film can be utilized as a power source film. The biocompatibility of polymers could incorporate such devices as power sources in vivo with low-impact.

Herein, MIC with ECMD in PPy freestanding films and Au-coated membrane (Au-membrane) composites with or without PPy deposition were investigated. MIC characteristics were investigated in PPy/Au-membrane composites as functions of the thickness of PPy, type of electrolyte and electrolyte concentration. The change in the magnitude of MICs in terms of the diffusive characteristics of the mobile ion with ECMD behaviors was also discussed. A two-electrode MIC device was also fabricated to investigate the output characteristics and the MIC generation functionality in buffer saline solution for practical use.

2. Experimental

The basic experimental conditions can be found in the literature [14]. The pyrrole monomer was distilled, and the other chemicals were used as received. The normal saline solution (NSS) was purchased from Otsuka Pharmaceutical Co., Ltd. The electrodeposition was performed in a dodceylbenzene sulfonate (DBS) solution galvanostatically at 1.0 mA/cm^2 at a range of times points to vary the concentration of the PPy coating. The ECMD, CV and MIC measurements were obtained using samples with the same rectangular shape in a single compartment of an electrochemical cell as previously reported (Fig. 1) [14]. The MIC was generated by modulating the load of 1.0 MPa under the application of a base load of 0.1 MPa. The supporting electrolyte was dissolved in degassed distilled water at the standard concentration of 1.0 M unless otherwise noted.

3. Results and discussion

3.1. Contribution of the electronic double layer on the MIC

Fig. 2 shows the induced current vs. electrochemical potential applied on an Au-membrane film without the PPy deposition. The figure illustrates that a MIC can be generated without PPy. The MIC potential map shows a proportional increase as a function of the absolute potential vs. polarity switch around the zero-potential region. These features are unlike those found in literature [5,14] which indicated that the MIC observed herein was attributed to the (dis)charging of the electronic double-layer capacitor with the modulation of the surface area caused by the tensioning load. However, the current level of this MIC was approximately one order of magnitude smaller than that in the PPy/Au-membrane composite described later in this document. Although the double layer charge was involved to some extent, the latter suggested that the MIC was dominated by the redox component. The dual components of the redox and the double layer charges have been already confirmed via electrochemical studies of conducting polymers [8–10]. It was important to note the duality between the charging behaviors in the MIC and the redox characteristics as it revealed the correlation between the MIC and ECMD via the electrochemistry of conducting polymers.

3.2. Surface morphology effect

The contribution of the surface porosity on the MIC was investigated in the PPy/Au-membrane and in the freestanding PPy films. The electrodeposition of PPy was tuned to control the weight per area of PPy to be 0.9 mg/cm^2 for both the PPy/Au-membrane and PPy freestanding films. Fig. 3 shows the potential map of the MIC,

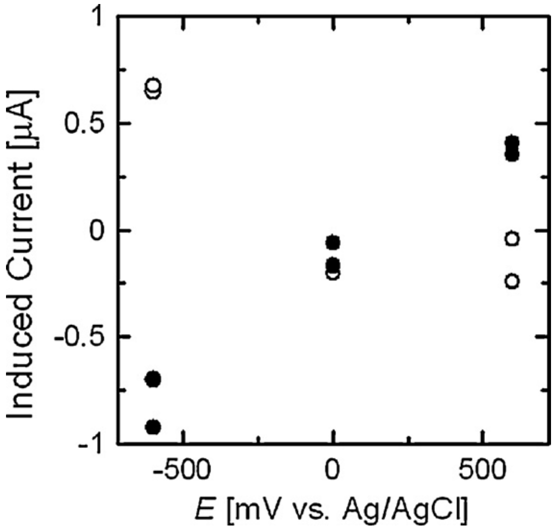

Fig. 2. Potential dependence of the MIC in a Au-membrane film. Solid circles and open circles represent MICs generated when applying and releasing a 1 MPa load, respectively.