



## New fabrication technique of conductive polymer/insulating polymer composite films and evaluation of biocompatibility in neuron cultures

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### ABSTRACT

Poly(vinyl alcohol), PVA, produces a flexible composite polymer film with electrical, optical and electrochemical properties very similar to those of polypyrrole (PPy). The rate of electrochemical polymerization depends on the diffusion rate of the electrolyte across the PVA film to the indium tin oxide (ITO) electrode. In particular, a solvent with a hydrophilic nature easily penetrates into the PVA film. By applying this new process, we demonstrate a unique method of forming an electrically conductive pattern in PVA film. It will be possible to develop electrodes for electrical stimulation of the nervous system using the conducting polymer, PPy. Then, by applying a similar technique, we fabricated poly(3,4-ethylenedioxythiophene), PEDOT/PVA, composite films and investigated their basic electrochemical properties. Moreover, in this study, in order to develop a novel cell-culture system which makes it possible to communicate with cultured cells, fibroblasts were cultured on PPy- and PEDOT-coated ITO conductive glass plates for 7 days. The result reveals that the PPy and PEDOT films support the secretory functions of the cells cultured on its surface. The PPy- and PEDOT-coated electrodes may be useful to culture the cells on.

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### 1. Foreword

Conductive polymers with extensive  $\pi$  electron conjugated systems in their main chain are considered to be organic semiconductors with relatively small bandgaps, and are being intensively studied as new materials in the field of physical chemistry. To date, various applications of conductive polymers, such as in semiconductor devices and optoelectronic devices, have also been proposed. Unfortunately, except for rechargeable batteries and capacitors, these applications have not yet been developed to the stage of practical use [1].

In order to fully exploit the potential offered by polymers, the device material must have good environmental stability and be processable in its polymeric form, while also having excellent electrical, optical, mechanical and other properties. However, many of these conducting polymers, which consist of rigid conjugated double bonds, show strong interchain interaction and generally are difficult to process due to their nonfusibility and insolubility. This is a serious problem in their practical utilization. However, by appropriate modification of the molecular structure of these polymers, such as the introduction of long alkyl side chains, the investigation of the polymerization process, and other developments, they have been made soluble in any solvent, and even fusible at relatively low

temperatures, and reveal good environmental stability. Accordingly, the study of conductive polymers has now reached a new stage.

A way to overcome the lack of processability of conductive polymers and to improve their electrical stability in air is to prepare composite materials based on conventional thermoplastic materials. That is, by some method, for example, by mixing and combining or connecting more than two kinds of materials with different characteristics, the fault of a single material can be compensated, and such a combined material that has characteristics not obtainable with a single material is called "a composite". *In situ* polymerization, involving the impregnation of a suitable insulating polymer with a catalyst, has been reported to give homogeneous conductive polymer/insulating polymer composites [2,3].

To date, various conductive polymers have been synthesized, but polypyrrole (PPy), the molecular structure of which is shown in Fig. 1, is the most stable after doping and is one of the most attractive materials, together with polyaniline (PAn), because of its good environmental stability and relatively high electrical conductivity.

Recently, when the electrochemical polymerization was performed using pyrrole as a working electrode of the ITO substrate coated by the insulating polymer, in that case, the polymerization current that might be from the insulating working electrode is observed, and the conductive polymer/insulating polymer composite film was found to be uniformly generated on the working electrode. In the present work, we elucidate the detailed characteristics of fabrication processes in order to gain a good understanding of the physical properties of composite films, and also, the functional applications of the obtained composite films were examined.

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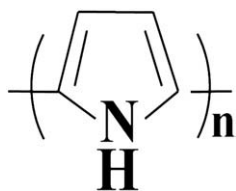


Fig. 1. Molecular structure of polypyrrole, PPy.

## 2. Electrochemical polymerization technique

In general, electrochemical polymerization technique is performed with the electrochemical polymerization equipment shown in Fig. 2. If the aromatization compound monomer that is to be polymerized is dissolved into a solvent containing a suitable supporting electrolyte and an appropriate voltage is applied to the electrode pair immersed into this solution, the monomer is oxidized or reduced on the surface of the anode or cathode, respectively, and it polymerizes in the form of a powder or a film and at times may show arborization [4]. The case in which the monomer is oxidized and polymerized on the anode surface is called an electrochemical oxidation polymerization. On the other hand, the case in which the monomer is reduced and polymerized on the surface of the cathode is called electrochemical reduction polymerization. The reference electrode might be immersed in the solution if necessary.

The most important point in this polymerization method is that the composition of the electrolyte, that is, the kind of solvent, the kind of supporting electrolyte, and the monomer, and the difference in the concentrations exert a strong effect on the polymerization reaction. Even when the same monomer is used, if the composition of the electrolyte is different, the form of the product might also differ greatly, and at times, the product might not be obtained at all. Besides this as a predominant factor of such an electrochemical polymerization reaction, it is likely that the applied voltage, the current density and the polymerization temperature, and, depending on the circumstances, the material of the electrode and the distance between electrodes, might also be periodic strong effects.

In order to obtain good-quality conductive polymer films by the electrochemical polymerization technique, it is necessary to examine the above predominant factors in detail and to understand the optimal electrochemical polymerization condition. Moreover, the conductive polymer can be reversibly electrochemically doped and dedoped and the dopant concentration can be widely adjusted by limiting the

voltage, enabling a film that has an arbitrary electric conductivity to be obtained.

## 3. Mechanism of electrochemical polymerization reaction

The reaction mechanism of conductive polymer synthesis by electrochemical polymerization has not been clarified, because various factors, such as the composition of the electrolyte and the electrolytic conditions, interact very complexly with the electrode reaction. Therefore, the polymerization reaction condition differs for each individual conductive polymer and the optimum conditions are determined through trial and error. However, qualitatively, the following reaction mechanisms are accepted in general. The dynamic movement of the molecule, which takes part in the monomer, and the electrolytic ion formed by the transfer of an electron from the solvent are caused at the interface between the electrode and the electrolyte in the electrochemical polymerization technique. Usually, 2–2.5 electrons are consumed in the electrochemical polymerization reaction, and ultimately, two pieces of electrons are used in the polymerization reaction and the remainder is used in the doping. As a result, the same number of protons ( $H^+$ ) that as the number of electrons used for the polymerization will accumulate in the polymerization liquid. Therefore, the polymerization reaction occurs as a result of the removal of the electron from the monomer, and the coupling reaction, in which the generated radical cation (positive ion) is assumed to be the activated species, and the deprotonation reaction are thought to progress repeatedly. The polymerization reaction is thought to be either reaction 1, the parent electron substitution coupling reaction, or reaction 2, the radical coupling reaction (Here, M indicates a monomer), as shown in Fig. 3. However, the structure analysis of the obtained polymer is difficult because the polymer is nonfusible and nonsoluble. Then, the polymerization reaction mechanism itself becomes very complex and a united opinion is not obtained, because electrochemical polymerization is a reaction of a nonuniform system that progresses in a limited area in the neighborhood of the electrode, and it is necessary to consider the supply of monomers and electrolytic ions to that area. That is, the electrochemical polymerization is thought to begin with the oxidizing or reducing reaction of the monomer in the electrolyte upon applying potential, followed by the generation of the radical cation or the radical anion in the aromatic compounds, and subsequently, the polymerization progresses repeated the coupling and the deprotonation reaction. It is necessary to prevent the solvent from undergoing the electrochemical reaction with the monomer at a low voltage, because the effects of the various factors such as the type of solvent, the supporting electrolyte, the polymerization voltage, and the polymerization temperature, on the electrochemical polymerization reaction are not yet fully clarified.

## 4. Experimental methods

As shown in Fig. 4, polyvinyl alcohol (PVA; saponification level: 78–82 mol%, the mean degree of polymerization: about 2000) was dissolved in distilled water. It was adjusted to the concentration of 20% and then spin-coated to a suitable thickness (about 300–900 nm) onto the ITO-coated glass substrate. The electrical conductivity of the obtained PVA film was about  $10^{-12}$  S/cm at room temperature.

The electrochemical polymerization was performed using an ITO-coated glass substrate with a working electrode of PVA a Ni plate as a counter electrode and an Ag wire as a reference electrode of the electrochemical cell shown in Fig. 2. The composition of the polymerization liquid used for the electrochemical polymerization is 0.1 mol/l pyrrole (Tokyo Kasei Inc., purity 98%) as the monomer, acetonitrile (Wako Pure Chemical Industries, Ltd., purity 99.5%) as the solvent and four-fluorinated boric acid tetrabutylammonium

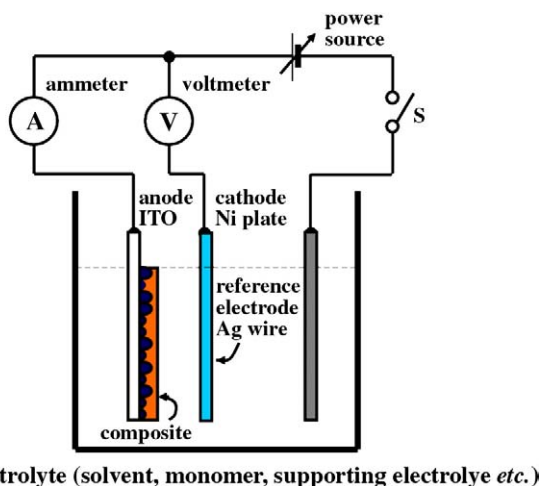


Fig. 2. Equipment of electrochemical polymerization.

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