CHEMISTRY LETTERS, pp. 687-690, 1986.

# CHARGE-CONTROLLABLE MEMBRANE.
# POLYPYRROLE-POLYELECTROLYTE COMPOSITE MEMBRANE THROUGH ANODIC DOPING PROCESS

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A new **PPy** composite membrane with **PE** was prepared by electropolymerization of **py** in the presence of **PE**. The **PPy/PE** film had highly tensile strength, and played a role as 'charge-controllable membrane'. A novel idea on the immobilized polymer dopant of **PPy** was presented.

Polypyrrole (**PPy**) and its analogs have been, very recently, expected not only as a promising candidate of low-dimensional conducting polymers but also as new materials with high performances.[1)] Convenience of electrochemical preparation and high resistance against moisture, air, and heat, have accelerated their advancement. Especially, their electrochemically anodic doping should be emphasized as their peculiar properties. The anodic doping mechanism can be placed a broad construction that the dopant is not necessarily an adopted supporting electrolyte anion, and that other negatively-charged molecules, even if it has much larger size, can be incorporated into **PPy** matrix as a 'dopant' only on electropolymerization. Some negatively-charged functional molecules have been incorporated into **PPy** matrix on electropolymerization of pyrrole (**py**) together with those functional molecules.[2-10)] We have been establishing this procedure systematically by adopting a wide variety of functional molecules as a dopant.[1,7)] Here, new **PPy** composite membrane (**PPy/PE**) doped with anionic polyelectrolytes (**PE**) was prepared.[8)] The **PE** reinforced **PPy** matrix by forming a polyion complex and played a significant role as an immobilized charge in a charge-controllable **PPy/PE** membrane.

A typical **PPy/PE** was obtained when **py** (0.2 mol $dm^{-3}$) was electropolymerized in water in the presence of **PE** (0.01 mol $dm^{-3}$), e.g., potassium poly(vinylsulfate) (**PVSK**, MW=$2.5 \times 10^5$), sodium poly(styrenesulfonate) (**PSSNa**, MW=$1.0 \times 10^5$). Sodium 1-pentanesulfonate (**ps**) was adopted as a low-molecular-weight dopant compared with **PE**. The **PPy/PVS** surface looked more homogeneously and more densely than the **PPy/ps**. (Fig. 1) The **PPy/PE**'s had as high conductivity ($\log \sigma = 0-1$) as an ordinary **PPy/Cl$^-$** prepared electrochemically in water ($\log \sigma = 1$), and they had 2-5 times more highly tensile strength (21 N/mm$^2$ for **PPy/PVS** and 49 N/mm$^2$ for **PPy/PSS**) than the **PPy/ps** (10 N/mm$^2$).[11)] The **PE** was incorporated into **PPy** chains with entanglement, so that the mechanical property was improved. Moreover, this specific composite structure scarcely affected its native conducting mechanism.

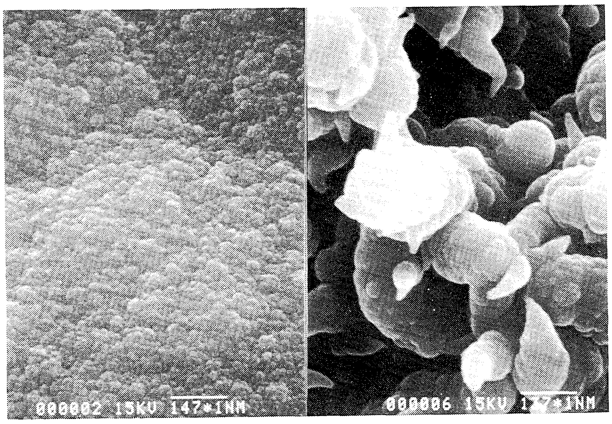

Fig. 1. The scanning electron microscopic images of the **PPy/PVS** composite film surface (left) and the **PPy/ps** film surface (right). The bars in the figures were $1.47\times10^{-7}$ m (left) and $1.37\times10^{-7}$ m (right).

The ratios of negativelly-charged groups of **PE** to a pyrrole unit of **PPy** (**S/py**-ratio) were 0.112 for **PPy/PVS** and 0.177 for **PPy/PSS**, from sulfur contents of 4.96 wt.% for **PPy/PVS** and 5.82 wt.% for **PPy/PSS**. Diaz et al. reported on the ratios of usual dopants ($Cl^-$, $BF_4^-$, etc.) to a pyrrole unit in the ordinary doped **PPy** being 0.25-0.33.12) The agreement, though a little smaller, of the **S/py**-ratios with Diaz's ratios indicated that the **PE** formed a 'polyion complex' with the oxidized **PPy** matrix through their electrostatic interaction. In short, **PE** functioned as a 'polymer dopant' (**PD**). However, the incorporated **PE** was scarcely undoped, i.e., released, (<2%) even when reducing the **PPy/PE** at -1.0 V vs. SCE for >1 h, different from an ordinary dopant. This incomplete undoping of the **PE** in **PPy/PE** implies a tight network of specific composite structure of twining **PE** with **PPy** matrix. This was also shown in a dopant-exchange reaction by cyclic potential sweep method. **PPy/PVS**-, **PPy/PSS**-, **PPy/ps**-, and ordinary **PPy/Cl**$^-$-coated (1400-3300 A) Pt wire electrodes (0.047 $cm^2$) showed $E_{1/2}$=-335 mV ($\Delta E_p$=210 mV), -370 mV (260 mV), -510 mV (360 mV), and +165 mV (170 mV) vs. SCE, respectively, in their cyclic voltammograms (200 mV/s of sweep rate) in aqueous solution containing 0.1 mol $dm^{-3}$ of each dopant as a supporting electrolyte.13) In 0.1 mol $dm^{-3}$ KCl aqueous solution, **PPy/PVS**- and **PPy/PSS**-electrodes reproduced their original cyclic voltammograms even during >500 potential sweeps between -0.8 V and 0.4 V. This observation illustrated that the incorporated **PVS** and **PSS** were scarcely exchanged with $Cl^-$ in the electrolytic solution. On the contrary, the cyclic voltammogram of **PPy/ps** was immediately changed into that of **PPy/Cl**$^-$, under the same condition. The **PPy/ps** showed an efficient dopant-exchange reaction (80% exchange yield from **ps** into $Cl^-$ within 10 cycles' sweep), similar to an ordinary **PPy**. The **ps** worked as a usual exchangeable dopant. The **PE** such as **PVS** and **PSS**, had low diffusional mobilities in **PPy** matrix. Conversely when an ordinary **PPy/Cl**$^-$-coated electrode was treated under cyclic potential sweep in aqueous solution containing each dopant (0.1 mol $dm^{-3}$) as a supporting electrolyte, the $Cl^-$ dopant was exchanged with **ps** at once but not with **PE**. A very low mobility of **PE** in **PPy/PE** matrix should be regarded as a unique and typical property of 'polymer dopant'.

So, how is the charge balance in the reduced **PPy/PE** kept? The incorporation of a supporting electrolyte cation into the reduced **PPy/PE** as a counterion should become an issue. The incorporated $K^+$ was detected ($5.0\times10^{-5}$ mol /g)14) for **PPy/PVS** reduced at -1.0 V in 0.1 mol $dm^{-3}$ KCl aqueous solution, while the oxidized **PPy/PVS** had no $K^+$. Of course, $K^+$ was not detected (<$1.0\times10^{-7}$ mol/g) in both the oxidized and the reduced **PPy/ps**'s. The incorporation and the release of $K^+$ balanced the immobilized charges of **PPy/PE** during redox reaction of **PPy**.

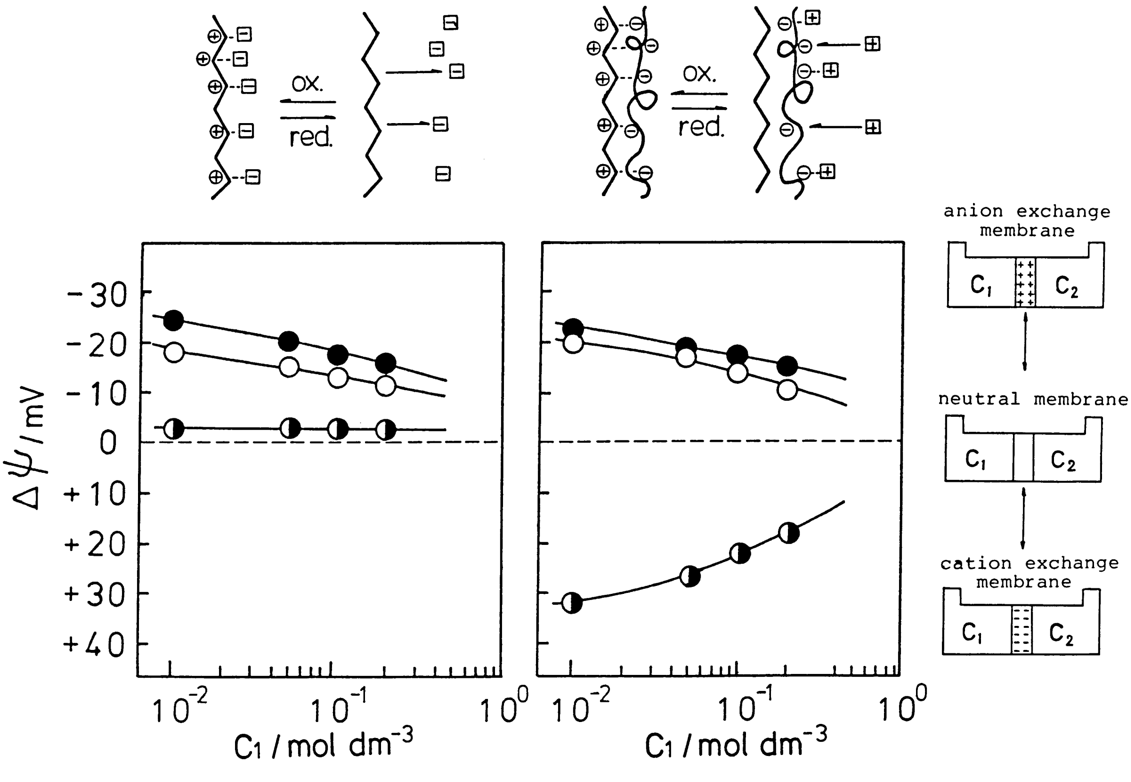

Fig. 2. The polarity changes of the fixed charges in the **PPy/ps** membrane (left) and the **PPy/PVS** membrane (right) for the oxidized and the reduced states, which were suggested by the membrane potential ($\Delta\psi$) measurement in KCl-concentration cell.15) (●): the prepared membrane, (◑): the reduced membrane at -1.0 V vs. SCE, (○): the oxidized membrane at +2.0 V. The negative $\Delta\psi$ meant the existence of a fixed positive charge in the membrane.

In this case, the small cation ($K^+$) behaved as a cathodic 'pseud-dopant'. The fact that the small cation is penetrated and is released along with reduction-oxidation of **PPy/PE** allowed us to regulate the polarity of the fixed charges in the **PPy/PE** matrices. The polarity was expected to be inverted reversibly toward the electrode potential. We terms the **PPy/PE** a 'charge-controllable membrane'. After preparing the **PPy/PE** or when oxidizing it at >0 V vs. SCE, two types of the fixed charges, the oxidized **PPy** and the **PE**, existed in the **PPy/PE** matrix, while on reducing it (<-0.6 V) the fixed negative charge of the **PE** remained in the matrix. The polarity change of the fixed charges in the **PPy/PE** was realized directly by measuring its membrane potential ($\Delta\psi$) in KCl concentration cell.15) The original, the reduced, and the re-oxidized **PPy/PVS** membranes (prepared by 18 C/cm$^2$ of electropolymerization, ca. 0.1 mm of thickness) had -22 mV, +32 mV, and -20 mV of $\Delta\psi$, while the **PPy/ps** membrane had -25 mV, -3 mV, and -18 mV, respectively, at $C_1$=0.01 mol dm$^{-3}$ and $C_2$=0.001 mol dm$^{-3}$ KCl aqueous solution.(Fig. 2) The inversion of $\Delta\psi$ polarity on reducing the **PPy/PVS** strongly suggested that the fixed negative charges of the **PE** stayed on. A $\Delta\psi$ change of **PPy/ps** means the appearance and disappearance of the fixed positive charge of the **PPy**, which corresponded to ac-impedance change of an ordinary **PPy** doped with $Cl^-$.16) The present **PPy/PE** having a wider range of $\Delta\psi$ change than an ordinary **PPy** has practical potential for the application to new types of an ion-selective-permeable membrane and an ion-exchange adsorbent in which the fixed charges are controlled electrically.

This study provided a novel idea on the immobilized dopant in the doping-undoping process of **PPy**. Also, we firstly (i) prepared a conducting **PPy/PD** film with highly tensile strength and (ii) demonstrated a pseud cathodic doping process of a supporting electrolyte cation in the **PPy/PE**. A considerably negative value of $\Delta\psi$ of the original and the re-oxidized **PPy/PE's**, which is against a primitive speculation that the $\Delta\psi$ should be essentially zero, can be interpreted at present by the oxidized **PPy** having more fixed, naked, and desolvated charges than the incorporated **PE**. A detailed study on the nature of fixed charges of the **PPy/PE** and on the dependences of the dopant size and charge on its diffusional mobility in **PPy** matrix is in progress.

This work was supported by Grant-in-Aid from Ministry of Education of Japan.

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13) $E_{1/2}$ and $\Delta E_p$ are half-wave potential and peak separation between anodic and cathodic peaks in cyclic voltammetry, respectively.
14) The incorporated $\mathbf{K^+}$ in the film was soaked out with 2 N HCl and its amount was measured with an atomic absorption analysis.
15) In the present study the negative $\Delta\psi$ means the existence of a fixed positive charge in the matrix. The **PPy** membrane (18 C/cm$^2$ of electropolymerization, about 0.1 mm of thickness) was put between two KCl aqueous solutions ($C_1$ and $C_2$) contacted with two Ag-AgCl reference electrodes through KCl-saturated agar bridges. A $\Delta\psi$ was measured as a potential difference of both electrodes when $C_1$ was changed from 0.01 mol dm$^{-3}$ to 0.2 mol dm$^{-3}$ with $C_1/C_2=10$.
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(Received January 31, 1986)