

# Junction Properties of Polypyrrole Containing a Small Amount of Poly(ethylene oxide) with Indium

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## INTRODUCTION

With a low work function metal such as indium,<sup>1</sup> *p*-type polypyrrole (PPY) is expected to form a rectifying contact, which has been given consideration by some researchers.<sup>2,3</sup> Still, the fact remained that during the evaporation process involved in the making of a sandwich-type device a contact may sometimes occur between two metal electrodes separated by a PPY layer,<sup>2,4,5</sup> as PPY is comparatively porous. To eliminate this defect, flexible and tough (PPY) containing a small amount of poly(ethylene oxide) (PEO) was prepared.

This paper is concerned with the electrical properties of the PPYs containing a small amount of PEO and their junction properties with indium.

## EXPERIMENTAL

### Materials and Reagents

PPY monomer and acetonitrile were supplied by Nakarai Chemicals and purified by distillation. Perchlorotetraethylammonium (PCTEA) from Nakarai Chemicals was used as received. PEO (Alcox E-45, MW 450,000) was supplied by Meisei Chemicals.

### Electrochemical Polymerization of Pyrrole in the Presence of PEO

The electrochemical polymerization of pyrrole was carried out in an electrolyte solution (100 mL of acetonitrile and 0.001 mol of PCTEA) containing a small amount of PEO. The polymerization conditions were as follows: polymerization temperature, 0°C; polymerization time, 60 min; for electrodes, a

sheet of conducting glass (Iwaki Glass, Glass EC) was used as an anode and a platinum plate as a cathode; and voltage, 1.0 volt against SCE. The PPY films containing a small amount of PEO (PPY-PEO) were washed with cold water for 1 h followed by cold methyl alcohol for 1 h, air-dried, and dried in vacuum at 50°C for 4 h.

### Heat Treatment

The PPY-PEO films were peeled from the electrode and heat-treated at 80°C for 8 h in nitrogen atmosphere or in air.

### Conductivity Measurements

The conductivities were measured both in a planar direction and in a vertical direction, with a digital multimeter (Takeda Riken TR-8853) or with an electrometer (Takeda Riken TR-8651) using gold electrodes.

### Fabrication of a Sandwich-type Device (Indium/PPY-PEO/Gold)<sup>6</sup>

A schematic representation of the device is shown in Figure 1.

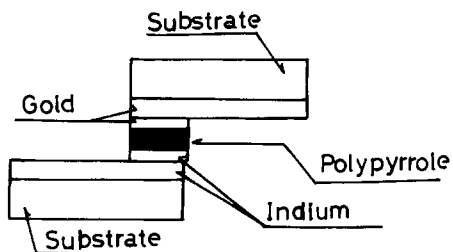
### Measurement of the Current Density-Voltage (*J*-*V*) Characteristics

The *J*-*V* characteristics were measured with a function generator (Kikusui Corporation, 458A) and recorded using an X-Y recorder (Watanabe Sokki Corporation, WX-4401).

### Measurement of the Capacitance-Voltage (*C*-*V*) Characteristic

The *C*-*V* characteristic was measured with an impedance analyzer (Yokogawa Hewlett-Packard, YHP-4192, LCZ meter).

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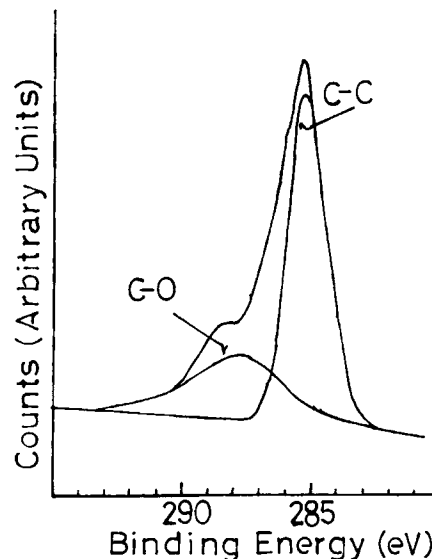


**Figure 1** Schematic representation of an indium/PPY/gold device.

## RESULTS AND DISCUSSION

### Preparation of PPY-PEO Films and Their Electrical Properties

The PPY-PEO samples were prepared by electrochemical polymerization of pyrrole in the presence of PEO. The preparation conditions and their conductivities are shown in Table I. The conductivity (conductivity reported: ca. 10–100 s/cm [Ref. 7]) decreased with increasing PEO contents in the electrolyte solution. It is estimated that the decrease in conductivity is due to an increased amount of insulating material, such as PEO. PEO in the sample was recognized qualitatively by XPS measurement (see Fig. 2). The weight losses after extracting both with hot water and by hot methyl alcohol were also measured and the results are shown in Table I. It is apparent that samples prepared in solutions containing increased amounts of PEO were increasingly rich in PEO. These results reveal that weak bonds (hydrogen bonds) become established on mixing



**Figure 2** X-ray photoemission spectroscopy of PPY-PEO.

PEO and PPY. After the preparation, the conductivity of PPY generally decreases as a function of time. For the above-mentioned four samples, the changes in conductivity were compared after keeping them for 1000 h at room temperature in a desiccator. Although the conductivity of the PPY-PEO mixture was reduced to about 80% of the original one, the value recorded for PPY prepared as a reference was reduced to 60%. The changes in conductivity after heat treatment at 80°C were also compared (see Table I). Though the conductivity of PPY was reduced to a large extent by the heat treatment,<sup>8</sup> that of the (PPY-PEO) compositions was comparatively stable. From these results, it seems that the structure of PPY-PEO was strongly improved by a combination of PPY with PEO. The conductivities were measured both in a vertical direction and in a planar direction using gold electrodes (Ohmic contact was confirmed for each sample) and are also shown in Table I. A difference was found between the conductivities in a vertical direction and in a planar direction: 5.1–11.7 s/cm for a planar direction and  $1.5 \times 10^{-3}$ – $5.0 \times 10^{-3}$  s/cm for a vertical direction (see Fig. 3). It is considered that PPY molecules have a tendency to orient along the electrodes in the electrical polymerization at a high voltage,<sup>9</sup> so that an anisotropy of conductivity can be observed. The temperature dependence of the conductivity (–100 to +100°C) is shown in Figure 3. Generally, the conductivity increases with increasing temperature and is semiconductorlike.<sup>10</sup>

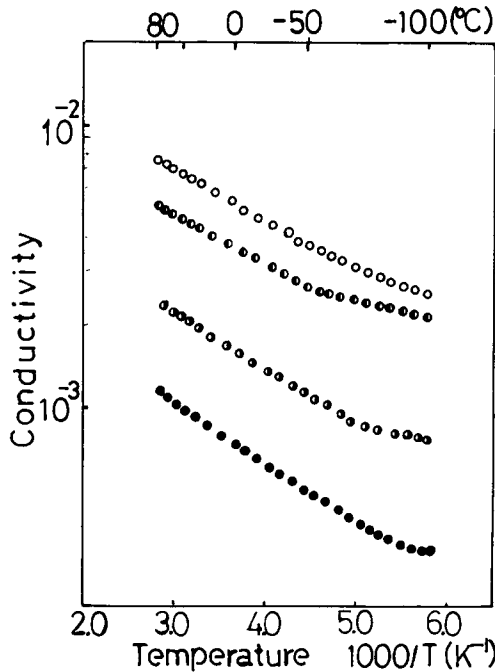
**Table I** Preparation Conditions of PPY-PEO Samples and Their Conductivities

Sample	PEO Conc'n/ PEO Content <sup>b</sup> in Solution <sup>a</sup>		Conductivity	
	wt %	wt %	No Heat Treatment (S/cm)	80°C <sup>c</sup> (s/cm)
P-0	—	—	31.8	5.0
P-1	0.5	0.6	11.7	8.4
P-2	1.0	1.5	5.9	3.0
P-3	1.5	2.5	5.1	2.6

<sup>a</sup> Electrolyte solution : pyrrole, 0.01 mol; acetonitrile, 100 mL;  $(C_2H_5)_4NClO_4$ , 0.01 mol.

<sup>b</sup> Determined by extraction for 10 h both with hot methyl alcohol and hot water.

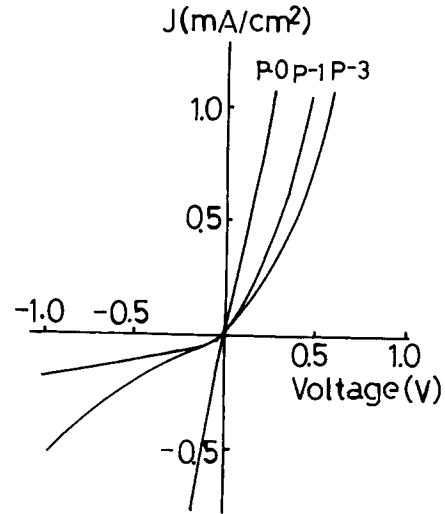
<sup>c</sup> In nitrogen.



**Figure 3** Relationship between conductivity and  $1/T$  for PPY and PPY-PEO: (○) P-0; (◐) P-1; (◑) P-2; (●) P-3.

#### Junction Properties of PPY-PEO with Indium

Sandwich-type devices were prepared with three kinds of PPY-PEO and PPY. The devices of as-prepared PPY-PEO samples as well as that prepared with PPY did not give stable rectifying contacts for indium, but a rectifying contact was observed when the heat-treated PPY-PEO composition samples were used in the devices. The  $J$ - $V$  characteristics of devices obtained from P-1 to P-3 are shown in Figure 4, compared with a device prepared with PPY (P-0). It is apparent that in the device made from PPY-PEO samples higher PEO contents exhibited an outstanding rectifying property. It was considered that the rectifying property is due to increasing uniformity of the films thus formed, as PEO molten above the melting point of PEO ( $70^{\circ}\text{C}$ ) was finally mixed with PPY by heat treatment. It has also reported<sup>11,12</sup> that a rectifying contact of poly(*N*-methyl pyrrole) with indium was improved by heat treatment and the rectifying property was due to the oxide layer formed during the heat treatment. Accordingly, the discrepancy between the after heat treatment in air and the after heat treatment in nitrogen was compared, but hardly any difference was observed. In this case, the physical conditions of the film are probably important.



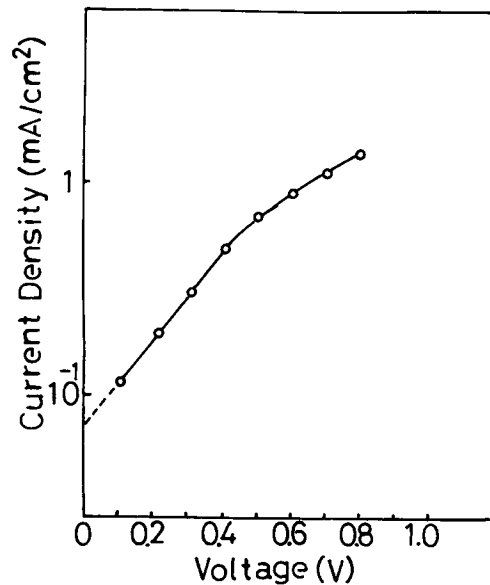
**Figure 4**  $J$ - $V$  characteristics for indium/PPY or PPY-PEO/gold devices at  $25^{\circ}\text{C}$ .

According to the thermionic emission theory, the rectifying properties are expressed as follows:

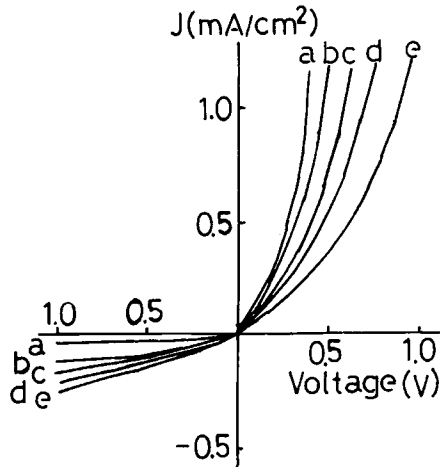
$$J = J_0 \exp(qV/\eta kT) \quad (1)$$

$$J_0 = A^* T^2 \exp(-q\phi_b/kT) \quad (2)$$

where  $J$  is the current density;  $J_0$ , the reverse current density;  $V$ , the bias voltage;  $\eta$ , the ideal factor;  $A^*$ , the Richardson constant, and  $\phi$ , the barrier height.

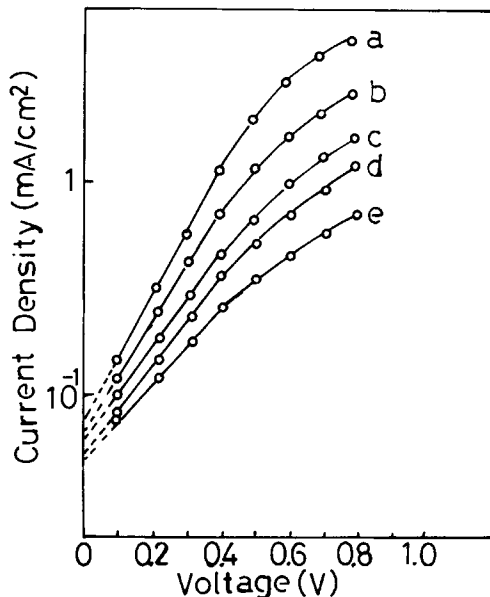


**Figure 5** Log  $J$ - $V$  plots for indium/PPY-PEO (P-3)/gold devices at  $25^{\circ}\text{C}$ .

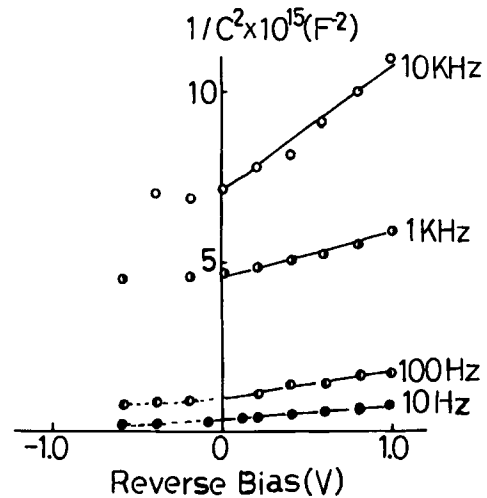


**Figure 6**  $J$ - $V$  characteristics for indium/PPY-PEO (P-3)/gold devices at various temperatures: (a) 373 K; (b) 323 K; (c) 273 K; (d) 233 K; (e) 193 K.

In Figure 4, the logarithm of the current density is plotted against the bias voltage, and the relationship is shown in Figure 5. In the 0.1–0.4 V range, the relation was found to be linear as predicted from eqs. (1) and (2). The  $J$ - $V$  characteristics of indium/PPY-PEO (P-3)/gold at different temperatures are shown in Figure 6. At each temperature, the relation between the logarithm of the current density and the bias voltage is also linear (see Fig. 7).



**Figure 7** Log  $J$ - $V$  plots for indium/PPY-PEO (P-3)/gold devices at various temperatures: (a) 373 K; (b) 323 K; (c) 273 K; (d) 233 K; (e) 193 K.



**Figure 8**  $1/C^2$  vs. reverse bias plots for indium/PPY-PEO (P-3)/gold.

From these results, it was estimated that Schottky barriers were formed between PPY-PEO and indium at each temperature. Using eqs. (1) and (2), the ideal factors and the barrier height were calculated: The barrier height was in the 0.4–0.8 range, and the ideal factor, in the 6–8 range. Judging from the ideal factor, the Schottky barrier is probably imperfect. On the other hand, the Schottky barrier was also discussed on the basis of capacitance measurements. The capacitance–reverse bias voltage relationship is shown in Figure 8. The capacitance of the junction (P-3) increased with increased reverse bias voltage. This suggests that the Schottky barrier is formed between PPY-PEO and indium. The numerical analysis, however, was difficult because the ideal factors were too high and the Schottky barrier was not perfect.

## CONCLUSION

Polypyrroles containing a small amount of poly(ethylene oxide) (PPY-PEO) were prepared by electrochemical polymerization of pyrrole in the presence of PEO. The conductivity decreased with increasing PEO contents of the PPY-PEO samples. The PPY-PEO samples, however, were more stable and the change in conductivity resulting from aging or heat treatment was comparatively small.

The devices were fabricated with the PPY-PEO materials and indium and the junction properties were measured. The rectifying contacts between

PPY-PEO and indium were observed in heat-treated PPY-PEO samples. From the capacitance-voltage measurement, it is estimated that a Schottky barrier is formed.

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Received November 10, 1988

Accepted March 13, 1991