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Technical Notes

New Four-Band Electrode Fabrication To Measure in Situ Electrical Property of Conducting Polymers

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A simple and renewable four-band platinum electrode for in situ conductivity measurement of polymers is described. A model is developed to evaluate contact resistance between the electrode and polyaniline film and calibrate the film resistances obtained by two-probe and four-probe methods. The conductivity of the film is calculated from the calibrated resistance. By comparing the effects of band thickness, gap width, and film thickness, it is found that the ratio K of the middle gap width to the thickness of the internal two platinum bands is the most important parameter to characterize one four-band electrode. An ideal four-band electrode should have large K and wide middle gap as possible so long as the film can uniformly cover the electrode. Under this case, the influence of contact resistance on the four-probe measurement of film resistance is negligible. It is shown that contact resistance depends on the oxidation state of the film. It rises nonlinearly with increasing film resistance.

Conducting polymers have been a subject of intensive research in the last 2 decades. Their conducting properties strongly depend on the doping level. A large number of different methods to characterize conducting polymers have been devised. One of the most important characteristics of a conducting polymer is its conductivity. The methods to measure the conductivity can be classified as ex situ and in situ methods. The ex situ conductivity of a conducting polymer is usually determined by the conventional four-point probe technique.¹ The main limitation of this technique is the lack of information about the behavior of the conductivity as a function of the applied potential. Moreover, some irreversible changes such as air oxidation, contamination, and mechanical damage might occur, which damages the conducting property of polymers. Hence, it is always desirable to apply in situ methods to measure conductance of conducting polymers.

A few in situ two-probe methods to measure the conductance of conducting polymers have been also proposed.^{2–20} The different geometrical dimension electrodes such as microelectrode array,^{2,3,5} twin electrode thin-layer cell,^{4,5} sandwich electrode,^{5,6} dual-disk microelectrode,⁷ and double-band electrode^{14–17} were devised. Zotti and co-workers^{17–20} described a renewable double-band microelectrode for in situ measurement of some polymers such as polypyrrole, poly(*N*-methylpyrrole), polythiophene, and poly(ethylenedioxythiophene). They electrochemically deposited conducting polymer onto two closely spaced platinum bands so that the polymer covered the electrodes and the insulating gap between the electrodes. The construction of the electrode allows easy renewal of the surface for repeated measurements. A chosen potential is applied on a Pt band by one potentiostat, while the conductivity is determined using a small dc voltage applied by a second potentiostat. Although relatively widely used, the two-probe method used by Zotti and co-workers only gives relative conductivity. An external reference polymer has to be used to measure

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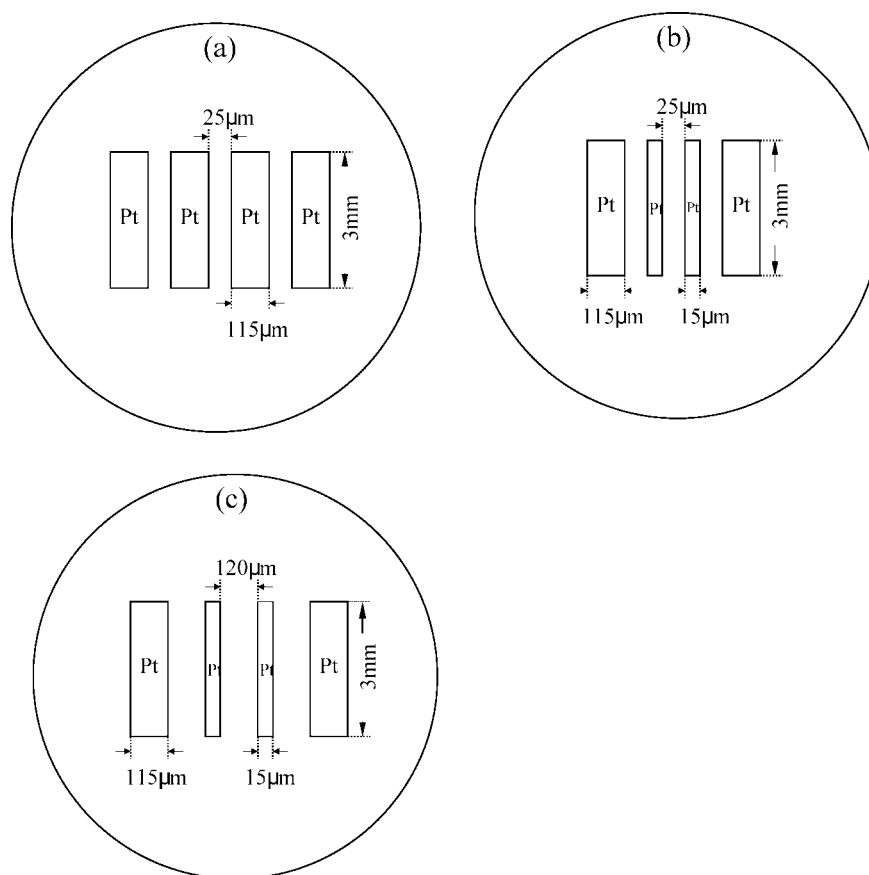


Figure 1. Schematic diagram of the four-band platinum electrodes: (a) electrode A; (b) electrode B; (c) electrode C.

the so-called cell constant under semi-infinite volume condition. The conductivity of this reference polymer must be accurately determined by other techniques.

Cai et al.²¹ measured the conductivity of conducting polymer using an in situ four-probe method. Four platinum lines with a diameter of 0.5 mm were put in parallel with gap width of 0.1 mm and sealed into a tube. The polymer was deposited on the cross section of the tube. It is actually a four-disk electrode. However, it is obviously not a better electrode design because the real gap width between adjacent platinum lines and the film width could not be exactly given for this kind of electrode. Hence, it is necessary to devise a new electrode for in situ four-probe measurement, which can exactly and conveniently calculate the film conductivity.

In most papers about in situ conductance measurement of conducting polymers, the contact resistance between the polymer film and metal electrode is regarded as negligible. An electropolymerized polymer on an electrode for in situ four-probe resistance measurement is usually different from a standard ex situ four-point probe sample, and then the effect of contact resistance should be considered. Therefore, it is interesting to analyze the effect of contact resistance on conductance measurement of polymers for in situ two-probe or four-probe methods under different doping potentials. Papers about this topic are rarely published.

In this paper we report the construction of a simple four-band electrode for repetitive and reproducible in situ measurements

of the conductivity. By comparing the resistances of polyaniline film measured by two-probe and four-probe methods, a model is elaborated to evaluate the influence of contact resistance between the electrode and polyaniline film and calibrate the measured resistance. The construction parameters of an ideal four-band electrode for in situ conductivity measurement by the four-probe method are proposed.

EXPERIMENTAL SECTION

All chemicals were purchased from Tokyo Kasei Co. Aniline and acetonitrile (MeCN) were used after distillation. Tetraethylammonium perchlorate (Et_4NClO_4) was purified by recrystallization from ethanol. Polyaniline (PANI) films were prepared on a four-band electrode by cycling the potential between -0.2 and 1.0 V versus $\text{Ag}/\text{AgCl}/\text{saturated NaCl}$ at a sweep rate of 100 mV/s in a 2.3 M perchloric acid solution with 1.3 M aniline. The platinum bands and gaps were uniformly covered by the polyaniline film.^{22,23} After polymerization, the films were rinsed thoroughly with distilled water and dried in air. They were then transferred to MeCN solution containing 0.1 M TEAP and subsequently dedoped at -0.7 V for 30 min. In situ measurements were performed on the film from reduced to doped state. This applied potential is referred to as the doping potential.

Three types of four-band platinum electrodes were fabricated

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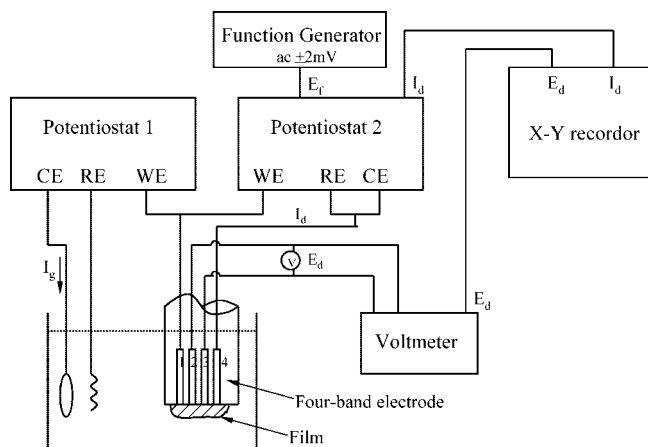


Figure 2. Schematic illustration of the electrochemical apparatus for in situ conductance measurement in MeCN + 0.1 M TEAP.

as shown in Figure 1. Four platinum foils 3 mm wide and 15 or 115 μm thick are separated by thin insulating mica film. The complete system was embedded in epoxy resin at the end of a glass tube. The end of the sealed tube was first ground with fine emery papers and then polished with alumina powder (0.3 μm). The four-band system has a high open-circuit resistance (>20 M Ω). Three electrodes of different Pt band and gap widths are called electrodes A, B, and C, respectively. Before the coating is fabricated, the four-band electrode is always polished again.

The film resistance measurements were performed with the apparatus illustrated in Figure 2. The PANI film was first brought to the desired potential by potentiostat 1 (Hokuto Denko HAB-151). After I_g is close to zero, a constant current I_d is applied between the outer two bands of the four-band electrode by potentiostat 2 (Hokuto Denko HAB-151) and registering the voltage E_d between the internal two platinum bands. So the film resistance R and conductivity σ are calculated by the following formula:

$$R = \frac{E_d}{I_d} \quad (1)$$

$$\sigma = \frac{L}{Rlh} \quad (2)$$

where L is the gap width between the internal two bands, l is the Pt band length of 3 mm, and h is the film thickness. In order to decrease the applied current I_d and the influence of interface capacitance and improve the measurement accuracy, a triangular wave E_f of ultralow frequency of 10–50 mHz with amplitude of 2 mV is applied between the outer two bands. It is generated by one function generator and input into potentiostat 2 as shown in Figure 2. In fact, the current I_d changes slowly with E_f . The E_d between the internal two bands will also change correspondingly with I_d . The E_d and I_d are simultaneously recorded on one X–Y recorder. A straight line is drawn on the section paper; thus, the film resistance can be exactly calculated from the slope of the straight line.

For comparison, if the output lines of potentiostat 2 in Figure 2 are connected with the internal two bands instead of the outer two bands, Figure 2 becomes a schematic diagram of a two-probe measurement. Hence, in this work we may compare the resis-

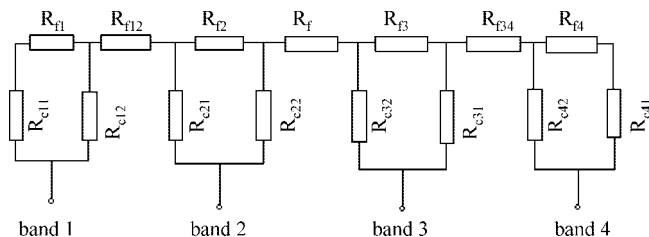


Figure 3. Equivalent circuit of film resistance measurement on a four-band electrode by two-probe and four-probe methods.

tances obtained by two-probe and four-probe methods for one sample, then contact resistance and film resistance will be calculated and calibrated as described in following section. Usually, the electrosynthetic film thickness is estimated by the charge amount of polymerization or other indirect methods.^{7,21} In this work, the thickness of the PANI film is directly measured by a shift of the focus plane of an optical microscope (Olympus BH2-UMA) as done in metallography. In order to improve the measurement accuracy of the coating thickness, the shift scale of the focus plane of this microscope was verified using a standard glass plate of 100 μm thickness. The film thickness on the whole electrode is observed, and it is found that the non-uniformity of film thickness at different positions of the electrode under the above polymerization conditions is less than 10%. In following sections, the average thickness of each film was used.

FILM RESISTANCE MODEL ON THE FOUR-BAND ELECTRODE

A simplified equivalent circuit of film resistance on a four-band electrode is illustrated in Figure 3. R_{f12} , R_f , and R_{f34} are the resistances of the film on the three gaps. R_{f1} , R_{f2} , R_{f3} , and R_{f4} refer to the resistances of the film on the four platinum bands, respectively. R_{c11} , R_{c12} , ..., R_{c42} are contact resistances between the band and film. A microarray electrode fabricated by photolithography has a high resistance for the electrode itself due to coating very thin Pt or Au film as the electrode.^{2,3,13} It will not be able to be used if the film resistance is much lower than that of the electrode itself. In this work, the thickness of platinum bands of over 15 μm thick are utilized and their resistance is negligible.

During resistance measurement by two-probe and four-probe methods, the real current distribution in the film on a four-band electrode is complex. When a potential is applied on one platinum band the current transfers from this band to the film. To simplify the treatment, it is assumed that this current is divided into two components. One component passes the interface between the film and band into the film on this platinum band, then into the film on the insulating gap. Another component transforms directly from the interface to the film on the gap. For example, the first part of the current transforms from band 1 to R_{c11} , R_{f1} , then into R_{f12} . Another part passes from band 1 to R_{c12} and then to R_{f12} . Thus, the contact resistance R_{c1} of band 1 is divided by two parallel resistances of R_{c11} and R_{c12} ($R_{c1} = R_{c11}R_{c12}/(R_{c11} + R_{c12})$).

For two-probe measurement, the small bias voltage V_{23} is applied between band 2 and band 3, and the corresponding current I_{23} is detected. The R_{23} is inferred according to the equivalent circuit in Figure 3 as follows:

$$R_{23} = \frac{V_{23}}{I_{23}} = R_f + \frac{R_{c22}(R_{f2} + R_{c21})}{R_{f2} + R_{c21} + R_{c22}} + \frac{R_{c32}(R_{f3} + R_{c31})}{R_{f3} + R_{c31} + R_{c32}} \quad (3)$$

Similarly, for four-probe measurement, a tiny current I_{14} is passed from band 1 to band 4, and the potential difference V_{23} between band 2 and band 3 is measured. As shown in Figure 3, R_{f2} and $R_{c21} + R_{c22}$, R_{f3} , and $R_{c31} + R_{c32}$ form two parallel circuits. It is assumed that the current can transfer from the film to the platinum band, output from the band to the other side of the film again. R_a by the four-probe method is inferred from this equivalent circuit as follows:

$$R_a = \frac{V_{23}}{I_{14}} = R_f + \frac{R_{f2}R_{c22}}{R_{f2} + R_{c21} + R_{c22}} + \frac{R_{f3}R_{c32}}{R_{f3} + R_{c31} + R_{c32}} \quad (4)$$

So the resistance difference ΔR of two-probe and four-probe measurements may be inferred from eqs 3 and 4:

$$\Delta R = R_{23} - R_a = \frac{R_{c21}R_{c22}}{R_{f2} + R_{c21} + R_{c22}} + \frac{R_{c31}R_{c32}}{R_{f3} + R_{c31} + R_{c32}} \quad (5)$$

If band 2 and band 3 have the same dimensions and the film on the four-band electrode is uniformly covered, then

$$R_{f2} = R_{f3} \quad (6)$$

$$R_f = KR_{f2} \quad (7)$$

We here define that K , the ratio of the gap width between band 2 and band 3 to the thickness of platinum band 2 or 3, is the geometric factor of a four-band electrode. The K 's of electrodes A, B, and C in Figure 1 are 0.217, 1.67, and 8, respectively.

Moreover, in order to make the calculation of the above equations feasible, we assume:

$$R_{c21} = R_{c22} = R_{c31} = R_{c32} = 2R_{c2} \quad (8)$$

R_{c2} is the contact resistance of band 2 or band 3 with the film. So eqs 3–5 are simplified into eqs 9–16.

$$R_{23} = R_f + \frac{4R_{c2}\left(2 + \frac{R_{f2}}{R_{c2}}\right)}{4 + \frac{R_{f2}}{R_{c2}}} \quad (9)$$

$$R_a = R_f + \frac{4}{\frac{4}{R_{f2}} + \frac{1}{R_{c2}}} = KR_{f2} + \frac{4}{\frac{4}{R_{f2}} + \frac{1}{R_{c2}}} \quad (10)$$

$$\Delta R = R_{23} - R_a = \frac{8R_{c2}}{4 + \frac{R_{f2}}{R_{c2}}} \quad (11)$$

Solving eqs 9–11, the film resistance R_f on the middle gap and contact resistance R_{c2} are obtained as

$$R_f = R_a - \frac{2R_a}{(K+1) + \sqrt{(K+1)^2 + \frac{2K(R_a)}{\Delta R}}} \quad (12)$$

$$R_{c2} = \frac{\Delta R(K-1) + \sqrt{\Delta R^2(K+1)^2 + 2K(\Delta R)(R_a)}}{4K} \quad (13)$$

where K is a constant for one four-band electrode. R_a , R_{23} , and ΔR are obtained from experiment. Therefore, R_f and R_{c2} can be calculated from eqs 12 and 13. Then the conductivity of the film is calculated from eq 2, where R_f substitutes R_a . The difference of R_a and R_f is expressed as

$$\frac{R_a - R_f}{R_a} = \frac{2}{(K+1) + \sqrt{(K+1)^2 + \frac{2K(R_a)}{\Delta R}}} \quad (14)$$

However, the validity of this model for calibrating the measurement resistance of film on a four-band electrode will have to be experimentally verified by changing the widths of the middle gap and platinum band and film thickness. If the model can explain the changes of R_{23} and R_a under various conditions, the assumptions to infer the above model will be acceptable.

RESULTS AND DISCUSSION

Resistance Measurement of Polyaniline Film under Different Doping Potentials. Before discussion, it is noteworthy to point out the reproducibility of the measurements is considerably satisfactory. The variations were not higher than 10–20% among different samples electrosynthesized under the same condition and much less changes in the same sample for different runs.

Figure 4 depicts the dependence of R_{23} , R_a , and R_f on doping potential for the polyaniline film. R_{23} and R_a are measured by two-probe and four-probe methods, respectively. R_f is calculated from eq 12. The film thicknesses in Figure 4, parts a, c, and e, are only 35–45 μm . On the contrary, the films in Figure 4, parts b, d, and f, are very thick with 180–250 μm . Electrode A (Figure 4, parts a and b) and electrode B (Figure 4, parts c and d) have a same middle gap width of 25 μm and a different platinum bandwidth of 115 and 15 μm , respectively. However, the middle gap width of electrode C (Figure 4, parts e and f) increases to 120 μm while the narrow Pt bands of 15 μm for band 2 and band 3 are used as well as electrode B.

The doping level of the polyaniline film rises with increasing doping potential,^{22,23} and then the resistivity of the film decreases correspondingly. Hence, the film resistance rapidly reduces several orders of magnitude with an increase of doping potential as shown in Figure 4a–f.

Figure 4 also responds to the effect of gap width, bandwidth, and film thickness on the film resistance. When Figure 4, parts a, c, and e, is compared with Figure 4, parts b, d, and f, the difference of R_{23} and R_a enlarges while increasing the film thickness. For a sample with a large bandwidth and relatively thin film (see Figure 4a), R_{23} and R_a are almost the same. However, if decreasing the width of internal two bands, the difference of R_{23} and R_a will enlarge (see Figure 4c). On the other hand, when R_f is compared with R_a , it is found that their

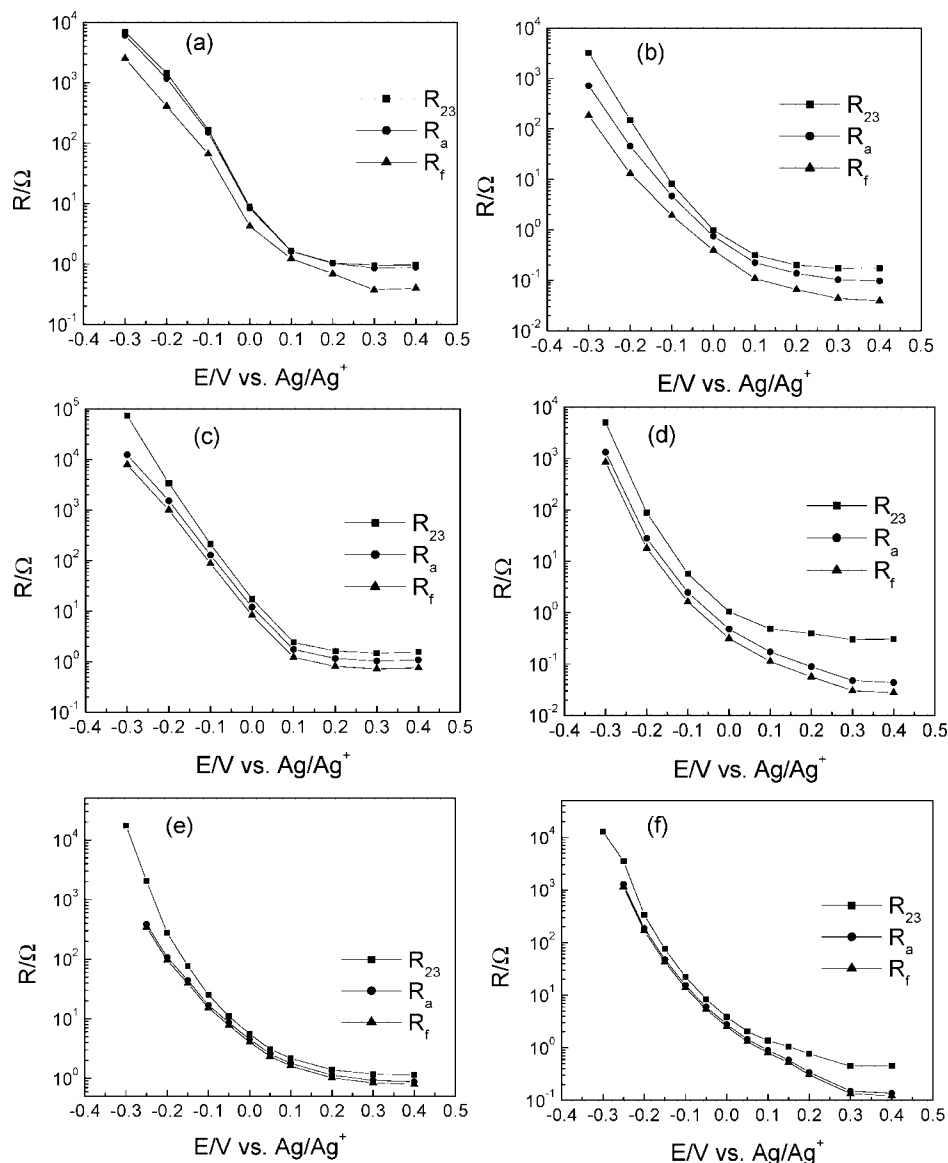


Figure 4. Dependence of resistances R_{23} , R_a , and R_f on doping potential for polyaniline film: (a) electrode A (film thickness 35 μm); (b) electrode A (film thickness 240 μm); (c) electrode B (film thickness 45 μm); (d) electrode B (film thickness 180 μm); (e) electrode C (film thickness 45 μm); (f) electrode C (film thickness 250 μm).

difference for electrode A is the largest among the three electrodes. On the contrary, the resistance difference of R_f and R_a for electrode C with a wide gap and narrow platinum band is much smaller than that for electrodes A and B. It will be explained using the change of geometric factor K in a later section.

Contact Resistance at the Electrode–Film Interface. Contact resistance between PANI film and band 2 is calculated from eq 13. Its dependence on doping potential is described in Figure 5. When Figure 4 is compared to Figure 5, R_{c2} , R_{23} , and R_a have a similar tendency to change with doping potential. Figure 5 shows that the contact resistance at the electrode–polyaniline interface is not a fixed value and changes in a large range with doping potential. It implies that the contact resistance is related to the film resistance. Under higher doping potential, the contact resistance as well as the film resistance is very small. When the doping potential reduces, the film resistance increases rapidly due to low doping level; in this case, the contact resistance increases several orders of magnitude as illustrated in Figure 5.

On the other hand, the contact resistance for electrode C seems to be independent of film thickness (see Figure 5c). However, the contact resistance of the thin film for electrodes A and B is not equal to that of the thick film; their difference is larger under low doping potential (see Figure 5, parts a and b). It is usually considered that the contact resistance for one electrode under an ideal case should be independent of film thickness, whereas Figure 5 shows that the contact resistance is not a steady value, and there are other factors to influence it besides the film resistance.

Figure 6 illustrates the relationship of resistance difference ΔR by two-probe and four-probe measurements and contact resistance R_{c2} . Linear regression is carried out for these measurement points under different doping potentials, and the fitted parameters are given in the plots. It is found that for the electrode system with different gap widths, bandwidths, and film thicknesses, $\log_{10} \Delta R$ to $\log_{10}(R_{c2})$ is always a linear relation. Nevertheless, the standard deviation of regression for electrode A is larger than that for electrodes B and C. The data points in

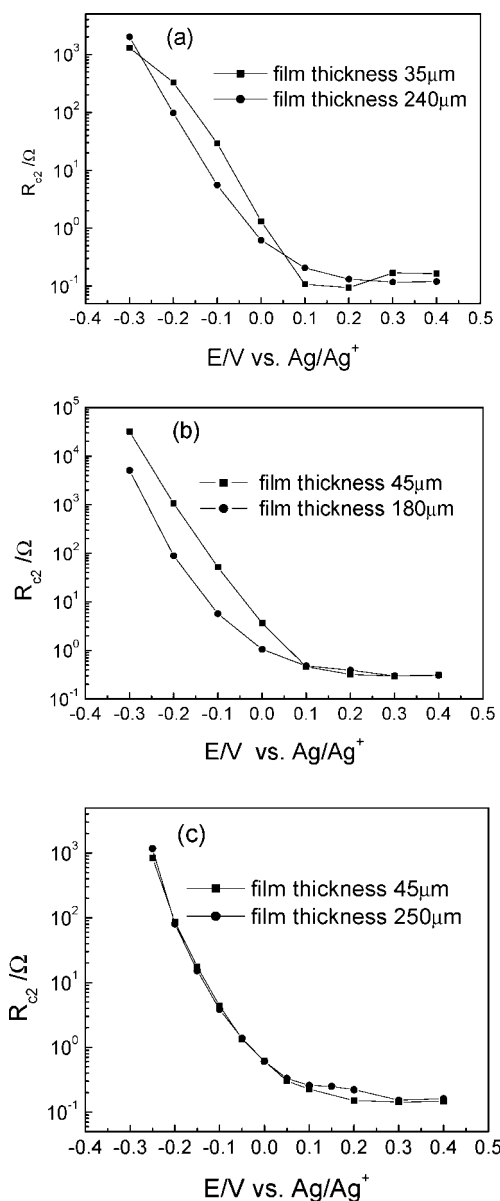


Figure 5. Dependence of contact resistance on doping potential: (a) electrode A; (b) electrode B; (c) electrode C.

Figure 6a deviate the fitting line much more than in Figure 6, parts b and c. For the electrode A with a small gap and wide band ($K = 0.217$), two parallel fitting lines appear while changing film thickness as shown in Figure 6a. However, the fitting lines under different film thicknesses for electrode C ($K = 8$) nearly overlap (see Figure 6c). Therefore, the higher the K of a four-band electrode, the smaller is the effect of film thickness on the relation of ΔR and R_{c2} .

The slope of the fitting line for the $\log_{10} \Delta R$ and $\log_{10}(R_{c2})$ relation under different electrode and film thicknesses is close to unity. The slope of the fitting line is about 1.10 for electrode A and 1.02 for electrode C. It means that ΔR and R_{c2} are nearly a linear relation, especially for a four-band electrode with high geometric factor K . Hence, it is believed that the resistance difference by two-probe and four-probe measurements on a four-band electrode mainly results from the contact resistance at the interface of the electrode and film.

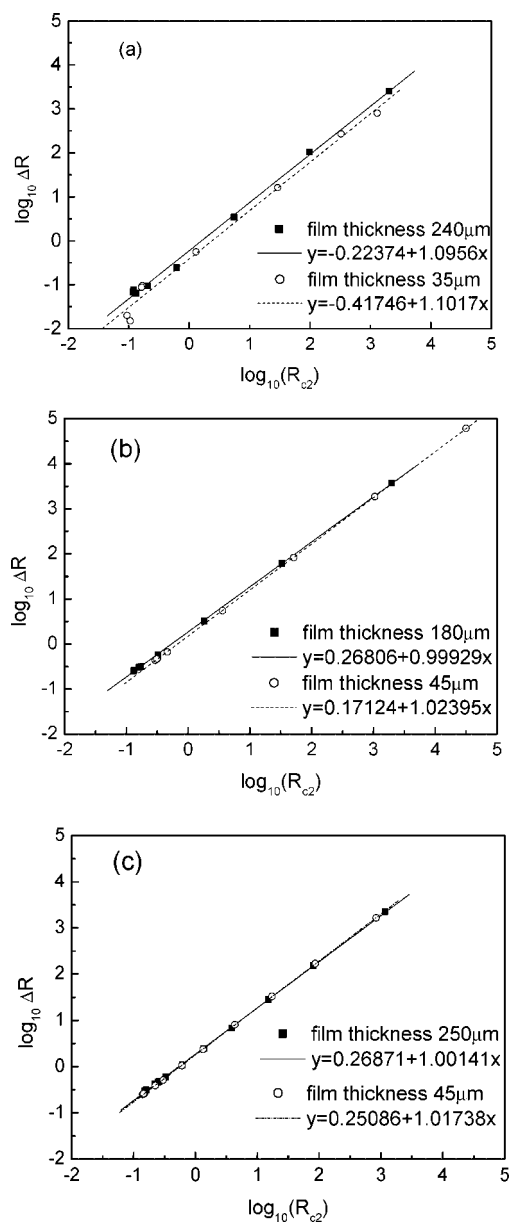


Figure 6. Dependence of resistance difference by two-probe and four-probe measurements on contact resistance: (a) electrode A, $K = 0.217$; (b) electrode B, $K = 1.67$; (c) electrode C, $K = 8$.

The intercept of the fitting line changes from -0.42 of electrode A to 0.27 of electrode C. It increases with geometric factor K . If K is large enough, this intercept will be close to 0.30 ; then ΔR is equal to $2R_{c2}$.

In order to analyze the relation of contact resistance and film resistance, Figure 7 exhibits the effect of doping potential on the ratio of film resistance on the platinum band to contact resistance. When the doping potential reduces, both the film resistance and contact resistance will rapidly increase at the same time as described in Figures 4 and 5. However, Figure 7a shows that they are not a linear relation, and R_{f2}/R_{c2} changes with doping potential. A peak appears at a same doping potential of 0.0 V for the three electrodes A, B, and C, where the conductivity increases suddenly. It is found that the curves for electrodes B and C in Figure 7a almost overlap, and R_{f2}/R_{c2} for electrode A is much larger than them. It results from different bandwidths of the electrodes. The band 2 and band 3 in both the electrodes

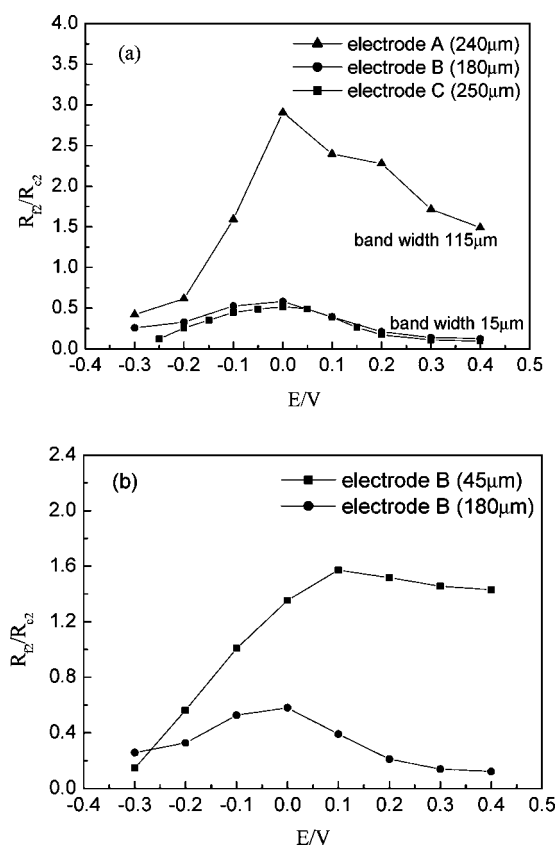


Figure 7. Dependence of R_f/R_{c2} on doping potential: (a) thick films; (b) electrode B with different film thicknesses.

B and C use a same platinum foil of $15\ \mu\text{m}$ thickness, but it is $115\ \mu\text{m}$ thick for the electrode A. The wide platinum band will lead to an increase of film resistance R_f on the band and a decrease of contact resistance R_{c2} . Moreover, the overlap of curves for electrodes B and C indicates that the gap width between bands 2 and 3 have not an obvious effect on the ratio of R_f/R_{c2} .

The film resistance for one electrode reduces with increasing film thickness, and the effect of thickness on film resistance is larger than on contact resistance. Hence, as shown in Figure 7b, R_f/R_{c2} for the thinner film is higher than for the thick film on electrode B, especially in higher doping potential. So are the results of the electrodes A and C.

When the thickness of internal two platinum foils of a four-band electrode reduces significantly, its contact resistance R_{c2} increases and film resistance on the band decreases correspondingly. Thus, R_f/R_{c2} reduces largely as shown in Figure 7a. According to eq 11 ($\Delta R = 8R_{c2}/(1 + R_f/R_{c2})$), the resistance difference ΔR of two-probe and four-probe measurements will enlarge while the bandwidth decreases. It is well consistent with experimental results in Figure 4. On the other hand, this equation shows ΔR is less than $2R_{c2}$. If the thickness of band 2 and band 3 of the electrode decreases significantly, R_f/R_{c2} is rather small. Then ΔR is close to $2R_{c2}$, and the intercept of the fitting line of $\log_{10} \Delta R$ to $\log_{10}(R_{c2})$ is approximately equal to 0.30. That explains the intercept change of the fitting lines in Figure 6, where the intercept increases from -0.42 of electrode A to 0.27 of electrode C. Furthermore, the effect of film thickness on R_f/R_{c2} for electrode A with a wide band is larger than for

electrodes B and C with a narrow band. Therefore when the film thickness increases, the intercept difference of the fitting line for electrode A is larger than for the other electrodes. It becomes insensitive to film thickness for electrode C with the narrow band and larger K . The corresponding fitting line tends to overlap for the samples of different film thicknesses. That is in good accordance with the result in Figure 6.

The conducting property of a conducting polymer depends on doping level rather than the electrode and measurement method. Contact resistance, however, is influenced by many factors including the Pt surface state, adhesion strength of the film with the electrode, and polymer properties besides film feature. For one same electrode, a tiny change of its original film-free surface state and adhesion strength of the film might lead to the larger difference of contact resistance R_{c2} even if the same conditions of polymerization and doping are kept. The four-probe method can avoid the effect of contact resistance on the film resistance measurement as much as possible, but it has to be considered in the two-probe measurement on a double-band electrode.

Zotti et al.¹⁷ measured resistances of conducting polymers using three double-band electrodes with different gap widths; the intercept is regarded as the contact resistance while the gap width is extrapolated into zero. Then the film resistance is verified by getting rid of the contact resistance. It is thought that the two-probe measurement is still valid for the determination of bulk conductivity after calibration with a standard sample. However, this calibration is very inaccurate due to the effect of three factors. At first, the contact resistance is not proportional to polymer resistance as indicated in Figure 7, and their ratio changes with doping potential. That does not conform to the presupposition of calibration in their work. Moreover, the contact resistance might not only depend on its bulk resistance changed with doping level but also on the species of conducting polymer. So this calibration by one standard sample could not be applied to all polymers. On the other hand, according to eq 9, when the gap width decreases, the film resistance R_f will decrease correspondingly, but the second part of the right side of this equation keeps no change. Therefore, this so-called intercept is actually the second part of eq 9 rather than contact resistance while gap width is extrapolated into zero. In fact, the resistance after calibration should correspond to R_f . Nevertheless R_f is not utilized to calculate the conductivity. In their work, the semi-infinite volume condition is required, and the measured resistance related to both R_f on the gap and R_{c2} on the band must be used to calculate the cell constant of a double-band electrode. So this calibration method cannot get rid of contact resistance, and then the accuracy of the measurement has not been improved.

Conductivity Evaluation of Polyaniline Film. Our destination for the above model is to obtain the film resistance R_f from the R_a by four-probe measurement and calculate the conductivity of the film. Figure 8 describes the dependence of $(R_a - R_f)/R_a$ on doping potential. For electrode A with a narrow gap and wide platinum band, $(R_a - R_f)/R_a$ changes in a larger range and is about 60% on average. It is found that $(R_a - R_f)/R_a$ is significantly influenced by the geometric factor K of the four-band electrode. With increasing K of an electrode, $(R_a - R_f)/R_a$ decreases obviously and approaches to 10% for electrode

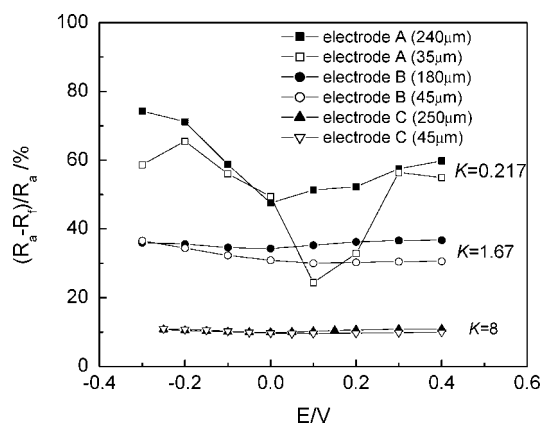


Figure 8. Change of $(R_a - R_i)/R_a$ with doping potential for polyaniline film under different film thicknesses and four-band electrodes.

C. It means that the R_a by four-probe measurement is much closer to the film resistance on the middle gap when the four-band electrode has the wide middle gap and narrow platinum band.

On the other hand, for electrode A with small geometric factor, $(R_a - R_i)/R_a$ under different film thicknesses fluctuates largely with doping potential. The larger the geometric factor K , the smaller is the effect of film thickness on $(R_a - R_i)/R_a$. When K is equal to 8, the curve of $(R_a - R_i)/R_a$ versus doping potential for thick film almost overlaps with that for thin film.

Equation 14 shows that $(R_a - R_i)/R_a$ is related to K , R_a , and ΔR . The K is constant for one four-band electrode and independent of film thickness and properties. On the contrary, R_a and ΔR are determined by many factors such as film properties and electrode dimension. Therefore, when K is much larger, the relative effect of $R_a/\Delta R$ on $(R_a - R_i)/R_a$ is small and $(R_a - R_i)/R_a$ mainly depends on the K . That is in good accordance with the results in Figure 8. Furthermore, as shown in eq 10, if the absolute value of R_i is increased, the relative proportion of the second part in the right side of the equation will reduce. Hence, it is necessary to enlarge the middle gap width as much as possible so long as the film can uniformly cover on the electrode.

According to the above analysis, it is necessary to choose a four-band electrode with a wide middle gap and narrow internal Pt band to measure the conducting property of polymer film in order to improve measurement accuracy and decrease the effect of film thickness. We here choose the sample of electrode C ($K = 8$) with film of 250 μm thickness to calculate the conductivity of polyaniline film by eq 2. Figure 9 displays the dependence of conductivity of polyaniline film on doping potential. Curves 1–3 depict the conductivities calculated from R_{23} , R_a , and R_i , respectively. Curves 1 and 2 correspond to the results measured by the two-probe method and four-probe method. Curve 3 is the calibrated conductivity from curve 2 in terms of the above model. It is found that the conductivity of film increases several orders of magnitude with doping potential. That is consistent with the previous result of polyaniline film measured by the two-probe method on a two-band electrode.²³ The maximum conductivities on curves 1–3 reach 3.6, 11.7, and 13.2 S cm^{-1} , respectively. These data are comparable with the reported conductivities for electrosynthesized polyaniline films (ca. 11.6 S cm^{-1}) measured by the in situ four-probe method²¹ and the

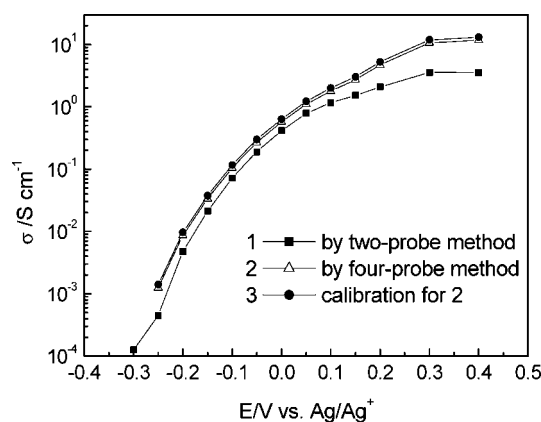


Figure 9. In situ conductivity of polyaniline film vs doping potential for electrode C with film of 250 μm thickness.

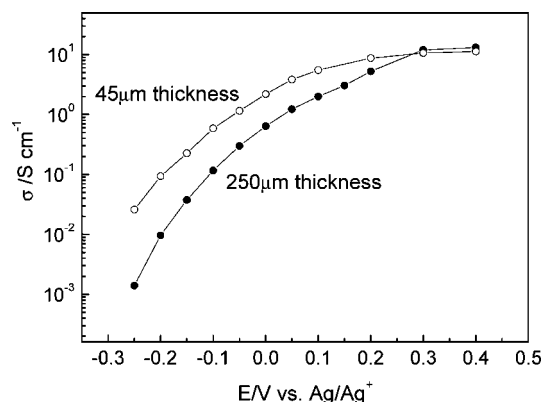


Figure 10. Calibrated conductivity of polyaniline film vs doping potential for electrode C with different film thicknesses by the four-probe method.

conductivities (17.7 ± 10.5 S cm^{-1}) measured by the ex situ van der Pauw method for chemically polymerized polyaniline films.²⁴ Due to the larger geometric factor of this electrode, the calibrated conductivity on curve 3 is close to the result of the four-probe measurement on curve 2. Hence, for the electrode with larger geometric factor, we may approximately replace the film resistance on the gap by the resistance of the four-probe measurement to calculate the conductivity.

Although relatively widely used, the two-probe method used by Zotti and co-workers only gives relative conductivity. An external reference polymer has to be used to measure the so-called cell constant under semi-infinite volume condition, which the film grows as thickly as possible. However, the conductivity of this reference polymer must be accurately determined by other techniques.

Different from the two-probe method used by Zotti under semi-infinite volume condition, this four-probe method may be used to evaluate the dependence of conductivity on film thickness. Figure 10 shows the conductivities of the thin film (45 μm) are higher than the thick film (250 μm) in the low and intermediate doping regions. As the doping potential increases, the conductivity difference tends to reduce. After the potential exceeds 0.3 V, both films have almost the same conductivity.

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Grennan et al. have shown that conductivity decreases with increasing film thickness for electrogenerated polyaniline films.²⁵ Such phenomenon was reported elsewhere for electrogenerated poly(3-methylthiophene) films,²⁶ in which it was attributed to the increase of morphological disorder accompanying the progress of the electropolymerization. Therefore, the higher conductivity observed for the thin film (45 μm) in Figure 10 should be also assigned to the more ordered structure of the polyaniline film formed in the early stage of electrochemical polymerization in comparison to the thick film at the end of polymerization. On the other hand, the conductivity of the polymer film is the sum of two contributions: interchain and intrachain charge transport processes. In the low doping region the film conductivity is mainly controlled by an interchain charge carrier hopping process, which depends greatly on the arrangement of polymer chains in the film,^{13,14} whereas in the high doping region the conductivity is mainly determined by intrachain charge transport, which is mainly related to the mean conjugation length of the polymer chain rather than the stacking structure of polymer chains. So the conductivity difference variation of 45 and 250 μm films with doping potential in Figure 10 can be reasonably explained in terms of the above conducting mechanism.

In comparison with the two-band electrode, the four-band electrode retains its advantages of convenient in situ measurement for conducting property of conducting polymers, but the measurement of the four-probe method on a four-band electrode is more accurate due to the tiny effect of contact resistance at the electrode–film interface. An ideal four-band electrode should have larger K and wider middle gap. The result for in situ resistance measurement of polyaniline film proves the above model is acceptable to calibrate the measurement resistance and evaluate the contact resistance. In fact, the fabricated four-band electrode and the suggested model are applicable for not only

conducting polymers but also other materials, so long as a uniform film can be covered on the electrode.

CONCLUSIONS

- (1) The above investigation shows that in situ conductivity of conducting polymers may be efficiently and conveniently determined with a reusable four-band electrode of simple and cost-effective construction by the four-probe method. The ratio K of middle gap width to platinum bandwidth is the most important parameter to characterize one four-band electrode. One ideal four-band electrode has large K and wide middle gap as much as possible. The influence of film thickness on measurement value of resistance decreases with increasing K .
- (2) The difference of resistances obtained by two-probe and four-probe methods mainly results from contact resistance at the polyaniline film and Pt electrode interface. For larger K , the resistance measured by the four-probe method is much closer to the resistance of the film on the middle gap. Under this case, the influence of contact resistance on R_a can be negligible.
- (3) The contact resistance between the polyaniline film and Pt band depends on the doping potential. It rises with increasing the film resistance, but they are not a linear relation.
- (4) The suggested model for the four-band electrode is available to calibrate film resistance and evaluate contact resistance. The conductivity of the film can be calculated from the calibrated resistance instead of R_a .

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