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Some dynamic regression simulated equations for electrochemical doping processes of polypyrrole

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Polypyrrole films in the oxidized state are positively charged, so the anions of sulphuric acid and *p*-toluensulphonic acid with a certain electrochemical activity were selected as dopants for the polypyrrole film. When the anions were electrochemically incorporated in commercial polypyrrole films at constant temperature (20° C) and constant voltage (3.0 V), the conductivities increased from 67 to 165 and 94 S cm^{-1}, respectively. Dynamic regression simulation of the electrochemistry of the doping process was performed. A new parameter, *r*, was introduced, and the dynamic equation $dS_A/dC_t = f(S_A)$ for the electrochemical doping of the polypyrrole films with sulphuric acid and *p*-toluensulphonic acid was obtained.

1. Introduction

Generally speaking, polypyrrole films in the reduced state are electrically neutral (PP°) and insulating, while in the oxidized state, the films are positively charged, highly conducting [1, 2], often containing some negatively charged intercalation substance or dopant. The dopant is very important for charge equilibration with the positively charged polypyrrole film. Obviously, there is electrostatic interaction between the positively charged polypyrrole and the negatively charged intercalation substance; however, to date no detailed mechanism has been proposed for the electrostatic interaction and for any chemical interaction.

In the present study, the anions of sulphuric acid and *p*-toluensulphonic acid of a certain electrochemical activity were selected as dopants for the polypyrrole film. The anions were incorporated into commercial polypyrrole films at constant temperature (20° C) and constant voltage (3.0 V). Experimental results showed that the conductivity of the polypyrrole film improved after doping [3].

This may be related to the valence of the anions incorporated into the film and the nature of the interaction between the donor and acceptor. Because of the large π conjugation system of the charged positive polypyrrole film and the electron donor properties of the doped anion species, $(FG)^{m-} \rightarrow PPyr^{n+}$ interactions are likely. On the other hand, since the *N* atoms in the polypyrrole film are not only stronger π donors, but also stronger σ acceptors, there is a stronger electrostatic interaction between the $(FG)^{m-}$ and $PPyr^{n+}$. In a separate paper, we have shown that when sulphuric acid and $CH_3C_6H_4SO_3H \cdot H_2O$ were chosen as dopants, the polypyrrole film with its *N* atoms of the stronger σ, accept electrons of the anion donor so that the electrons of the whole system can be freely conducted, thereby increasing the conductivity of the polypyrrole film. It was observed, however, that the polypyrrole films are oxidized and halogenated with increasing anion concentration [4]. The conductivity of the polypyrrole film decreases when the extent of oxidation and halogenation is too high. To better describe the electrochemistry of the doping process, a statistical approach [5, 6] was adopted using multiphase and multifactor dynamic regression simulation for the electrochemical reaction; the relationship between the conductivity, S_A, and the dopant concentration, C_t, was obtained. Dynamic equations of the form $dS_A/dC_t = f(S_A)$ for the electrochemical doping of the polypyrrole film with sulphuric acid and *p*-toluensulphonic acid are presented in this paper.

2. Experimental details

The polypyrrole films employed in this study were provided by BASF (Lutamer West Germany Elektr Leitfahigkeit Ca). The thickness of the films was approximately 65 μm. The doping vessel employed had dimension (ϕ 2.5 cm × 10 cm) and the polypyrrole samples were 2 cm × 2 cm. An AMEL model 551 potentiostat and Escort EDM-1135 multimeter were employed to maintain a constant voltage between the polypyrrole, which was connected to the anodic terminal, and the cathode, which consisted of a copper plate.

Samples were doped electrochemically for 1 h at a constant temperature of 20° C and a constant voltage

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Table 1. Conductivity (S_A) of polypyrrole films doped with sulphuric acid of various concentrations (C_t)

Code: N	*1*	*2*	*3*	*4*	*5*	*6*
C_t/M	0.5	1.0	1.5	2.0	2.5	3.0
S_A/S cm^{-1}	94.8	110.9	134.7	154.5	159.7	164.6

of 3.0 V in solutions of various sulphuric acid and *p*-toluensulphonic acid concentrations, with distilled water as solvent. The films were then washed with distilled water and vacuum dried for 4 h before measurement of their conductivity using the 4-probe method [7].

3. Data treatment and results

The experimental values of conductivity obtained for the doped films are presented in Tables 1 and 2. The relationship between S_A and C_t is shown in Figs 1 and 2 for the H_2SO_4 and *p*-toluensulphonic acid doped films, respectively.

From the plots of S_A against C_t in Figs 1 and 2, it can be seen that the relationship between the conductivity and dopant concentration can be expressed in terms of the relation:

$$Y = [f(a + b \exp(-X^r)]^{-1}$$
$$= [a + b \exp(-X^r)]^{-1} \qquad (1)$$

where $Y = S_A$, $X = C_t$ and r is a new parameter.

Let

$$Y = \frac{1}{Y} = \frac{1}{S_A}$$

and

$$X = \exp(-C_t^r) \qquad (2)$$

therefore

$$Y = a + bX \qquad (3)$$

The dopant parameters a, b and r for the sulphuric acid or *p*-toluensulphonic acid can thus be calculated after the basic equations are determined.

3.1. *Preliminary estimation of a′ and b′*

3.1.1. *Calculation of a and b for sulphuric acid dopant.*

$S_{A(1)} = 94.8$ and $C_{t(1)} = 0.5$

$$a' = \frac{1}{S_{A(6)}} = 6.06 \times 10^{-3}$$

substituting a', $S_{A(1)}$ and $C_{t(1)}$ into Equation 1

$$b' = 7.37 \times 10^{-3}$$

therefore

$$S_A = (6.06 \times 10^{-3} + 7.37 \times 10^{-3} \exp(-C_t^r))^{-1} \qquad (4)$$

3.1.2. *Preliminary estimation of a′ and b′ for p-toluensulphonic acid dopant.* Using the same method as for 3.1.1.

$$a' = 1.06 \times 10^{-2}$$

and

$$b' = 8.94 \times 10^{-3}$$

where a', b' and r are parameters, therefore

$$S_A = (1.06 \times 10^{-2} + 8.94 \times 10^{-3} \exp(-C_t^r))^{-1} \qquad (5)$$

3.2. *Estimation of the new parameter r*

3.2.1. *Estimation of r for sulphuric acid dopant.* According to the mid-value point or median, we may further obtain from Equations 1, 2 and 4, and the values of $S_{A(3)}$ and $C_{t(3)}$

$$r = 1.1328$$

3.2.2. *Estimation of r for p-toluensulphonic acid dopant.* Using Equations 1, 2 and 5 and the values $S_{A(6)}$ and $C_{t(6)}$

$$r = 0.3717$$

3.3. *Final determination of a and b values*

3.3.1. *Determination of a and b for sulphuric acid dopant.* From

$$X = \exp(-C_t^r), \qquad Y = a + bX$$

$\Sigma X = 1.4092$, $\Sigma X^2 = 0.5963$, $\Sigma Y = 0.0466$ and $\Sigma XY = 130.56$, we can calculate the sum of the squares of the deviation (see Appendix)

$$L_{XX} = 0.2653, \qquad L_{XY} = 0.0021$$

therefore

$$b = 7.9 \times 10^{-3}, \qquad a = 5.9 \times 10^{-3}$$

3.3.2. *Determination of a and b for p-toluensulphonic acid dopant.* From

$$X = \exp(-C_t^r), \qquad Y = a + bX,$$
$$\Sigma X = 1.8847, \qquad \Sigma X^2 = 0.3986$$

$\Sigma Y = 0.1336$, and $\Sigma XY = 0.00236$, the sum of the

Table 2. Conductivity (S_A) of polypyrrole films doped with p-toluensulphonic acid of various concentrations (C_t)

Code: N	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
$C_t \times 10^{-1}$/M	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0
S_A/S cm^{-1}	72.0	75.0	78.0	82.0	84.4	86.5	88.5	90.0	91.8	92.8	94.0

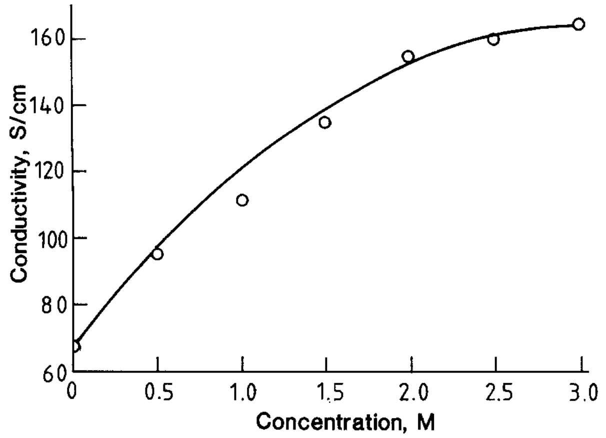

Fig. 1. The influence of H_2SO_4 concentration on the conductivity of the polypyrrole film.

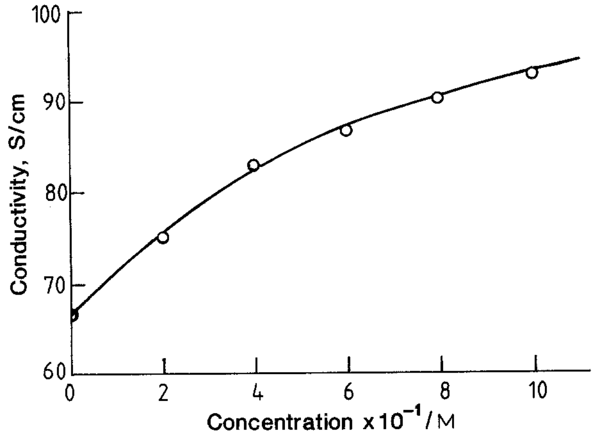

Fig. 2. The influence of p-toluensulphonic acid concentration on the conductivity of the polypyrrole film.

squares of the deviation are

$$L_{XX} = 7.56 \times 10^{-2}$$

$$L_{XY} = 7.00 \times 10^{-4}$$

therefore

$$a = 1.06 \times 10^{-2}$$

$$b = 9.00 \times 10^{-3}$$

3.4. *Dynamic integral formulae*

3.4.1. Dynamic integral formula for sulphuric acid dopant. Substituting the a, b and r values for sulphuric acid dopant into Formula 1, respectively, the integral formula for sulphuric acid dopant is given by

$$S_A = (5.90 \times 10^{-3} + 7.90 \times 10^{-3} \exp(-C_t^{1.1328}))^{-1} \quad (6)$$

3.4.2. Dynamic integral formula for p-toluensulphonic acid dopant. Using the same method as above

$$S_A = (1.06 \times 10^{-2} + 9.0 \times 10^{-3} \exp(-C_t^{0.3717}))^{-1} \quad (7)$$

3.5. *Calculation of the value for the dynamic integral formulae deviation with experimental data*

3.5.1. Calculation for the dopant sulphuric acid and p-toluensulphonic acid are summarized in Tables 3 and 4 below. From Tables 3 and 4, it can be seen that, apart from point 9, the percentage errors for all the points are all less than 5%.

3.5.2. Transformation of formulae. The above dynamic integral formulae may each be transformed into corresponding differential formulae in order that the doping process for the sulphuric acid and p-toluensulphonic acid dopants can be better described and understood. From Equation 1

$$\left(\frac{S_A b}{1 - aS_A}\right)^{1/r} = \exp C_t \quad (8)$$

Differentiating S_A with respect to C_t in Equation 8

$$\frac{dS_A}{dC_t} = rS_A(1 - aS_A) \ln\left(\frac{S_A b}{1 - aS_A}\right)^{r-1/r} \quad (9)$$

The differential formula for sulphuric acid dopant is thus

$$\frac{dS_A}{dC_t} = 1.1328 S_A(1.59 \times 10^{-3} S_A) \times \ln\left(\frac{7.9 \times 10^{-3} S_A}{1 - 5.9 \times 10^{-3} S_A}\right)^{0.1172} \quad (10)$$

while the differential formula for the dopant p-toluensulphonic acid is

$$\frac{dS_A}{dC_t} = 0.3717 S_A(1.106 \times 10^{-2} S_A) \times \ln\left(\frac{9.0 \times 10^{-3} S_A}{1 - 1.06 \times 10^{-2} S_A}\right)^{-1.690} \quad (11)$$

4. Conclusions

(i) Polypyrrole films in the oxidized state were doped with the anions of sulphuric acid and p-toluensulphonic acid, and the conductivities increased from 67 to 165 and 94 S cm^{-1}, respectively.

Table 3. Standard deviation calculation for H_2SO_4 doping

C_t/M	*0.5*	*1.0*	*1.5*	*2.0*	*2.5*	*3.0*
Exp. S_A/S cm^{-1}	95.0	110.0	135.0	155.0	160.0	165.0
Calc. S_A/S cm^{-1}	91.74	113.64	133.30	147.50	157.00	162.30
Absolute error	−3.26	+3.64	−1.70	−7.50	−3.00	−2.70
Relative error	−0.034	+0.033	−0.0126	−0.048	−0.018	−0.016
Pecentage error/%	−3.4	+3.3	−1.26	−4.8	−1.8	−1.6

Table 4. Standard deviation calculation for p-toluensulphonic acid doping

$C_t \times 10^{-1}$	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
Exp. $S_A/\mathrm{S\,cm^{-1}}$	72.0	75.00	78.50	82.80	84.41	86.50	88.5	90.0	91.8	92.8	94.0
Calc. $S_A/\mathrm{S\,cm^{-1}}$	71.94	76.34	79.36	82.92	84.10	84.75	85.47	86.21	86.97	90.9	91.0
Absolute error	−0.06	+1.34	+0.86	+0.12	−0.31	−1.75	−3.03	−3.79	−4.83	+1.90	−3.00
Relative error	−0.0008	+0.018	+0.011	+0.0015	−0.0036	−0.020	−0.0034	−0.042	−0.052	+0.020	−0.031
Pecentage error/%	−0.08	+1.80	+1.10	+0.15	−0.36	−2.0	−3.4	−4.2	−5.2	+2.0	−3.1

(ii) A new parameter r was introduced into the mathematical regression simulation allowing the relationship between conductivity and dopant concentration to be obtained for the chemical reaction process.

(iii) From the functional relational formula

$$S_A = [f(a + b\exp(-C_i^r))]^{-1}$$

it can be seen that when C_t is sufficiently large, the exp $(-C_t^r)$ term in the formula will tend to zero. The values a, b and r were thus determined from the peak, the middle and last sections of the experimental curves. The preliminary a' and b' values can be used to determine r if the variability of the middle section of the curves in Figs 1 and 2 is small, and satisfactory calculation results can be obtained.

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Appendix

$$L_{XX} = \sum_{i=1}^{n} (X_i - \bar{X})^2$$

$$= \sum_{i=1}^{n} X^2 - \frac{1}{N}\left(\sum_{i=1}^{n} X\right)^2$$

$$L_{XY} = \sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})$$

$$= \sum_{i=1}^{n} XY - \frac{1}{N}\left(\sum_{i=1}^{n} X\right)\left(\sum_{i=1}^{n} Y\right)$$

$$b = \frac{\sum_{i=1}^{n} X_i Y_i - n\bar{X}\bar{Y}}{\sum_{i=1}^{n} X_i^2 - 2\bar{X}^2}$$

$$= \frac{\sum_{i=1}^{n} (X_i - \bar{X})(Y_i - \bar{Y})}{\sum_{i=1}^{n} (X_i - \bar{X})^2}$$

and

$$a = \frac{1}{N}\left(\sum Y - b\sum X\right)$$