# The Optimal Sulfonation Conditions of Self-doped Polyaniline Obtained by Using Experimental Strategies

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Abstract:    The optimal sulfonation condition of self-doped sulfonated polyaniline (prepared from leucoemeraldine base;  denoted as LEB-SPAN I) with a high electronic conductivity was obtained by experimental strategies,  including the fractional factorial design (FFD) and central composite design (CCD). From the FFD experiment,  the self-doped LEB-SPAN I prepared at a low temperature ($4^{o}$C),  a short reaction time (1 h),  and a small volume of fuming sulfuric acid (10 mL) showed a better conductivity (ca. 127 mS/cm).  In the CCD study coupled with a confirmation test,  the highest conductivity (ca. 141 mS/cm) of the LEB-SPAN I film was obtained under a sulfonation temperature of $4^{o}$C,  a sulfonation time of 75 minutes,  and a volume of 8 mL of 30% fuming sulfuric acid. The textural characteristics of self-doped LEB-SPAN I were characterized by Fourier transform infrared (FTIR) spectroscopy,  four-point probe method,  and X-ray photoelectron spectroscopy (XPS). The sulfonation rate and degree of LEB-SPAN I were found to be dependent upon the acid used in the polymerization step of PAN I

Keywords:    Self-doped polyaniline, Sulfonation, Conductivity, Fractional factorial design, Central composite design

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## 1    Introduction

Conducting polymers were widely investigated in the last two decades, especially aim to find suitable applications. Several fields, including rechargeable batteries, electromagnetic interference shielding, sensors, and electrochromic display devices[1-5], were shown to be of application potentials. Among all the conducting polymers, polyaniline (PAN I) is particularly an attractive material owing to its good electrical, optical, and electrochemical properties as well as good environmental stability[6-8]. In addition, PAN I was known to provide the faradaic pseudocapacitance for an electrochemical capacitor due to the redox transitions between different oxidation structures[9,10]. Furthermore, through means of protonation/de-protonation and doping/de-doping processes, the electronic properties of PAN I can be reversibly controlled[7]. However, PAN I in the acid (doped) form is insoluble in common organic solvents, which limits the applications of polyaniline because of the difficulty in processing. Accordingly, PAN I-based polymers with a good processing property are worthy being developed.

Recently, Yue et al[7] introduced a sulfonic acid group onto the polymer chain of emeraldine base (EB), which makes PAN I become a self-doped conducting polymer. As a result of a sulfonic acid group on the polymer chain, the electronic, chemical, and optical properties of sulfonated polyaniline (SPAN I) differ significantly from those of the parent polymer[7,11]. Moreover, the solubility of PAN I is obvi-

ously improved by the presence of a sulfonic acid group[7,8], which showed the application potential in rechargeable batteries[12,13], light emitting diode devices[14] etc. In fact, Wei et al[8]. used leucoemeraldine base (LEB) as the polymer precursor to synthesize a high-density sulfonated polyaniline (denoted as LEB-SPAN I). They found that LEB-SPAN I exhibited a higher sulfur-to-nitrogen (S/N) ratio and a better conductivity than that of EB-SPAN I and PNB - SPAN I (PNB = pernigraniline base)[8].

The experimental strategy is a sequential procedure to reach the reliable optimum preparation conditions of interest[15-17]. This methodology is based on the assumption that the response variable (denoted as $Y$; e. g , the electronic conductivity of LEB-SPAN I in this work) is a function of quantitative and controllable variables (denoted as $X_i$). Since the starting point of preparation conditions is usually remote from the optimal conditions and several factors may influence the response variable, screening experiments are used to find the key factors affecting the response variable. In order to efficiently find the key variables, a fractional factorial design (FFD) is often utilized because the response variable is believed to be primarily driven by certain effects of main factors and low-order interactions[15-20]. Based on FFD, the relationship between response variable and key variables, $Y = f(X_i)$, close to the starting point is presumably described by a first-order model. This model is used to approach the vicinity of the optimal conditions through means of the methodology of the steepest ascent path. Finally, the central composite design (CCD) is employed to model the apparent curvature of response variable against the key factors at the vicinity of optimum. This mathematic model, represented as contour lines or a plane in graphs to find the location of optimum conditions, belongs to the response surface methodology (RSM).

One of key factors determining the practical applications of LEB-SPAN I is the electronic conductivity. Our approach is to search the optimal experiment conditions for the preparation of LEB-SPAN I with high conductivity, which will be applied in solid -

state electrolytic capacitors[5]. The fractional factorial design was employed to efficiently find the key variables affecting the conductivity. The key variables were subjected to the central composite design (CCD) coupled with the response surface methodology (RSM) in order to investigate the relationships near the optimal experimental settings for the LEB-SPAN I synthesis. The oxidation state and doping level were examined by FTIR (Fourier transform infrared) spectroscopy and XPS (X-ray photoelectron spectroscopy).

## 2 Experimental

To avoid the attack of Al by the presence of chloride anions, nitric acid was employed as the acid for preparing the emeraldine base (EB). Ammonium persulfate (0. 26 mol/L) was added into a stirred solution with 0. 2 mol/L aniline and 1mol/L HNO₃ at 4 . This solution was stirred for 2 h to get the emeraldine salt. The precipitated emeraldine salt was filtered, washed with water, and then stirred with acetone and obtained by filtration. After drying overnight in a vacuum oven at room temperature, the emeraldine salt was suspended in 1mol/L NH₄OH solution and stirred for 24 h. The EB was obtained after filtration and then was dried in a vacuum oven at room temperature.

The process for synthesizing LEB-SPAN I is similar to that described in reference[8]. A mixture consisted of 0. 5 g EB and 5mL phenylhydrazine was stirred for 1 h, then washed with ethyl ether, and dried in a vacuum oven at room temperature. The dried LEB was sulfonated in the fuming sulfuric acid and then transferred to an icy water bath to precipitate the LEB-SPAN I product. The filtrated cake was dried under vacuum for 24 h. During the sulfonation process, five factors, i e. , reaction temperature, reaction time, volume of fuming sulfuric acid, the concentration of fuming sulfuric acid, and the stirring rate were considered in the FFD study.

The conductivity measurements were obtained from LEB-SPAN I pressed pellets by using a four-point probe (Conductance Meter Model CM-308, Elchema, USA). The FTIR spectra of LEB-SPAN I were recor-

ded by a Fourier transform infrared spectroscopy (FT-IR-8101M, Shimadzu, Japan) from KBr pellets with the weight ratio between polymer and KBr equal to 1 : 1000. The XPS spectra were collected on a Fison (VG) ESCA 210 system with Al $K$ X-ray source (1 486.6 eV).

# 3 Results and Discussion

## 3.1 Fractional Factorial Design (FFD)

To efficiency find the key variables of sulfonation affecting the conductivity of LEB-SPAN I, the fractional factorial design (FFD) is introduced to screen out these key variables. This experiment design can find the influences of each sulfonation variable at a variety of other variable levels, as well as the interactions among these variables on the conductivity of LEB-SPAN I because a system or process is likely to be driven primarily by some of main factors and low-order interactions[15～20].

Tab. 1　Factors and level for the $2^{5-1}$ fractional factorial design

| Factor | Variable | Level | |
| --- | --- | --- | --- |
| | | + | - |
| A | Temperature/ | 25 | 4 |
| B | Time/h | 24 | 1 |
| C | Volume/mL | 40 | 10 |
| D | Fuming sulfuric acid comcentration/% | 30 | 20 |
| E | Stirring rate/r·min$^{-1}$ | 80 | 40 |

Effects of the following sulfonation variables on the conductivity of LEB-SPAN I were investigated in the FFD study: (A) sulfonation temperature; (B) sulfonation time; (C) volume of the fuming sulfuric acid; (D) concentration (i.e., the $SO_3$ percentage) of the fuming sulfuric acid; and (E) stirring rate. The fixed levels of these five variables are listed in Table 1 where the low and high levels of A, B, C, D, and E are denoted as "-" and "+" respectively. In addition, the $2^{5-1}$ design matrix with levels and results of the conductivity for various LEB-SPAN Is are shown in Table 2. According to the defining relation I = ABCDE (introduced by Box et al[15～17]), the $2^{5-1}$ fractional factorial design is obtained by writing

down the full $2^4$ factorial matrix as the basic design and then equating factor E to the ABCD interaction[16] (i.e., A = A· I = A· ABCDE = $A^2$BCDE = BCDE). According to A = BCDE, the combination of observations used to estimate the effect of the main factor A (sulfonation temperature) is identical to that used to estimate the four-factor interaction effect of the aliases B (sulfonation time), C (volume of the fuming sulfuric acid), D (concentration of the fuming sulfuric acid) and E (stir rate); denoted as B ×C ×D × E. Thus, the main effect of factor A and the interaction effect of B ×C ×D × E are confounded[15,16]. From the principle of the sparsity of effects[16], a system is likely to be driven primarily by main-factor and low-order interaction effects. Effects of the high-order (e.g., three and higher order) interactions are assumed to be negligible. Thus, the main effect of factor A can be isolated from the confounded effects by this FFD experiment. Similar analyses are also applicable for facts B to E.

Tab. 2　Design matrix and experiment data for the $2^{5-1}$ fractional factorial design with the defining relation I = ABCDE

| Run | Factor | | | | | Conductivity |
| --- | --- | --- | --- | --- | --- | --- |
| | A | B | C | D | E | /mS·cm$^{-1}$ |
| 1 | - | - | - | - | + | 108.2 |
| 2 | + | - | - | - | - | 30.5 |
| 3 | - | + | - | - | - | 64.9 |
| 4 | + | + | - | - | + | 34.1 |
| 5 | - | - | + | - | - | 84.0 |
| 6 | + | - | + | - | + | 3.5 |
| 7 | - | + | + | - | + | 44.3 |
| 8 | + | + | + | - | - | 2.8 |
| 9 | - | - | - | + | - | 125.9 |
| 10 | + | - | - | + | + | 39.3 |
| 11 | - | + | - | + | + | 52.4 |
| 12 | + | + | - | + | - | 19.0 |
| 13 | - | - | + | + | + | 89.8 |
| 14 | + | - | + | + | - | 0.7 |
| 15 | - | + | + | + | - | 0.1 |
| 16 | + | + | + | + | + | 13.6 |

From an examination of the last column in Table 2, the conductivity of LEB-SPAN I varies from 0. 1 to 126 mS/cm, indicating that the conductivity of LEB-SPAN I is strongly dependent on these sulfonation variables. To obtain the quantitative information of each factor (including main factors and their two-factor interactions), analysis of variance (ANOVA) is carried out on the basis of the $2^{5-1}$ design matrix in Table 2. The result of ANOVA is listed in Table 3.

Tab. 3 Analysis of variance for the conductivity of LEB-SPAN I in $2^{5-1}$ fractional factorial design

| Source | Sum of square | d f | Mean square | F |
| --- | --- | --- | --- | --- |
| A | 11442. 86 | 1 | 11442. 86 | 104. 84 |
| B | 3874. 48 | 1 | 3874. 48 | 35. 50 |
| C | 3458. 73 | 1 | 3458. 73 | 31. 69 |
| AB | 3646. 56 | 1 | 3646. 56 | 33. 41 |
| BD | 494. 73 | 1 | 494. 73 | 4. 53* |
| Error | 1091. 43 | 10 | 109. 41 | |
| Total | 24008. 80 | | | |

$F_{0.05}$ (1, 10) =4. 96; $R^2$ =0. 9545; * : marginal significance.

The concept of ANOVA is based on a partitioning of total variability ($SST$) into its component parts (i. e. sum of square due to factors ($SSF$) and sum of square due to errors ($SSE$))[15, 17]. The quantities $MSF_i = SS_i / df_i$ and $MSE = SSE / df_{error}$ are respectively defined as the mean square of factor (or interaction) $i$ and the mean square of error. The $df_i$ and $df_{error}$ indicate the degree of freedom for factor (or interaction) $i$ and error, respectively. The test statistic, $F$, is the ratio of $MSF_i / MSE$. If the $F$ value is greater than that in the $F$ distribution table at a specific probability level (e. g. $F_{0.05}$ (1, 10) = 4. 96 and $F_{0.1}$ (1, 10) = 3. 29), the influence of factor (or interaction) on the conductivity of LEB-SPAN I is considered to be significant. Hence, from the ANOVA table, factors $A$, $B$, $C$, and interaction $A \times B$ are concluded to be the statistically significant effects on the conductivity of LEB-SPAN I. Note that interaction $B \times D$ is a marginally significant effect since its calculated $F$ value (4. 53) is between $F_{0.05}$ 4. 96 and $F_{0.1}$

(1, 10) and the other ten factors or interactions without statistic significance were lumped as the errors. In addition, the sequence of factors with respect to decreasing the significance on the conductivity is: $A > B > C > AB > BD$. Moreover, the multiple correlation coefficient, $R^2$, defined as $R^2 = SSR / SST$ provides useful information for the significance of the FFD experiments; where $SSR$ is the sum of square of regression (i. e., the lumped sums of significant factors and interactions; $SSR = \sum SSF_i$). $R^2$ is indicative of the proportion of variability in the data "explained" by the significant factors and interactions (i. e., the model). A $R^2$ value close to 1 means a good fit to the experiment data ($R^2 = 0. 9545$ in this study).
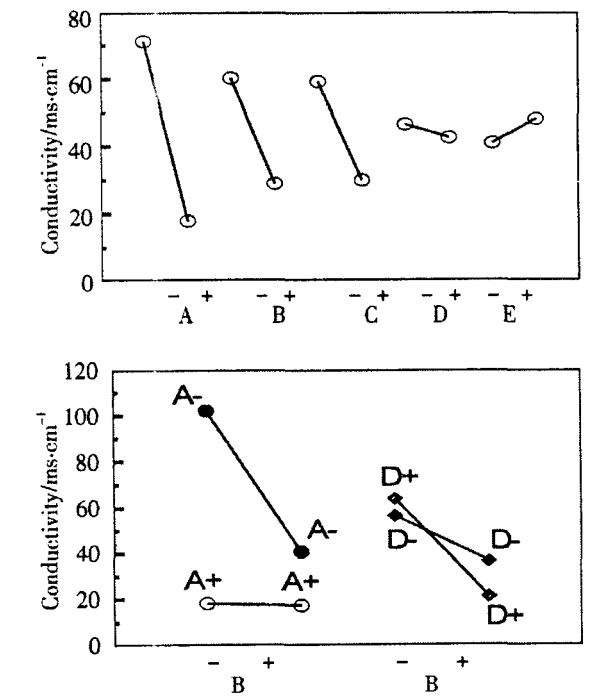


Fig 1 Effects of (a) main factors and (b) two-factor interactions with statistical significance on the conductivity of LEB-SPAN I

Calculation of the estimates for main factors and two - factor interactions is followed the procedure recommended by Box et al[15]. Effects of main factors and two - factor interactions with statistically significant influences on the conductivity of LEB-SPAN I are shown in Fig 1. In Fig 1a, main factors A, B and C

exhibit negative effects on the conductivity of LEB - SPAN I  Accordingly, sulfonation at 4   (low level of factor $A$) for 1h (low level of factor $B$) in the solution with 10 cm$^3$ fuming sulfuric acid (low level of factor $C$) promotes the electronic conductivity of LEB - SPAN I  The above results indicate that sulfonation at a lower temperature, a shorter time, and a smaller volume of fuming sulfuric acid is able to retard the hydrolysis of LEB.  On the other hand, the differences in conductivity due to factors D and E are considered to be the experimental errors since these two factors are statistically insignificant

From the ANOVA results shown in Table 3, the effects of two-factor interactions, A × B and B × D, are not negligible and further analyzed in Fig  1b. For the $A × B$ interaction, the conductivity of LEB - SPAN I is not significantly influenced by varying the reaction time (i e., factor $B$) from 1 to 24 h when factor $A$ is under the high level (i e  25  ). However, at 4  , the conductivity of LEB - SPAN I is sharply increased from 40 to 100 mS/cm by shortening the reaction time from 24 to 1 h  These phenomena suggest that the hydrolysis degree of the polymer chain becomes saturated under 25   although the sulfonation time is only 1h, revealing a very rapid hydrolysis rate at a relatively high temperature[7,21]. For the B × D interaction, the conductivity of LEB - SPAN I is less significantly influenced by increasing the reaction time (i e., factor $B$) from 1 to 24 h when factor $D$ is under the low level (i e  20% ). However, when the 30% fuming sulfuric acid is employed, the conductivity of LEB - SPAN I is more obviously increased from 20 to 65 mS/cm by shortening the sulfonation time from 24 to 1 h  The above results suggest that the conductivity of LEB - SPAN I is more seriously affected by the sulfonation time in a concentrated fuming sulfuric acid medium.  This is attributable to that the rate of hydrolysis is significantly affected by the $SO_3$ ratio of the fuming sulfuric acid since the hydrolysis degree of the polymer chain is believed to be the key factor dominating the conductivity of LEB - SPAN I  Accordingly, a combination of the negative adjustment in factors A, B, and C and the positive adjustment in factor D should obviously increase the conductivity of LEB - SPAN I  From all the above results and discussion, the conductivity of LEB - SPAN I should be not only dependent on the sulfonation degree but also the hydrolysis degree of polymers

## 3. 2   Central Composite Design

The purpose of a central composite design (CCD) is to provide enough degrees of freedom to fit the second-order model correlating key factors in a sulfonation reaction with the conductivity of LEB - SPAN I  According to the results and discussion in the FFD study, LEB - SPAN I prepared under the low levels of factors A, B, and C and the high level of factor D showed a conductivity of 126 mS/cm.  These conditions have been simply confirmed to be close to the vicinity of the optimal preparation conditions for LEB - PAN I with the highest conductivity.  Therefore, the central point of the CCD study is set at A  = 4   ; B  = 90 min; C  = 10 mL; D  = 30% fuming sulfuric acid; and E  = 80 r/min  Note that the low level of factor A is close to the freezing point of fuming sulfuric acid (i e  2  ).  Factor $A$ was kept constant (4  ) in this CCD investigation although the sulfonation temperature is concluded to be a key factor in the CCD study.  Accordingly, only factors B and C are considered in the CCD study.

A CCD study consists of a $2^k$ factorial design, 2k axial runs and $n_C$ center runs, which results in the total number of experimental runs equal to $2^k + 2k + n_C$.  In this design, experiments on the central point are repeated $n_C$ times ($n_C = 3$ in this work) in order to evaluated the pure error between each experiment[16].  Accordingly, only factors B and C are considered in this CCD study and the total number of experimental runs is equal to $2^2 + 2 × 2 + 3 = 11$.  In addition, the distance from the points in the factorial design and the axial runs to the central points is constant ($\sqrt{2}$).  A design with this property will leave a constant variance of the response variable at all experimental points when the design is rotated about the center[16].

The design matrix of CCD and the results are lis-

ted in Table 4. The coded variables, $X_1$ and $X_2$, represent the factors B and C, respectively. The relationship between the natural variables and the coded variables is defined as:

$$X_1 = [B - \frac{1}{2}(B_{high} + B_{low})] / \frac{1}{2}(B_{high} - B_{low}) \qquad (1)$$

$$X_2 = [C - \frac{1}{2}(C_{high} + C_{low})] / \frac{1}{2}(C_{high} - C_{low}) \qquad (2)$$

where $B_{high}$ and $B_{low}$ indicate the high and low levels of factor B in the natural unit, respectively. This definition is also applicable for factor C. According to the regression analysis and analysis of variance for the data shown in Table 4, a second-order model representing the dependence of conductivity on the sulfonation time ($X_1$) and the volume of 30% fuming sulfuric acid ($X_2$) was generated as follow:

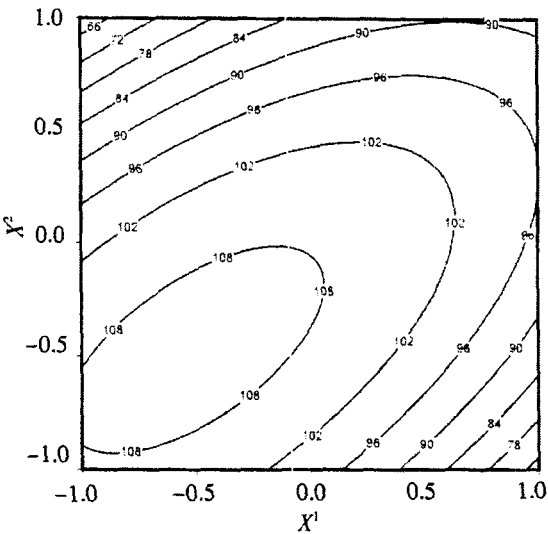$$Y = 107.7 - 2.76X_1 - 6.64X_2 - 10.23X_1^2 - 15.6X_2^2 + 16 X_1 * X_2 \qquad (3)$$



Fig 2 Contour plots for the conductivity of LEB-SPAN I against time of sulfonation ($X_1$) and volume of 30% fuming sulfuric acid ($X_2$)

where $Y$ indicates the conductivity of LEB-SPAN I. The negative signs in equation (3) corresponding to the coefficients of $X_1^2$ and $X_2^2$ indicate the existence of a maximum in this CCD work.

Tab. 4 Design matrix and experimental data for the conductivity of LEB-SPAN I for the central composite design with a quadratic form fit

| Rum | Natural variables | | Coded variables | | Conductivity |
|---|---|---|---|---|---|
| | Time/min | Volume/mL | $X_1$ | $X_2$ | /mS·cm$^{-1}$ |
| 1 | 60 | 14 | -1 | 1 | 56.3 |
| 2 | 120 | 6 | 1 | -1 | 75.0 |
| 3 | 60 | 6 | -1 | -1 | 127.5 |
| 4 | 120 | 14 | 1 | 1 | 67.8 |
| 5 | 132 | 10 | $\sqrt{2}$ | 0 | 94.1 |
| 6 | 48 | 10 | $-\sqrt{2}$ | 0 | 80.7 |
| 7 | 90 | 15.6 | 0 | $\sqrt{2}$ | 85.6 |
| 8 | 90 | 4.4 | 0 | $-\sqrt{2}$ | 67.7 |
| 9 | 90 | 10 | 0 | 0 | 101.6 |
| 10 | 90 | 10 | 0 | 0 | 114.4 |
| 11 | 90 | 10 | 0 | 0 | 107.0 |

A two-dimension contour plot for the conductivity of LEB-SPAN I constructed on the basis of equation (3) is shown in Fig 2. Note that the conductivity of LEB-SPAN I increases progressively with the direction of lowering volume and shortening time and reaches a maximum at (-0.5, -0.5). Since the conductivity of LEB-SPAN I at this point was not available in the CCD study, a confirmation test was carried out and the results are shown in Table 5. From Table 5, the conductivity reaches the maximum (ca 141 mS/cm) under the experimental settings of run 2 (i.e., A, 4; B, 75 min; C (30% fuming sulfuric acid), 8 cm$^3$, and E, 80 r/min). From the above sequential experimental strategies, including the FFD, CCD, and confirmation studies, the optimal sulfonation experiment settings for the highest conductivity of LEB-SPAN I were obtained.

Tab. 5 Points and the results of conductivity in the confirmation test

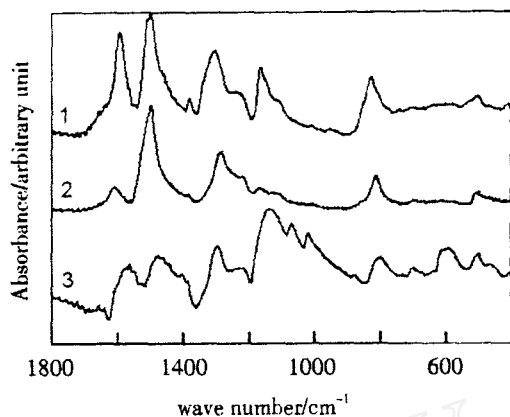| Run | Time/min | Volume/ml | Conductivity/mS·cm$^{-1}$ |
|---|---|---|---|
| 1 | 90 | 10 | 104.3 |
| 2 | 75 | 8 | 140.6 |
| 3 | 60 | 6 | 116.3 |
| 4 | 45 | 4 | 86.7 |

Fig 3 FTR spectra of (1) emeraldine base (2) leucoemeraldine base and (3) LEB-SPANI

## 3.3 Fourier Transform Infrared Spectroscopy

From the above results of FFD, CCD and the confirmation test, the highest conductivity of LEB-SPANI was successfully obtained while 141 mS/cm is obviously lower than the conductivity of LEB-SPANI (ca 1 S/cm) reported in the literature[8]. Moreover, the S/N ratio of this polymer acquired by the analysis of XPS is 0.46, which is obviously lower than that of a sulfonated leucoemeraldine base (S/N ratio (0.78) reported in Reference[8]. In order to gain a further understanding on these differences, FTR is employed to analyze the textural characterization of LEB-SPANI prepared in this work.

Figure 3 shows the FTR spectra of EB, LEB, and LEB-SPANI prepared from a nitric acid solution in this study. From spectrum 1 (for EB), the characteristic peaks of EB are centered at about 1600, 1500, 1380, 1330, and 830 cm$^{-1}$ while a sharp absorption peak corresponding to $NO_3^-$ is absent around 1350 1420 cm$^{-1}$ [22 26]. The latter result suggests that $NO_3^-$ should be completely expelled from EB in a 1mol/L $NH_4OH$ solution during the preparation of EB. The sharp peak between 1600 and 1500 cm$^{-1}$ is attributed to the typical C—C stretch form in a phenyl ring of quinonoid (the oxidation state of PANI) and benzenoid (the reduction state of PANI) units Therefore, the ratio of quinonoid to benzenoid units

can be used to infer the extent of the oxidation state. From a comparison of spectrum 1 with that of EB prepared in hydrochloric acid[8], the absorption between 1500 and 1600 cm$^{-1}$ in Fig 3 is more obvious than that of EB prepared in an HCl solution, attributable to influences of anions on the texture of EB. From spectrum 3 (for LEB-SPANI), the sulfonic acid group substituted on the PANI backbone is demonstrated by the presence of intrinsic peaks of SPANI at 1070, 1020, 702, and 610 cm$^{-1}$ [8,21].

During the synthesis of PANI in this work, PANI should be further oxidized by $NO_3^-$ in comparison with the PANI prepared in an HCl medium since $NO_3^-$ possesses an oxidative ability[22]. Thus, EB prepared from a nitric acid solution shows a higher mean oxidation state in comparison with that prepared in HCl Note that even when EB is reduced to LEB by phenylhydrazine, some quinonoid units are still visible on the polymer chain of LEB (see spectrum 2 in Fig 3). Since sulfonation of PANI is an electrophilic aromatic substitution reaction[8,27], the reactivity of the aromatic ring will increase with increasing the electron density of aromatic rings Based on the fact that some quinonoid units are still visible on the polymer chain of LEB prepared in this work, the lower electron density on the aromatic rings should decrease the sulfonation rate. In addition, the nitrogen atoms on quinonoid should be protonated in the fuming sulfuric acid solution. The positive charges delocalized in the protonated quinonoid units will deactivate the sulfonation reaction[8]. Consequently, the S/N ratio of LEB-SPANI prepared in this work cannot achieve the high sulfonation degree (e.g , S/N ratio (0.78).

## 3.4 X-ray Photoelectron Spectroscopy

The doping level of PANI was widely determined by using XPS analysis because it is a powerful analytical tool providing the information of chemical composition and oxidation structure of conducting polymers[28]. A typical XPS spectrum of LEB-SPANI is shown in Fig 4.

In fact, the N 1s spectrum has ever been fitted smoothly into four component peaks centered at 398.

2, 399. 3, 400. 9 and 402. 6 eV[23, 28  30]. However, the peak centered at 398. 2 eV does not exist in Fig 4, representing that the undoped imine units are completely transformed into cationic nitrogen atoms (polarons and bipolarons) corresponding to the peak centered at 400. 9 eV)[30]. The peak centered at 402. 6 eV is attributable to the protonated amine units Accordingly, the doping level of LEB-SPAN I can be determined from the sum of peak areas at 400. 9 and 402. 6 eV in comparing with the total peak area of the N 1s peak From this figure, the doping level of LEB-SPAN I is 0. 43, very close to the S/N ratio of LEB-SPAN I (i e., 0. 46), indicating that LEB-SPAN I is a good self - doped conducting polymer.
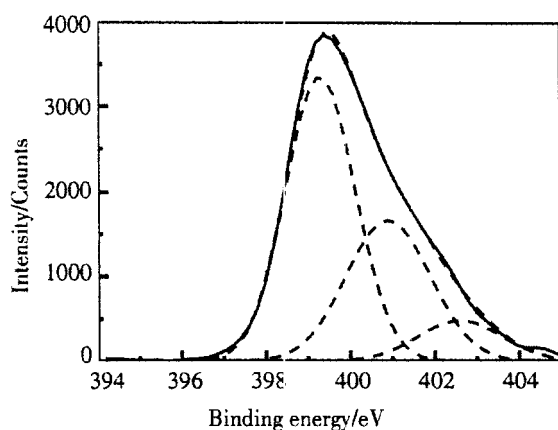


Fig 4   N 1s XPS spectrum of LEB-SPAN I synthesized from the sulfonation solution with adding 8 cm$^3$ 30% fuming sulfuric acid at 4    for 75 min

## 4   Conclusions

The key factors significantly influencing the conductivity of LEB-SPAN I, screened out in the FFD study, were concluded to be the sulfonation temperature, sulfonation time, as well as the volume and concentration of fuming sulfuric acid In the CCD study followed with a confirmation test, the LEB-SPAN I with a highest conductivity (ca 141 mS/cm) was obtained from the sulfonation solution with adding 8 mL 30% fuming sulfuric acid at 4    for 75 min From the results and discussion of FTIR and XPS spectra, the sulfonation degree and rate of LEB-

SPAN I were found to be significantly lowered when it was formed from the polymer precursors (i e., polyaniline) synthesized in HNO$_3$ in comparison with that prepared in HCl

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(                              ,          621,          )

:                                    ,                                          .

,              (4   )                (1 h)                  (10 mL)

(ca  127 mS· $cm^{-1}$);                                   ,              (ca  141 mS/cm)

4      75 min                   8 mL 30%              .                           (FTIR)              X

.        ,

:                        ;          ;          ;                ;