

Electropolymerization of Sulfonated Phenol by Cyclic Voltammetry

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ABSTRACT: In this work, electropolymerization of sulfonated phenol were performed by cyclic voltammetry (CV) on planar or nano-architecture substrates. The corresponding CV curves were analyzed and compared. The obtained polymer was characterized by SEM, EDX, and FTIR. The results suggested that it was feasible to electropolymerize sulfonated phenol on different substrates. The facility of electropolymerization on different substrates was as follows: graphite carbon > stainless steel plate > ZrO₂ nanotube. The peak current density of CV curve on stainless steel kept constant from the second cycle possibly attributed to the promoting effects of sulfonic acid groups: improving the ionic conductivity, changing the packing mode of polymer chains, and enhancing the permeability of the film to monomers. This work offered some insights into electrochemical synthesis of proton-conducting membrane for varied special applications, such as micro-sized fuel cell, sensor, battery, and other solid-state ionic devices. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1151–1156, 2013

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INTRODUCTION

Electropolymerization means that monomers are polymerized on the surface of the conductor or semiconductor by an electrochemical method.^{1–3} Generally, electropolymerization can endow the polymer film with a good binding force to the substrate surface, therefore, the as-synthesized composite materials have some unexpected advantages for applications with high integration and micro-sized requirements.⁴ It has been reported that some phenolic monomers can be easily electropolymerized on the surface of some substrates, mainly for metal corrosion protection, electrochemical or biological sensors, waste water treatment, and micro-sized battery.^{5–11} These polymer membranes can be insulating, electron-conducting, or uncommonly proton-conducting, mainly depending on the promoting effects of substituted groups on phenyl rings. For example, the polymer from amino-substituted phenol is electron-conducting due to the formation of long conjugated chains for transport of movable π -electrons, while the polymer from nonsubstituted phenol is insulating due to the unavailability of continuous transport channels. With the aid of some water, sulfonic acid group is known to dissociate protons and thus endow the polymer with some proton conductivity.^{12,13} In addition, sulfonic acid groups can also promote the swelling and polarity of the polymer, change the packing mode of polymer chain, and thus improve the access of the monomer to the

active sites on the interface between the electrode and electrolyte.⁹ However, compared with electron-conducting and insulating polymers, it was seldom reported about electropolymerization of sulfonated phenol.^{14,15} Up to now, to our best knowledge, only a few corresponding reports can be checked in literatures in which para-phenolsulfonic acid was used as monomer for electropolymerization, and the resultant main product was obtained by 1,2 coupling instead of 1,4 coupling for chain propagation, because para-position was occupied by sulfonic acid group.^{10,11} In this work, phenol was first sulfonated with concentrated H₂SO₄ (98%) at room temperature, and as main product, ortho phenol-sulfonic acid was then electropolymerized by cyclic voltammetry (CV) on different substrates including planar stainless steel, graphite carbon, and ZrO₂ nanotube. It was expected that the chain propagation was achievable by 1,4 coupling, that is, head-to-tail coupling. The corresponding CV curves were analyzed and compared. Furthermore, SEM, EDX, and FTIR were used to characterize the polymer film. The obtained results provided the experimental entry to design of micro-sized fuel cell, sensor, and batteries.

EXPERIMENTAL

Materials

Phenol (Sigma-Aldrich) and concentrated sulfuric acid (98%, Fisher Science) were used as received without further

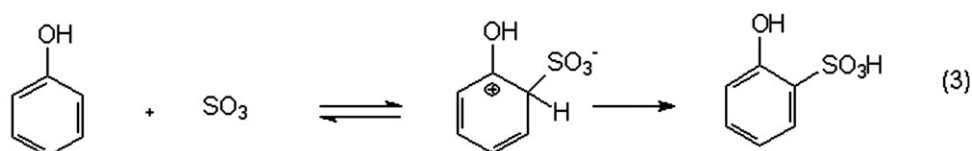
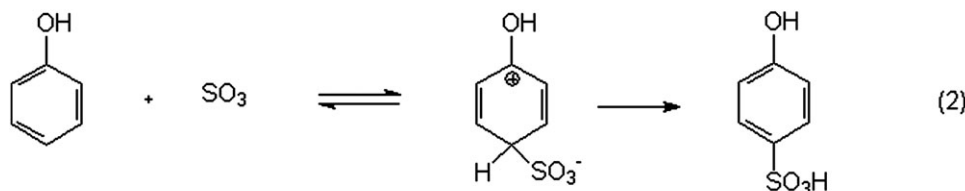
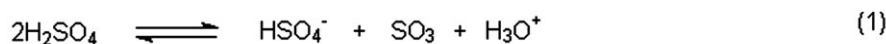


Figure 1. Scheme of sulfonation reaction of phenol.

purification. Sulfonated phenol was prepared by the following procedure: 4.7 g phenol (0.05 mol %) was dissolved in concentrated sulphuric acid (10 mL, about 0.2 mol %) and stirred for 3 h at room temperature. The obtained solution was diluted to 1 L with pure water. The resultant concentration of sulfonated phenol in the electrolyte was slightly less than 0.05M, because considering that side product of H_2O diluted the concentration of H_2SO_4 , sulfonation reaction should be not complete, and there was still small part of unsulfonated phenol.¹⁶ The rest unreacted H_2SO_4 was diluted and used as supporting electrolyte. The corresponding pH value of the electrolyte was measured to be about 1.25. ZrO_2 nanotube was prepared by anodization at 20 V of zirconium thin-films for 50 min, as reported elsewhere.¹⁷

Electropolymerization of Sulfonated Phenol

The electropolymerization of sulfonated phenol was performed by CV in a conventional three-electrode cell with planar stainless steel (304 L), graphite carbon or ZrO_2 nanotube as working electrode (effective area: 0.28 cm^2), a platinum sheet as counter electrode and saturated Ag/AgCl as reference electrode, respectively. A potentiostat/galvanostat (EG&G PARSTAT 2273) was used for all electrochemical experiments. The sweep rate was 20 mV s^{-1} ; the voltage range for carbon and ZrO_2 nanotube was from 0.4 to 1.8 V vs. Ag/AgCl ; for more clarity and avoiding the side reaction, the voltage range for more active stainless steel electrode was from 0.6 to 1.4 V. All experiments were performed at room temperature and atmosphere. The obtained polymer membranes were rinsed with ultra pure water before subsequent characterization.

Characterization of the Polymer

The photo of appearance, SEM image and EDX spectrum of the polymer were collected with a digital camera and scanning electron microscope (PHILIPS XL-30FEG), respectively. FTIR spectrum of the polymer was collected in transmission mode from 4000 to 400 cm^{-1} wavenumber with a Bruker Equinox 55 spectrometer.

RESULTS AND DISCUSSION

Sulfonation of Phenol

Hydroxyl is well known to be an ortho- or para-orienting group, so sulfonic acid group can only substitute for H atom

ortho or para to hydroxyl in phenol molecule. During the electrophilic sulfonation reaction, it is necessary to form carbonium ion. Sulfonation reaction at low temperature should be a kinetics-controlled process, that is, the product depends on the kinetics parameters such as concentration. The attack to ortho-H can directly result in the formation of a stable carbonium ion, therefore, *o*-phenolsulfonic acid is a main product at room temperature.¹⁸ *p*-phenolsulfonic acid can also form by resonance of carbonium ion as mentioned above. Higher temperature, for example, at 100°C , can facilitate the formation of thermodynamically stable *p*-phenolsulfonic acid. Figure 1 showed the possible sulfonation reaction mechanism of phenol, as discussed above.

Electropolymerization of Sulfonated Phenol on Stainless Steel

Figure 2 shows the CV curves (1–5 cycles) corresponding to the electropolymerization of sulfonated phenol on stainless steel plate. During the anodic scanning of the first cycle, a well-defined oxidative peak between 0.95 and 1.4 V vs. Ag/AgCl can be observed, while no reductive peak occurred during the cathodic scanning. This implied that electrochemical oxidation of sulfonated phenol is an irreversible process, similar to those of

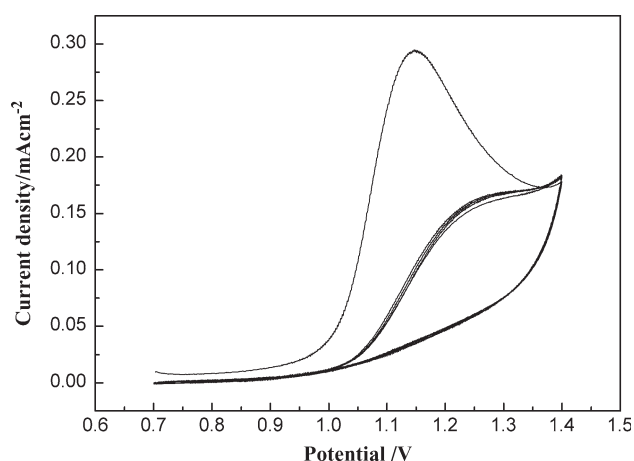


Figure 2. CV curves (1–5 cycles) during the electropolymerization of sulfonated phenol on stainless steel electrode surface.

Table I. Onset Potential, Peak Potential, and Peak Current Density during the Electropolymerization of Sulfonated Phenol on Different Substrates

| Parameters | Stainless steel | Graphite carbon | ZrO ₂ nanotube |
|---|-----------------|-----------------|---------------------------|
| Onset potential (V) | 0.95 | 0.8 | 1.1 |
| Peak potential (V) | 1.15–1.25 | 0.9 | 1.38 |
| Peak current density (mA cm ⁻²) | 0.3 | 0.4 | 0.01 |

other phenolic compounds. The corresponding onset potential, peak potential, and peak current density of the oxidative peak were listed in Table I. During the second cycle scanning, both the onset potential and peak potential shifted to the anodic direction, while the peak current density decreased, implying that the electrochemical oxidation began to become harder, similar to the electropolymerization of phenol.^{19,20} The possible reason was due to the formation of polymer membrane with higher resistance than steel electrode after the first cycle scanning. Thereafter, the peak current density did not decrease any more, similar to that of electron-conducting polymer from amino-phenol,²¹ while different with the continuous decrease of the peak current density during the formation of insulating polyphenol,¹⁴ implying the electropolymerization of ortho phenol-sulfonic acid was not self-limiting. The possible reasons are as follows: (i) sulfonic acid groups changed the packing mode of polymer chains and the polarity of polymer, allowing for the permeability to the monomers for continuous electropolymerization^{9,22}; (ii) probably, sulfonic acid groups also promoted the swelling and endowed the polymer film with some conductivity. After CV scanning, the stainless steel electrode was covered by a visible dense layer of pale yellow polymer membrane, as shown in Figure 3.

Electropolymerization of Sulfonated Phenol on Graphite Carbon

The CV curve about electropolymerization of sulfonated phenol on graphite electrode was shown in Figure 4. Compared with

CV curves of electropolymerization on stainless steel plate, the onset potential decreased from 0.95 to 0.8 V vs. Ag/AgCl, and the peak potential decreased from 1.15 to 0.9 V, while the peak current density increased from 0.3 to 0.4 mA cm⁻² (Table I). The peak potential was close to that on carbon electrode in literature.¹⁴ This indicated that the electropolymerization of sulfonated phenol occurred more easily on graphite carbon than on stainless steel, possibly due to the intrinsic attribution of the electrode materials. For example, the over-potential of electropolymerization of sulfonated phenol on stainless steel was slightly larger than that on graphite carbon, that is, graphite carbon facilitated the electrochemical oxidation of sulfonated phenol. However, from the second cycle, the peak current density on graphite carbon rapidly decreased. This problem may be related to the porosity of the electrode surface. It was expected that the situation may be improved by further modifying the carbon electrode or optimizing pH value of electrolyte, because the oxidative peak after the first cycle scanning was still visible during the electropolymerization of chlorophenol on carbon electrode.¹⁵

Electropolymerization of Sulfonated Phenol on ZrO₂ Nanotube

Recently, ZrO₂ nanotubes exhibited large advantages for many applications, because its large aspect ratio and small size can improve the sensitivity of sensors.¹⁷ ZrO₂ nanotubes were also used as substrate of electropolymerization by CV, as shown in Figure 5(a). It can be observed that the onset potential and peak potential were 1.1 and 1.38 V, respectively. Compared with those on stainless steel and graphite carbon, both of them shifted to the anodic direction, while the current density decreased by one order of magnitude, implying that sulfonated phenol can be electro-oxidized on ZrO₂ nanotube but more difficultly than on the other two materials. The peak current density also decreased greatly from the second cycle scanning, seeming a self-limiting electropolymerization. According to the literature,¹⁰ it can be speculated that the thickness of the polymer may be dozens of nanometers, which may be a potential composite material for nano-sized sensor or capacitor. Self-limiting process was probably related to the *n*-type conductivity

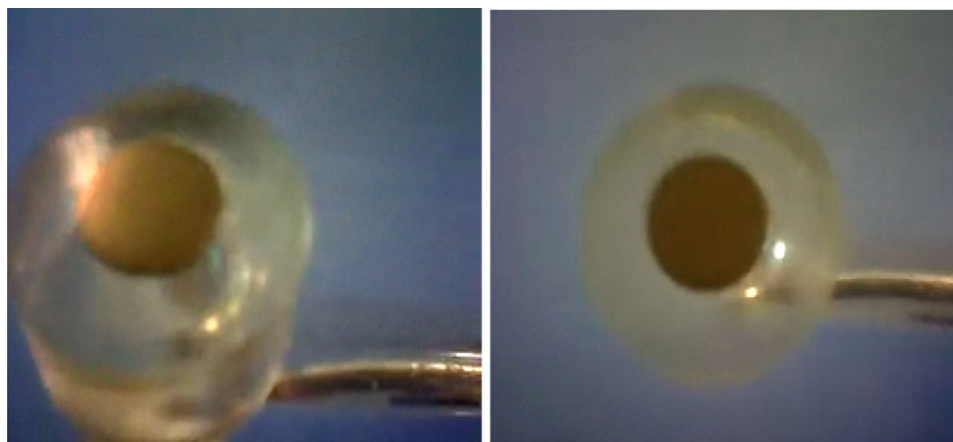


Figure 3. Photos of the sulfonated polyphenyl oxide membrane on stainless steel electrode after CV scanning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

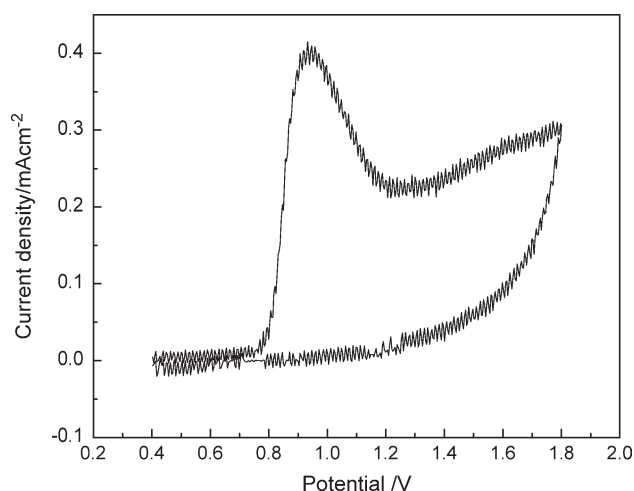


Figure 4. CV curve during electropolymerization of sulfonated phenol on graphite carbon electrode.

of the electrode or the morphology such as nozzle size and distribution of nanotubes. As shown in Figure 5(b), some dotted defects can be observed from SEM image of ZrO_2 nanotube substrate, near which the current cannot be well collected due to discontinuity-induced large electrical resistivity. The result may be improved after optimization of these structure parameters. Anyway, the interesting primary result afforded multiple concepts for designing the new structure of micro-sized fuel cells and other similar electrochemical solid-state ionic devices. Probably, in the case of ZrO_2 nanotubes, chronoamperometry at peak potential is a better method to obtain a dense polymer than CV scanning.

Morphology and Element Composition of the Polymer

The morphology and element composition of the obtained polymer were probed by taking the sample on stainless steel for an example, as shown in Figures 6 and 7, respectively. It can be

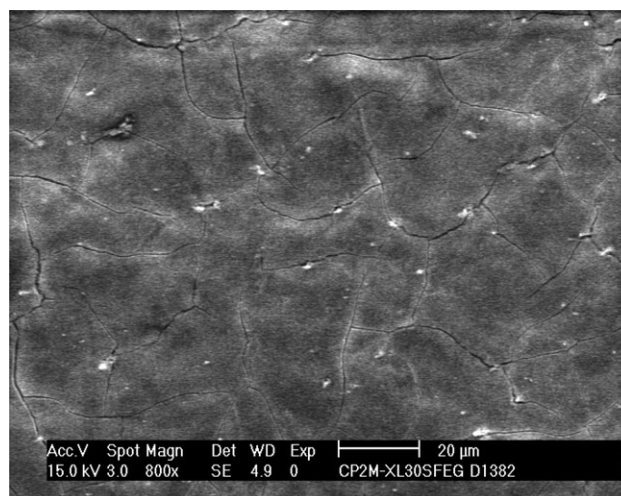


Figure 6. SEM image of sulfonated polyphenol on stainless steel electrode surface.

seen that a dense layer of sulfonated polyphenyl oxide was easily formed on the substrate surface by electrochemical oxidation. In addition, some small cracks on the polymer surface can be also observed, as reported elsewhere,²³ possibly due to the in vacuum of the dehydration sample during SEM and EDX test. According to EDX spectrum (Figure 7), beside the element signals (Fe, Ni, Cr, and Si) from stainless steel substrate, the interesting signals corresponding to S, O, and C from sulfonated polyphenyl oxide were also visible, and the order of peak strength was as follows: peak (C) > peak (O) > peak(S), which was reasonable and consistent with their relative contents by weight within sulfonated polyphenyl oxide. Especially, the C signal was much stronger than other element signals, corresponding to the main component of the polymer. No doubt, signal of sulfur element offered sufficient evidence that phenol was successfully sulfonated before electropolymerization.

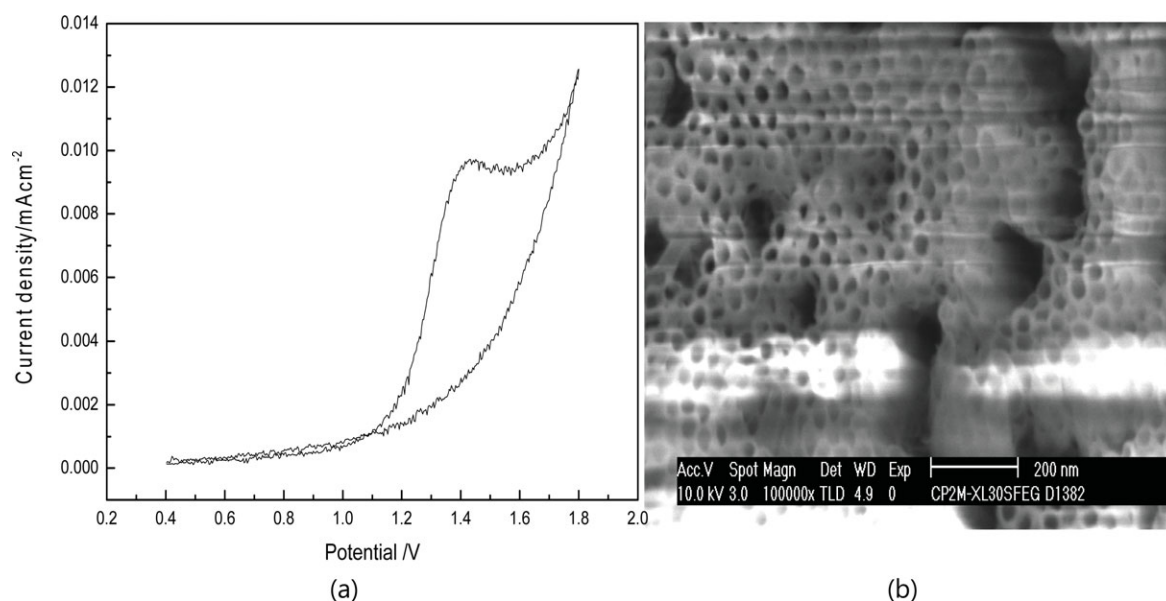


Figure 5. (a) CV curve during electropolymerization of sulfonated phenol on ZrO_2 nanotube and (b) SEM image of ZrO_2 nanotube substrate.

FTIR Spectrum of Sulfonated Polyphenyl Oxide

FTIR spectrum between 4000 cm^{-1} and 500 cm^{-1} of sulfonated polyphenyl oxide was shown in Figure 8. A broad peak centered at 3400 cm^{-1} was corresponding to stretching vibration of —OH from the ends of polyphenol chain as well as the presence of a little water. The peaks at 1648 cm^{-1} , 1590 cm^{-1} , 1488 cm^{-1} , and 1450 cm^{-1} can be attributed to stretching vibration of aromatic C—C bond.²⁴ The strong peak at about 1220 cm^{-1} was due to stretching vibration of aromatic ether chains (Ph—O—Ph),²⁵ corresponding to chain propagation during the electropolymerization of sulfonated phenol. The peaks at 834 cm^{-1} , 754 cm^{-1} , and 545 cm^{-1} correspond to C—H bond vibrations. The peaks at 1176 cm^{-1} , 1109 cm^{-1} , 1027 cm^{-1} , and 696 cm^{-1} can be assigned to the symmetric stretching vibrations of sulfonic acid groups and C—S bonds, respectively.^{26–30} The absence of the peak at 1700 cm^{-1} corresponding to carbonyl groups excluded the presence of quinone moiety and supported the formation of only polyether compounds. These results suggested that the concept and design were feasible and successful. Further optimization and deep exploration are underway.

CONCLUSIONS

Electropolymerization of sulfonated phenol was performed by CV on three substrates conductive stainless steel, semiconductor graphite, and semiconductor ZrO_2 nanotubes. The peak voltages on graphite carbon, stainless steel plate, and ZrO_2 nanotube were 0.8, 0.95, and 1.1 V vs. Ag/AgCl , respectively, so the facility of electropolymerization of sulfonated phenol on different substrates was as follows: graphite carbon > stainless steel > ZrO_2 nanotube. On stainless steel, the peak current density from the second cycle kept constant during the electropolymerization of sulfonic phenol, possibly attributed to the promoting effects of sulfonic acid group: improving the ionic conductivity, changing

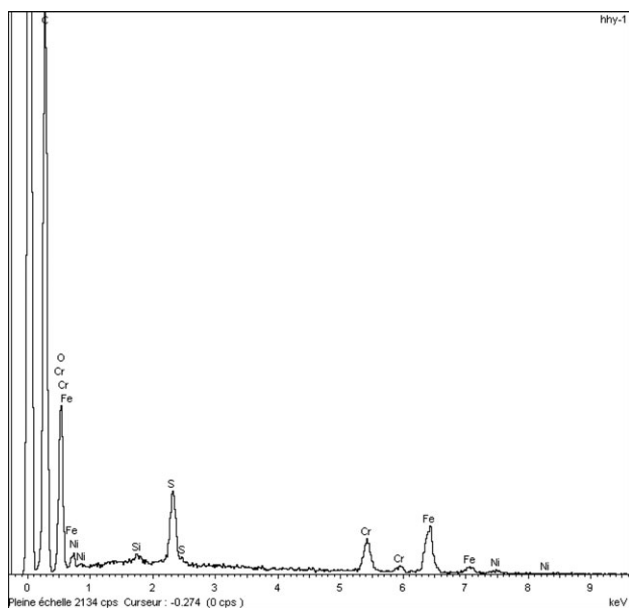


Figure 7. EDX spectrum of sulfonated polyphenol on stainless steel substrate.

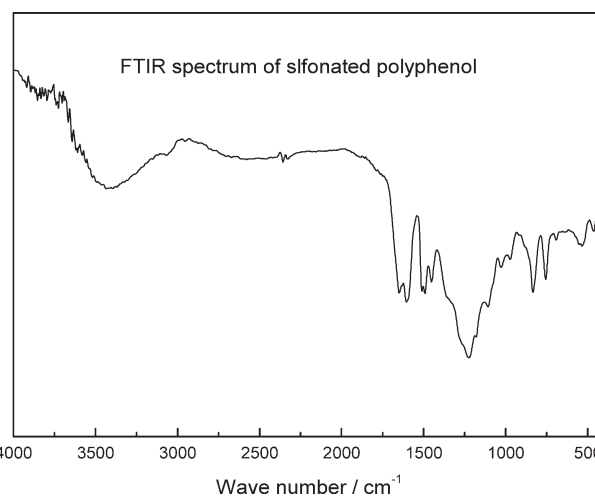


Figure 8. FTIR spectrum of sulfonated polyphenol.

the packing mode of polymer chains and enhancing the permeability of the film to monomers. For the moment, the dense polymer membrane was still not available on graphite carbon and ZrO_2 nanotube, thus further optimization was necessary. These results offered interesting insights into the electropolymerization of sulfonated phenolic compounds for application with high integration requirements such as micro-sized fuel cell, sensor, battery, and other similar solid-state ionic electrochemical devices.

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