

Preparation of P(AN-MMA)/SiO₂ Hybrid Solid Electrolytes

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ABSTRACT: Based on sol-gel methodology, poly(acrylonitrile-methyl methacrylate) [P(AN-MMA)]/SiO₂ hybrid solid electrolytes were prepared from AN, MMA, and tetraethyl orthosilicate with 3-methacryloxypropyl-trimethoxysilane (KH570) as silane coupling agent. From Fourier transformed infrared spectroscopy and x-ray photoelectron spectroscopy spectra, P(AN-MMA) and silica units are linked by covalent bonds in P(AN-MMA)/SiO₂ hybrid network. Differential scanning calorimetry result shows the glass transition temperature (T_g) of P(AN-MMA)/SiO₂ hybrid material is higher than that of P(AN-MMA) and

increases with the increase of silica content. From X-ray diffraction analysis, this hybrid solid electrolyte is amorphous. A study of ionic conductivity by AC impedance suggests that the ionic conductivity of P(AN-MMA)/SiO₂ hybrid solid electrolyte increases with the increase of the silica content and reaches a maximum value of $1.42 \times 10^{-3} \text{ S cm}^{-1}$ for 7 wt % SiO₂, and then decreases for SiO₂ > 7 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1365–1369, 2009

Key words: hybrid solid electrolyte; sol-gel methodology; preparation; ionic conductivity

INTRODUCTION

Solid electrolyte has been widely studied in energy conversion, chemical processing, sensing, and combustion control.^{1–4} Polymer electrolyte is a very important solid electrolyte, and the study of polymer electrolyte was launched by Fenton in 1973.⁵ So far, much work has been done to improve the ionic conductivity of polymer electrolyte, including blending, crosslinking, copolymerization, and plasticization.^{6–10} It is reported that the ionic conductivity of the polymer electrolyte can be increased by doping with inorganic particles, such as SiO₂, TiO₂, Al₂O₃, MgO, and so on, as well as a number of Lewis acid, such as AlCl₃, AlBr₃, and so on.^{11–13} Jiang et al.¹¹ prepared Li/polyurethane acrylate (PUA)-SiO₂/Li_{0.33}MnO₂ nanocomposite polymer electrolyte by doping with nanosilica in the PUA, and its ionic conductivity increased by 100%. Tambelli et al.¹² prepared PEO₈LiClO₄-Al₂O₃ composite polymer electrolyte by doping with Al₂O₃ powder and found that the Al₂O₃ powder decreased the poly(ethylene oxide) (PEO) crystallinity, at the same time its ionic conductivity improved obviously. Lin et al.¹³ doped 5% nanotitanium dioxide in PEO-10% LiClO₄ composite polymer electrolyte; as a result, ionic conductivity is increased from 1.03×10^{-5} to $1.40 \times 10^{-4} \text{ S cm}^{-1}$. These composite polymer elec-

trolytes were prepared by directly doping inorganic nanoparticles into the polymer matrix, resulting in being nonuniformly dispersed in the matrix of polymer electrolyte.

Organic and inorganic hybrid material is a well-dispersed multiphase material. The interfacial area between organic and inorganic phase is very large; at least one dimension of one phase is in nanometer size. The interfacial interaction may be covalent bond, which can improve the compatibility between organic and inorganic phase and keep inorganic nanoparticles dispersed uniformly in the polymer matrix. It is obvious that organic and inorganic hybrid electrolyte has an advantage over composite polymer electrolyte prepared by directly doping inorganic nanoparticles into the polymer matrix. In the present report, based on sol-gel technique, P(AN-MMA)/SiO₂ hybrid solid electrolytes were prepared with tetraethoxysilane (TEOS), acrylonitrile (AN), and methyl methacrylate (MMA) as starting material. In addition, the structure and thermal property of P(AN-MMA)/SiO₂ hybrid material, and the phase and ionic conductivity of P(AN-MMA)/SiO₂ doped LiClO₄ hybrid solid electrolytes were investigated.

EXPERIMENTAL

Materials

TEOS was obtained from Chemical Medical (Group) Shanghai Chemical Reagent (Shanghai

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City, China). 3-Methacryloxypropyl-trimethoxysilane (KH570) was obtained from Chenguang Chemical Industrial Research Institute (Chengdu, China). AN with analytical purity was purchased from Tianjin Damao Chemical (Tianjin City, China). MMA was obtained from Sinopharm Chemical Reagent (Shanghai City, China). AN and MMA were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Benzoyl peroxide (BPO) used as initiator was purchased from Shandong Laiwu Meixing Chemical (Shandong Province, China).

Sample preparation

With hydrochloric acid as catalyst, the partial hydrolysis and polycondensation of TEOS and KH570 (molar ratio employed was TEOS : KH570 : ethanol : H₂O = 4 : 1 : 12 : 16) were conducted at 45°C in a three-necked, round-bottomed flask for 3 h. Then, inert gas N₂ was introduced into the system, aliquot AN, MMA (molar ratio employed was AN : MMA = 1 : 1) and the first half of BPO (the amount of BPO was 0.1 wt % of the weight of AN, MMA, and KH570) were added, and the temperature was raised up to 75°C. Half an hour later, the second half of BPO was added and the temperature was kept constant at 75°C. Three hours later, a transparent homogeneous P(AN-MMA)/SiO₂ hybrid sol was obtained. Finally, 1 wt % LiClO₄ was added into P(AN-MMA)/SiO₂ hybrid sol, and then the hybrid sol was put into a model for aging until the hybrid sol was transformed into hybrid gel. After the hybrid gel was heat-treated in a vacuum oven at 40°C for 48 h, P(AN-MMA)/SiO₂ hybrid solid electrolytes was obtained. To investigate the ionic conductivity of the hybrid solid elec-

trolytes, the hybrid sol with 1 wt % LiClO₄ was put into a model cell with two opposite stainless steel plates; after aging for 24 h, the hybrid sol was transformed into the hybrid gel, and then the model cell was heat-treated in a vacuum oven at 40°C for 48 h.

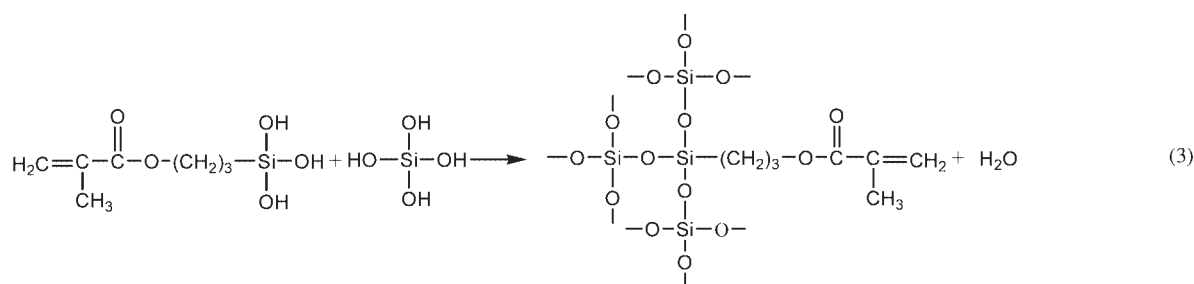
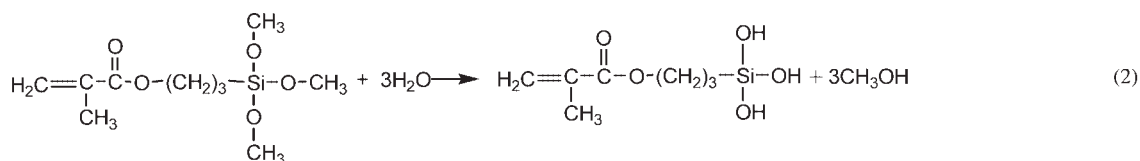
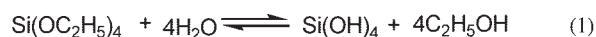
Measurements

Fourier transformed infrared spectroscopy (FTIR) spectra were measured with Nicolet (Madison, WI) Nexus-870 spectrometer, using KBr pellets. X-ray photoelectron spectroscopy (XPS) was performed using Mg K α radiation from a VG (West Sussex, UK) ESCALAB MKII X-ray photoelectron spectrometer. Differential scanning calorimetry (DSC) was conducted with a Mettler Toledo (Im Langacher, Switzerland) DSC-821E under nitrogen atmosphere at a flow of 80 mL/min. X-ray diffraction (XRD) analysis was recorded on a Risaku (Tokyo, Japan) diffractometer with D/max- γ B rotating Cu K α line ($\lambda = 0.15418$ nm), and the diffractograms were scanned in 2θ from 100° to 180° at a rate of 6°/min. The measurement of AC impedance was performed on an electrochemical workstation CHI660B (Shanghai, China) at a frequency range of 100 to 10⁵ Hz at room temperature.

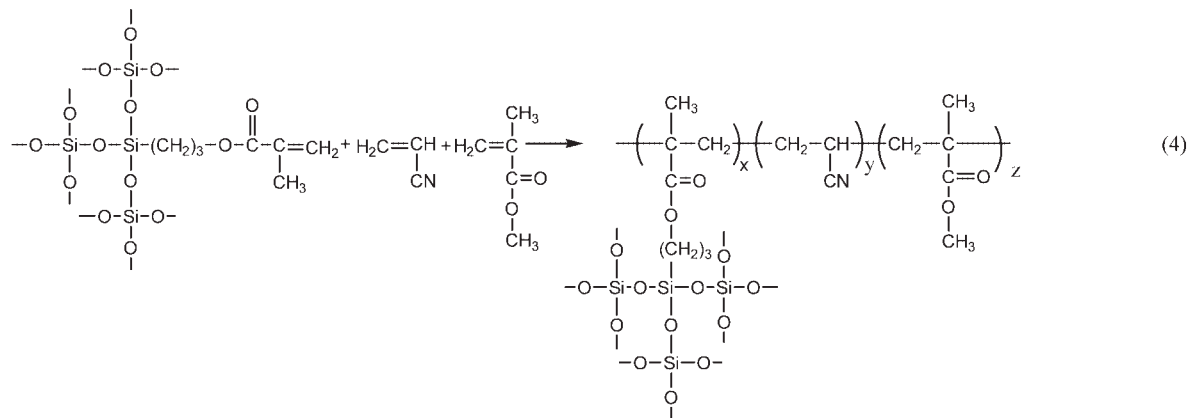
RESULTS AND DISCUSSION

P(AN-MMA)/SiO₂ hybrid mechanism

With HCl as catalyst, the active silica sol was synthesized by partial hydrolysis and polycondensation of TEOS and KH570 in ethanol medium as follows:



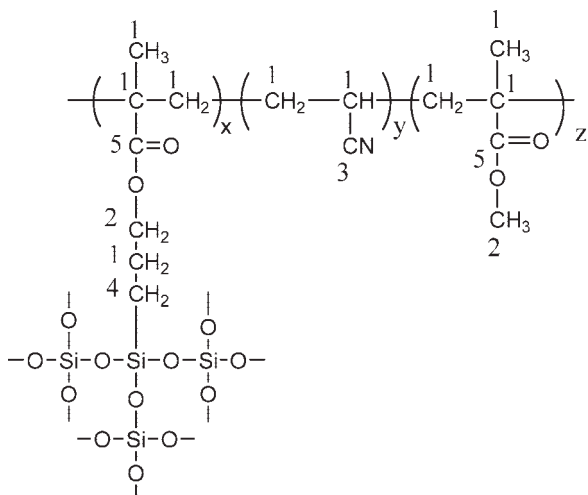
With BPO as initiator, P(AN-MMA)/SiO₂ hybrid sol was synthesized from active silica sol, MMA, and AN as follows:



Structure of P(AN-MMA)/SiO₂ hybrid material

Figure 1 shows the FTIR spectra of P(AN-MMA)/SiO₂ hybrid material. The characteristic peaks are present: $\nu(\text{-OH})$ at 3433 cm^{-1} and 1639 cm^{-1} , $\nu(\text{-CH}_3)$ at 2980 cm^{-1} , $\delta_s(\text{-CH}_3)$ at 1392 cm^{-1} , $\delta_{\text{as}}(\text{-CH}_3)$ at 1455 cm^{-1} , $\omega(\text{-CH}_2)$ at 956 cm^{-1} , $\nu(\text{-CN})$ at 2244 cm^{-1} , $\nu(\text{C=O})$ at 1734 cm^{-1} , $\nu_{\text{as}}\text{Si-O-Si}$ at 1153 cm^{-1} , and $\nu\text{Si-O-Si}$ at 1080 cm^{-1} , but no characteristic peak at $1670\text{-}1675 \text{ cm}^{-1}$ for $\nu(\text{C=C})$ is present, indicating that the active silica sol can be copolymerized with AN and MMA to form P(AN-MMA)/SiO₂ hybrid material.

Figure 2 illustrates the XPS full-scan spectrum of the P(AN-MMA)/SiO₂ hybrid material. In Figure 2, the peaks Si2p, C1s, N1s, and O1s are at 103.05, 284.80, 399.80, and 542.30 eV, respectively. When the peak C1s was fitted, five peaks at 284.81, 286.49, 286.64, 286.8, and 289.08 eV were obtained, as shown in Figure 3, corresponding to five different carbons (C1–C5) in the P(AN-MMA)/SiO₂ molecular structure as follows:



Peaks Si2p, C1s, N1s, and O1s proved that the P(AN-MMA)/SiO₂ hybrid material was made up of Si, C, N, and O elements, which implies that the

C=C groups of the active silica sol drawn from KH570 can be copolymerized with AN and MMA to form P(AN-MMA)/SiO₂ hybrid material.

Thermal property of P(AN-MMA)/SiO₂ hybrid material

Figure 4(a–d) is the DSC heating scan of P(AN-MMA) and P(AN-MMA)/SiO₂ hybrid materials for 3, 5, and 7 wt % SiO₂. The peak at about 134.2 in Figure 4(a) corresponds to glass transition temperature (T_g) of P(AN-MMA), whereas the peaks at about 137.3, 140.8, and 143.2°C in Figure 5(b–d) correspond to T_g of P(AN-MMA)/SiO₂ hybrid materials for 3, 5, and 7 wt % SiO₂, respectively. It was obvious that the T_g of P(AN-MMA)/SiO₂ hybrid materials is higher than that of P(AN-MMA) and increases with the increase of silica content. The reason is that the SiO₂ hybridized on P(AN-MMA)

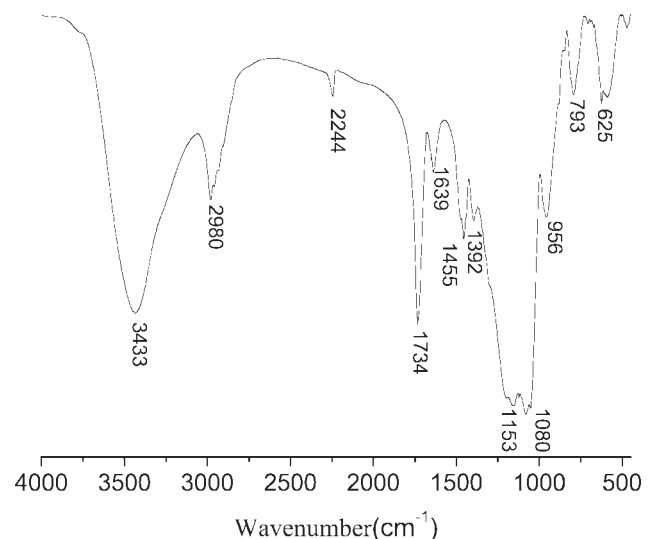


Figure 1 FTIR spectra of P(AN-MMA)/SiO₂ hybrid material.

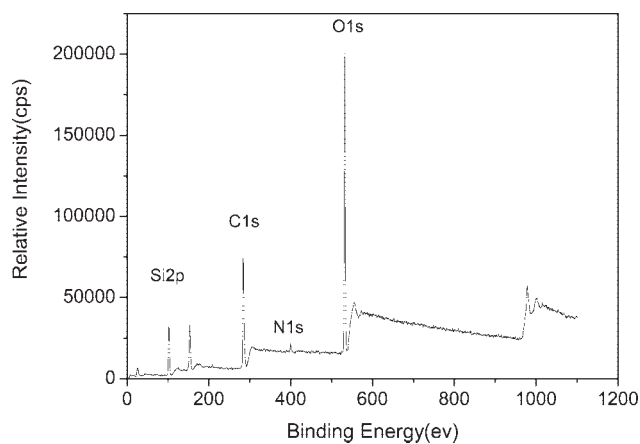


Figure 2 XPS full-scan spectrum of P(AN-MMA)/SiO₂ hybrid material.

chain limits the movement of P(AN-MMA) segments.

Ionic conductivity of P(AN-MMA)/SiO₂ hybrid solid electrolytes

Figure 5 is the AC impedance spectra of P(AN-MMA) and P(AN-MMA)/SiO₂ hybrid solid electrolytes. Each spectrum consists of a semicircle shown as Figure 6. In principle, a semicircle between the origin and the intercept would be observed if much higher frequency were used in the experiment, but the high-frequency limit used in this study (100 kHz is the upper limit for electrochemical workstation CHI660B) is not sufficient and caused the incomplete semicircle.¹⁴

Based on the intercept of each semicircle in each diagram in Figure 6 and eq. (5), the conductivities of P(AN-MMA) and P(AN-MMA)/SiO₂ solid hybrid electrolytes for 3, 5, 7, and 9 wt % SiO₂ can be esti-

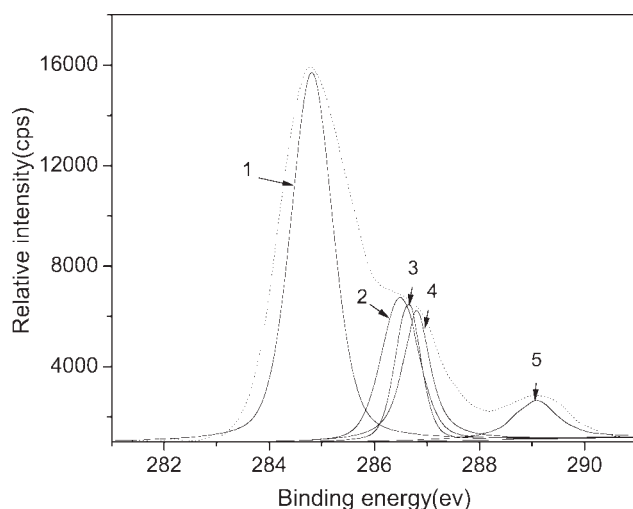


Figure 3 Curve-fitted XPS C1s spectrum of P(AN-MMA)/SiO₂ hybrid material.

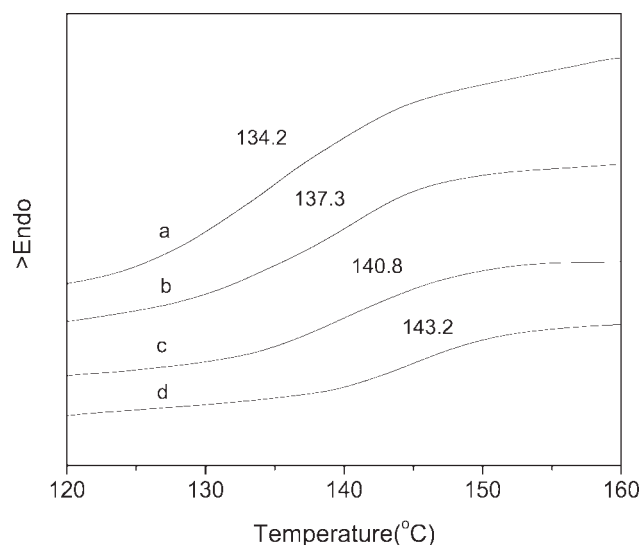


Figure 4 DSC curve of samples. (a) P(AN-MMA); (b) P(AN-MMA)/SiO₂ hybrid material for 3 wt % SiO₂; (c) P(AN-MMA)/SiO₂ hybrid material for 5 wt % SiO₂; (d) P(AN-MMA)/SiO₂ hybrid material for 7 wt % SiO₂.

ated to be 0.16×10^{-3} , 0.20×10^{-3} , 0.26×10^{-3} , 1.42×10^{-3} , and 0.18×10^{-3} S cm⁻¹, respectively.

$$\sigma = L/R \cdot S \quad (5)$$

where L is the distance between the stainless steel electrodes, S is the area of stainless steel electrode area, and R is the resistance of the sample. According to these data, the relationship between ionic conductivity and SiO₂ content was shown as Figure 6. It is obvious that the ionic conductivity of P(AN-MMA)/SiO₂ hybrid solid electrolyte increases with the increase of SiO₂ content and reaches a maximum value of 1.42×10^{-3} S cm⁻¹ for 7 wt % SiO₂, and then decreases for SiO₂ > 7 wt %. Figure 7(a,b) is

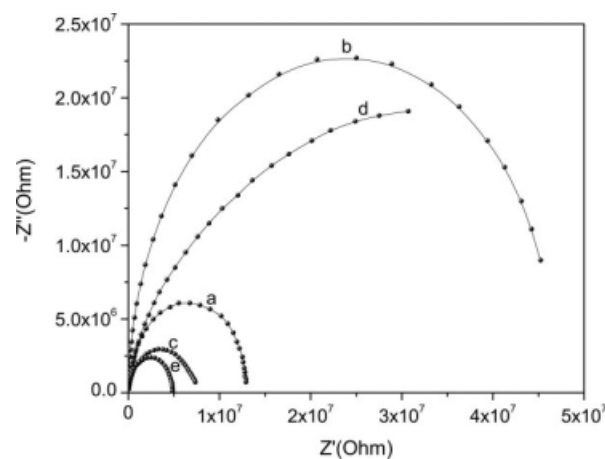


Figure 5 AC impedance curves of samples. (a) P(AN-MMA); (b) P(AN-MMA)/SiO₂ hybrid material for 3 wt % SiO₂; (c) P(AN-MMA)/SiO₂ hybrid material for 5 wt % SiO₂; (d) P(AN-MMA)/SiO₂ hybrid material for 7 wt % SiO₂; (e) P(AN-MMA)/SiO₂ hybrid material for 9 wt % SiO₂.

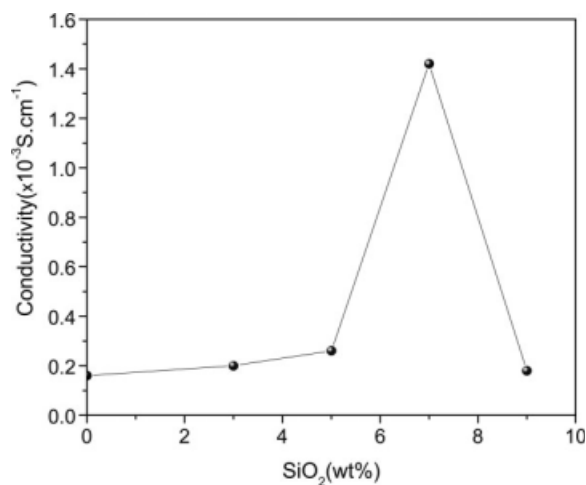


Figure 6 Relationship between ionic conductivity and SiO₂ content.

the XRD patterns for P(AN-MMA) and the P(AN-MMA)/SiO₂ solid hybrid electrolytes, respectively, and no significant difference is found between these two patterns. It is obvious that both P(AN-MMA) and P(AN-MMA)/SiO₂ solid hybrid electrolytes are amorphous, implying that the addition of SiO₂ did not change the form of P(AN-MMA), and this amorphous state will contribute to better lithium ion transfer. There exists a high ionic conductivity interfacial layer between polymer matrix and SiO₂. The area of interfacial layers increases with the increase of SiO₂ content; thus, the interfacial conductivity increases and the ionic conductivity is improved. Whereas SiO₂ content increases and exceeds 7 wt %, the insulation of SiO₂ appears to be more important and the ionic conductivity is lowered.¹⁵

CONCLUSIONS

Based on sol-gel technology, P(AN-MMA)/SiO₂ hybrid solid electrolytes were successfully prepared from AN, MMA, and TEOS with KH570 as silane coupling agent. P(AN-MMA), and silica units are linked by covalent bonds in P(AN-MMA)/SiO₂ hybrid network. The T_g of P(AN-MMA)/SiO₂ hybrid material is higher than that of P(AN-MMA) and increases with the increase of silica content. The ionic conductivity of P(AN-MMA)/SiO₂ hybrid solid electrolyte increases with the increase of the contents

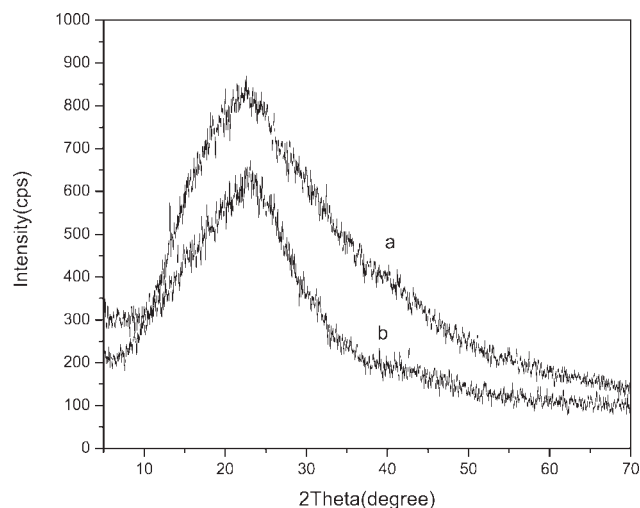


Figure 7 XRD patterns of samples. (a) P(AN-MMA) solid electrolyte; (b) P(AN-MMA)/SiO₂ solid electrolyte for 7 wt % SiO₂.

of SiO₂ and reaches a maximum value of $1.42 \times 10^{-3} \text{ S cm}^{-1}$ for 7 wt % SiO₂, and then decreases for SiO₂ > 7 wt %.

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