

Preparation of Poly(lactic acid)/Poly(methyl methacrylate)/Silicon Dioxide Degradable Hybrid Electrolytes

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ABSTRACT: On the basis of sol-gel methodology, a novel degradable hybrid electrolyte, poly(lactic acid) (PLA)/poly(methyl methacrylate) (PMMA)/silicon dioxide (SiO₂) hybrid electrolyte, was prepared from PLA, methyl methacrylate, and tetraethoxysilicon with 3-methacryloxypropyl trimethoxysilane as a coupling agent. As observed from Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy spectra, the PLA, PMMA, and silica units were linked by covalent bonds through the coupling agent in a hybrid network. Differential scanning calorimetry results show that the heat-resistance properties

of the hybrid electrolyte improved with increasing SiO₂ content. The hybrid electrolyte was shown to be amorphous by the X-ray diffraction results. From study of ionic conductivity by alternating-current impedance, the ionic conductivity of the PLA/PMMA/SiO₂ hybrid electrolyte increased with increasing silica content, reached a maximum value of 2.42×10^{-4} S/cm at 2 wt % SiO₂, and then decreased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2790–2794, 2010

Key words: composites; polyelectrolytes; polysilanes

INTRODUCTION

Polymer lithium-ion batteries used as polymer electrolytes instead of traditional liquid electrolytes are well adapted to various geometries and safety compared with liquid lithium-ion batteries.¹ The leakage of electrolyte solvent is a problem in polymer lithium-ion batteries that may result in a failure of the electrode/electrolyte contact and a reduction of the ionic conductivity (σ). Therefore, it is vital to look for some novel safe polymer electrolytes suitable for a new generation of high-performance lithium batteries. Among the polymer electrolytes reported so far, polymers such as poly(ethylene oxide), polyacrylonitrile, poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride), and poly(vinyl chloride) have been studied.^{2–5} PMMA has become a favorable polymer matrix for polymer electrolytes because of its distinct properties, including good compatibility with nonaqueous electrolytes; it can absorb much electrolyte, which leads to a high conductivity.⁶ Cui et al.⁷ studied the blend membranes of poly(vinylidene fluoride)/PMMA, whose ion conductivity

exceeded 10^{-3} S/cm. Saikia et al.⁸ showed that polymer electrolytes of P(VDF-HFP), lithium perchlorate (LiClO₄), and silica had fine mechanical stabilities and higher room-temperature conductivities.

It is well known that σ of a polymer electrolyte can be increased by doping with inorganic particles, such as silicon dioxide (SiO₂), TiO₂, Al₂O₃, and MgO, and with a number of Lewis acids, such as AlCl₃ and AlBr₃. Common composite polymer electrolytes have been prepared by the direct doping of inorganic nanoparticles into the polymer matrix, which results in nonuniform dispersion in the matrix of the polymer electrolyte. Although organic and inorganic hybrid materials are well-dispersed multiphase materials and interfacial interaction may be covalent bonds, they can improve the compatibility between the organic and inorganic phases and keep inorganic nanoparticles dispersed uniformly in the polymer matrix. Thus, hybrid electrolytes have an advantage over composite polymer electrolytes prepared by the direct doping of inorganic nanoparticles into the polymer matrix in σ . We prepared poly(acrylonitrile-methyl methacrylate)/SiO₂ hybrid solid electrolytes, and σ reached 10^{-3} S/cm.⁹ On the basis of the degradation of poly(lactic acid) (PLA) and hybrid function, we aimed to prepare a novel, degradable hybrid electrolyte, PLA/PMMA/SiO₂ degradable hybrid electrolyte, by a sol-gel methodology. The synthesis process, structure, thermal properties, crystallization, and σ of the polymer were investigated.

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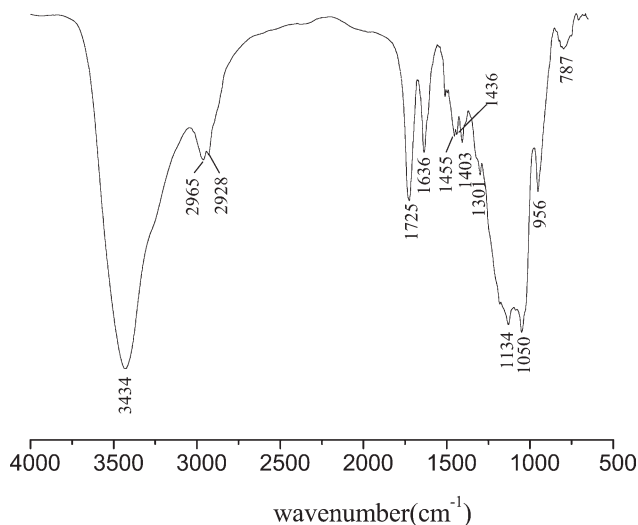


Figure 1 FTIR spectra of the PLA/PMMA/SiO₂ hybrid material.

for stretching, deformation, rocking, and wagging vibration, respectively; s and as stand for symmetrical and asymmetrical, respectively.): $\nu(\text{-OH})$ at 3434 cm^{-1} , $\nu(\text{C=O})$ and $\nu_{\text{as}}(\text{C=O})$ at 1725 and 1636 cm^{-1} , $\nu(\text{-CH}_3)$ at 2965 cm^{-1} , $\delta_{\text{as}}(\text{-CH}_3)$ at 1455 cm^{-1} , $\delta_{\text{s}}(\text{-CH}_3)$ at 1403 cm^{-1} , $\nu_{\text{as}}(\text{-CH}_2)$ at 2928 cm^{-1} , $\delta(\text{-CH}_2)$ at 1436 cm^{-1} , $\omega(\text{-CH}_2)$ at 1301 cm^{-1} , $\rho(\text{-CH}_2)$ at 787 cm^{-1} , $\nu_{\text{as}}(\text{C-O-C})$ at 1134 cm^{-1} , $\nu(\text{Si-O-Si})$ and $\nu_{\text{as}}(\text{Si-O-C})$ at 1050 cm^{-1} , and $\nu_{\text{s}}(\text{Si-O-C})$ at 956 cm^{-1} . Moreover, the characteristic absorbance for $\nu(\text{C=C})$ at 1670–1675 cm^{-1} was not found. Before FTIR spectroscopy was conducted, all of the samples were extruded with ethyl acetate over 24 h, and the uncrosslinked fragments were removed. Moreover, because of the steric hindrance, the C=C groups of KH570 structured on the active silica sol could hardly be self-polymerized. The spectra data indicated that the active silica sol may have reacted with PLA and MMA to form the PLA/PMMA/SiO₂ hybrid material.

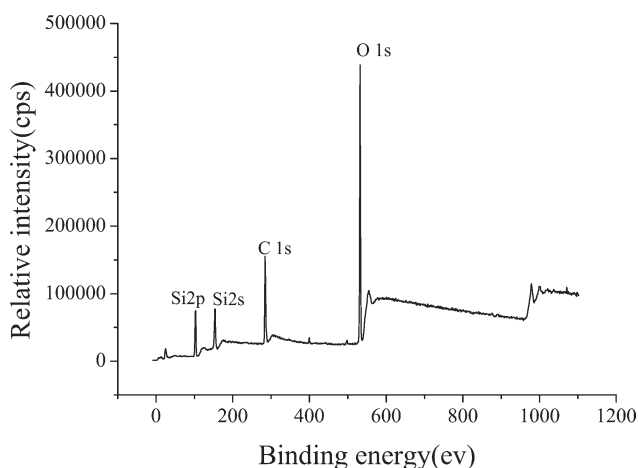
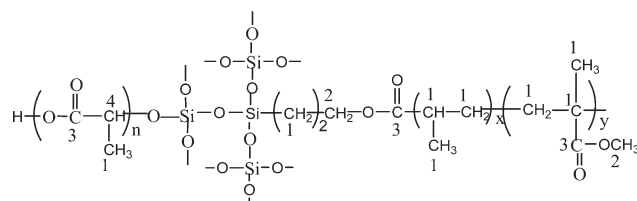


Figure 2 XPS full-scan spectrum of the PLA/PMMA/SiO₂ hybrid material.

XPS analysis

To confirm the composition and structure of the PLA/PMMA/SiO₂ hybrid material, XPS analysis was conducted. Figure 2 illustrates the XPS full-scan spectrum of the PLA/PMMA/SiO₂ hybrid material. The binding energy values of C1s, O1s, Si2s, and Si2p were 286.11, 532.86, 153.04, and 103.74 eV, respectively. When the C1s peak was fitted, typical spectra corresponding to the energy range of each of the considered elements are shown in Figure 3. Four peaks at 284.64, 286.13, 289.18, and 287.96 eV were obtained and corresponded to the four different carbons (C1–C4) in the PLA/PMMA/SiO₂ molecular structure as follows:



This molecular structure further confirmed the conclusions drawn from the FTIR analysis.

DSC analysis

To investigate the thermal properties of the PLA/PMMA/SiO₂ hybrid material, DSC was performed. Endothermic peaks at about 72, 92, 99, 105, and 113°C, corresponding to the melting of the PLA/PMMA/SiO₂ hybrid electrolytes for SiO₂ contents of 0, 2, 4, 6, and 8 wt %, respectively, were found and are shown in Figure 4. It was obvious that the heat-resistance properties of the hybrid electrolyte improved with increasing SiO₂ content. The reason has been the organic–inorganic networks from SiO₂ in the hybrid material.

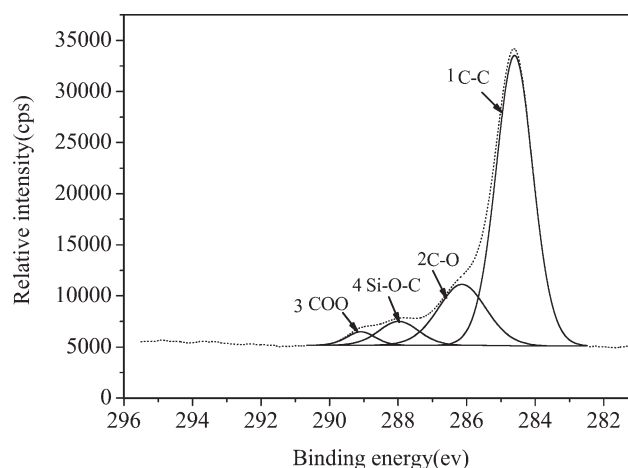


Figure 3 Curve-fitted XPS C1s spectrum of the PLA/PMMA/SiO₂ hybrid material.

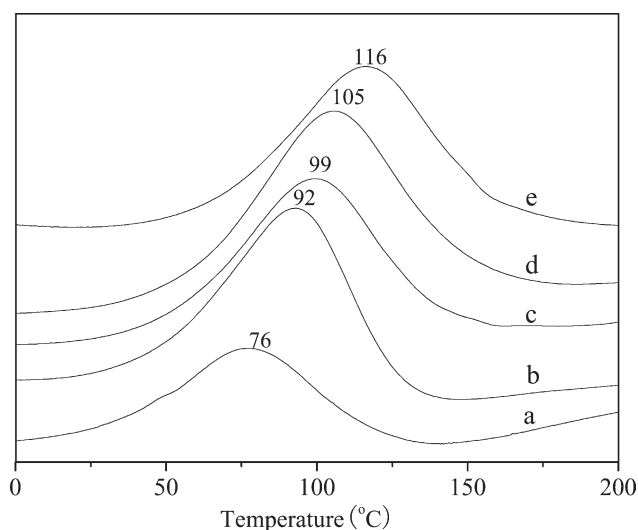


Figure 4 DSC curves of the PLA/PMMA/SiO₂ hybrid materials for different SiO₂ contents: (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt %.

ac impedance analysis

Electrochemical impedance spectroscopy is a sensitive method used to determine the conductivity of a polymer electrolyte. The measurement was carried out in the 100–10⁵ Hz frequency range, the initial impedance was 0.015 V, and the amplitude was 0.02 V. The electrolytes were sandwiched between two polished stainless-steel electrodes. The σ values were calculated from eq. (5):

$$\sigma = L/R_b A \quad (5)$$

where L (cm) is the thickness of the electrolyte film, R_b (ohm) is the bulk resistance of the film deter-

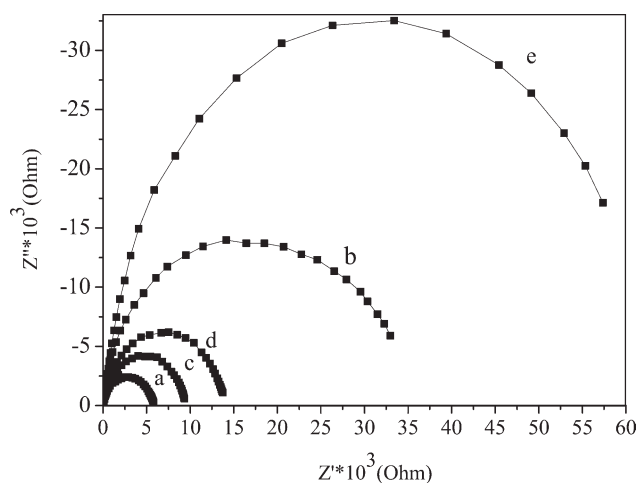


Figure 5 ac impedance curves of the PLA/PMMA/SiO₂ hybrid materials for different SiO₂ contents (Z' , Z'' are the real and imaginary part of impedance, respectively.): (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt %.

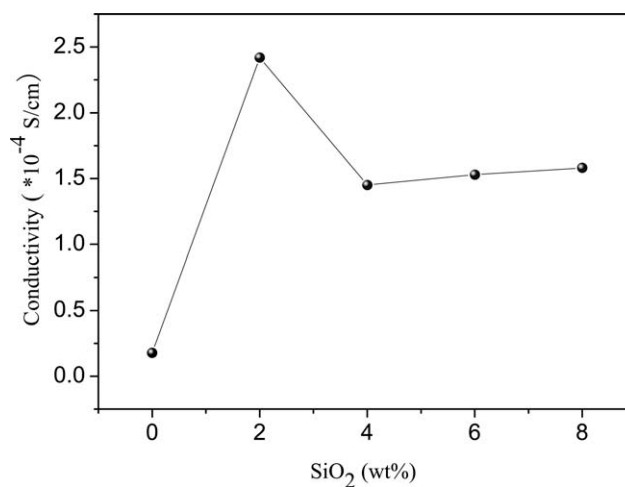


Figure 6 Relationship between σ and SiO₂ content.

mined by equivalent circuit analysis software, and A (cm²) is the area. Figure 5 shows the electrochemical impedance data (the average value of three time measurements is reported) for the PLA/PMMA/SiO₂ hybrid electrolytes for different SiO₂ contents. The calculated values of σ for the hybrid electrolytes were 0.178×10^{-4} , 2.42×10^{-4} , 1.45×10^{-4} , 1.53×10^{-4} , and 1.58×10^{-4} S/cm for 0, 2, 4, 6, and 8 wt % SiO₂, respectively. The relationship between σ and the SiO₂ content is shown in Figure 6. It was obvious that σ of the PLA/PMMA/SiO₂ hybrid electrolytes increased with increasing SiO₂ content, reached a maximum value of 2.42×10^{-4} S/cm for 2 wt % SiO₂, and then decreased. The area of the interfacial layer increased with increasing SiO₂ content; thus, the interfacial conductivity increased, and σ improved. Although the SiO₂ content increased and exceeded a certain value, the insulation of SiO₂

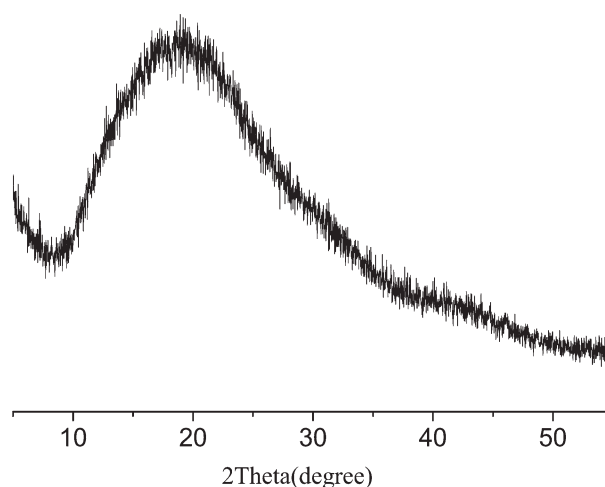


Figure 7 XRD curve of the PLA/PMMA/SiO₂ hybrid material of 2 wt % SiO₂.

appeared to be more important, and σ decreased.¹⁰ As shown in Figure 7, the PLA/PMMA/SiO₂ hybrid electrolyte was amorphous, and this amorphous state contributed to better lithium-ion transfer.^{7,8}

CONCLUSIONS

A PLA/PMMA/SiO₂ hybrid electrolyte was prepared by sol-gel methodology. PLA, PMMA, and silica units were linked by covalent bonds through a coupling agent in an organic-inorganic hybrid network. The heat-resistance property of the hybrid electrolyte improved with increasing SiO₂ content. σ of the PLA/PMMA/SiO₂ hybrid electrolyte increased with increasing silica content, reached a maximum value of 2.42×10^{-4} S/cm at 2 wt % SiO₂, and then decreased. The degradation and application of the PLA/PMMA/SiO₂ hybrid electro-

lyte will be investigated extensively in our next study.

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