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

Hualin Wang,¹ Liping Shu,¹ Shaotong Jiang²

¹School of Chemical Technology, Hefei University of Technology, Hefei, Anhui 230009, China ²School of Biotechnology and Food Engineering, Hefei University of Technology, Hefei, Anhui 230009, China

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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 tetraethoxylsilicon with 3-methacryloxy-propyl 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.

Correspondence to: H. Wang (hlwang@hfut.edu.cn).

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EXPERIMENTAL

Materials

All of the reagents used were analytical grade. Tetraethoxylsilicon (TEOS), LiClO₄, tetrahydrofuran, and methyl methacrylate (MMA) were purchased from Chemical Medical (Group) Shanghai Chemical Reagent Corp. (Shanghai City, China). 3-Methacryloxypropyl trimethoxysilane (KH570) was acquired from Chenguang Chemical Industrial Research Institute (Chengdu, China). Benzoyl peroxide (BPO), which was used as an initiator, was purchased from Shandong Laiwu Meixing Chemical Co., Ltd. (Shandong Province, China). PLA, with a weight-average molecular weight of 12,000, was made by ring-opening polymerization with stannous octoate as a catalyst in our laboratory.

Sample preparation

To obtain active silica sol, 2.48 g of KH570 and an amount of TEOS (the molar ratio used was TEOS : H_2O : ethanol = 1 : 2 : 4) were hydrolyzed and condensation-polymerized partially with hydrochloric acid as a catalyst in a three-necked, round-bottom flask at 45°C for about 12 h. Then, 20 g of MMA, 2 wt % PLA (dissolved in 20 mL of tetrahydrofuran solution), and the initiator BPO (the amount of BPO was 1 wt ‰ of MMA) were added to the active silica sol at 68°C under a nitrogen atmosphere. Five hours later, 2 wt % LiClO₄ was added. Finally, the hybrid sol was put into a model for aging until the hybrid sol was transformed into a hybrid gel. After the hybrid gel was heat-treated in a vacuum oven at 40°C for 48 h, PLA/PMMA/SiO₂ hybrid solid electrolytes were obtained.

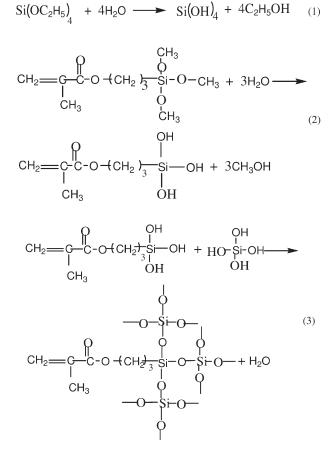
Measurements

Fourier transform infrared (FTIR) spectroscopy spectra were measured with a Nicolet Nexus-870 spectrometer (Madison, WI) in the region $650-4000 \text{ cm}^{-1}$ with KBr pellets. All of the samples were samples were extruded with ethyl acetate over 24 h. X-ray photoelectron spectroscopy (XPS) was performed with Mg Ka radiation with a VG ESCALAB MKII Xray photoelectron spectrometer (WestSussex, United Kingdom). Differential scanning calorimetry (DSC) was conducted with a Mettler Toledo DSC-851e (Im Langacher, Switzerland) under a nitrogen atmosphere. X-ray diffraction (XRD) analysis was recorded on a Risaku diffractometer (Tokyo, Japan) with a D/ max- γB rotating Cu K α line ($\lambda = 0.15418$ nm). The measurement of alternating-current (ac) impedance was performed on an electrochemical workstation CHI 660B (Shanghai, China) at a frequency range of 100–10⁵ Hz at room temperature.

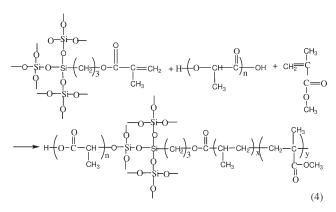
RESULTS AND DISCUSSION

PLA/PMMA/SiO₂ hybrid mechanism

With HCl as the catalyst, TEOS and KH570 were hydrolyzed and partially condensation-polymerized in an ethanol solution to form active silica sol, as shown in eqs. (1)–(3):



With BPO as the initiator, the PLA/PMMA/SiO₂ hybrid electrolyte was synthesized from active silica sol, PLA, and MMA as follows:



FTIR analysis

Figure 1 shows the FTIR spectra of the PLA/ PMMA/SiO₂ hybrid material. The following characteristic absorbances were present ($\upsilon \sigma \rho$, and ω stand

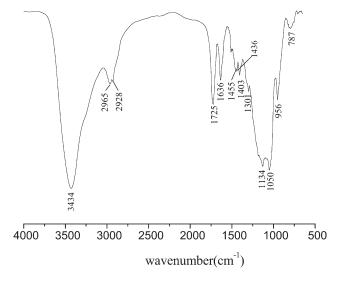


Figure 1 $\,$ FTIR spectra of the PLA/PMMA/SiO_2 hybrid material.

for stretching, deformation, rocking, and vagging vibration, respectively; s and as stand for symmetrical and asymmetrical, respectively.): v(-OH) at 3434 cm⁻¹ v(C=O) and v_{as}(C=O) at 1725 and 1636 cm⁻¹ 2965 cm^{-1} , $\delta_{as}(-CH_3)$ ν (-CH₃) at at 1455 cm⁻¹, δ_{s} (-CH₃) at 1403 cm⁻¹, v_{as} (-CH₂) at 2928 cm⁻¹ $\delta(-CH_2)$ at 1436 cm⁻¹, $\omega(-CH_2)$ at 1301 cm⁻¹, $\rho(-CH_2)$ at 787 cm⁻¹, $\nu_{as}(C-O-C)$ at 1134 cm⁻¹ v(Si-O-Si) and $v_{as}(Si-O-C)$ at 1050 cm⁻¹, and v_s (Si–O–C) at 956 cm⁻¹. Moreover, the characteristic absorbance for v (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.

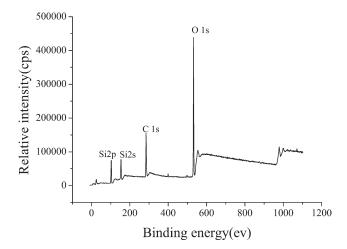
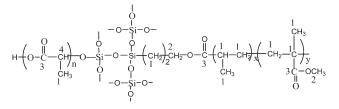


Figure 2 XPS full-scan spectrum of the PLA/PMMA/SiO₂ hybrid material.

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 rang 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. Endothermal 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 heatresistance properties of the hybrid electrolyte improved with increasing SiO₂ content. The reason have been the organic–inorganic networks from SiO₂ in the hybrid material.

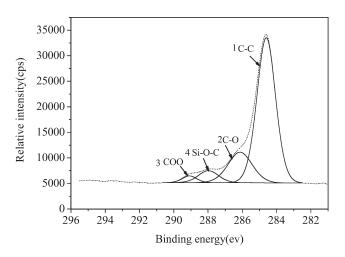


Figure 3 Curve-fitted XPS C1s spectrum of the PLA/ PMMA/SiO₂ hybrid material.

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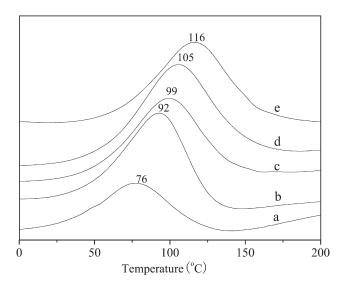


Figure 4 DSC curves of the $PLA/PMMA/SiO_2$ hybrid materials for different SiO_2 contents: (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt %.

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 $100-10^5$ 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):

$$\sigma = L/R_b A \tag{5}$$

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

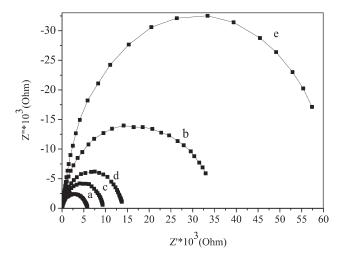


Figure 5 ac impedance curves of the PLA/PMMA/SiO₂ hybrid materials for different SiO₂ contents (Z', Z'' are the real and imaginary part of impedance, respectively.): (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt %.

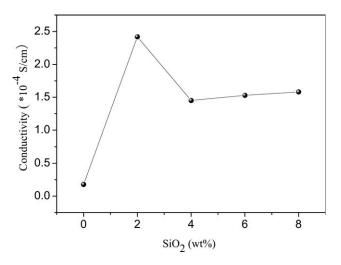


Figure 6 Relationship between σ and SiO₂ content.

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 SiO_2 content, reached a maximum value of 2.42 \times 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

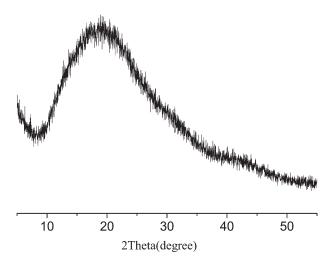


Figure 7 XRD curve of the PLA/PMMA/SiO_2 hybrid material of 2 wt % SiO_2.

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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 electrolyte will be investigated extensively in our next study.

References

- 1. Xiao, Q.; Wang, X.; Li, W.; Li, Z.; Zhang, T.; Zhang, H. J Membr Sci 2009, 334, 117.
- Basak, P.; Manorama, S. V.; Singh, R. K.; Parkash, O. J Phys Chem B 2005, 107, 1174.
- 3. Ma, W.; Zhang, J.; Wang, X. Appl Surf Sci 2007, 253, 8377.
- 4. Chiu, C.; Yen, Y.; Kuo, S.; Chen, H.; Chang, F. Polymer 2007, 48, 1329.
- 5. Ramesh, S.; Winie, T.; Arof, A. K. Eur Polym J 2007, 43, 1963.
- 6. Xiao, Q.; Li, Z.; Gao, D.; Zhang, H. J Membr Sci 2009, 326, 260.
- Cui, Z.; Xu, Y.; Zhu, L.; Wei, X.; Zhang, C.; Zhu, B. Mater Lett 2008, 62, 3809.
- Saikia, D.; Chen-Yang, Y. W.; Chen, Y. T.; Li, Y. K.; Lin, S. I. Desalination 2008, 234, 24.
- Wang, H.; Liu, X.; Yu, S.; Shi, T.; Jiang, S. J Appl Polym 2009, 114, 1365.
- 10. Quartarone, E.; Mustarelli, P.; Magistris, A. Solid State Ionics 1998, 110, 1.