

A Solid Solution-Based Tough Polymer Electrolyte for Structural Energy Storage Applications

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Abstract

Multifunctional structural energy storage components that can replace existing structural components while providing additional energy storage capability can ease the power demands of various electrically powered systems. The serious trade-offs between the mechanical and electrochemical performance of structural electrolytes are a challenge to realizing practical structural energy storage components. In this research, a solid polymer electrolyte with hydrates was created using polylactic acid and lithium salt. One of the compositions achieved a significant ionic conductivity ($3.11 \mu\text{S}/\text{cm}$) with an excellent toughness ($15.4 \text{ MJ}/\text{m}^3$) that is one order higher than the base polymer. This study demonstrates the possibility of incorporating electrochemical functionality into structural composites while maintaining or even enhancing mechanical functionality, guiding the design of future structural energy storage components.

Keywords

Structural energy storage; Supercapacitors; Solid polymer electrolyte; Multifunctionality.

Introduction

In electrically powered mobile systems, the heaviest components are energy storage devices and supporting structures. Taking an electric vehicle as an example, about 30% of the weight comes from the battery, and over 35% from structural components including frame, exterior, and interior. To further improve the operation time, travel range, and functionality of such systems, especially when the batteries are approaching their performance limit, one solution is to develop multifunctional structural energy storage components, which can replace existing structural components and provide extra energy storage capability. Researchers have demonstrated structural supercapacitors for this purpose¹. Most of these devices share the configuration of laminate fiber composites, in which two layers of carbon fiber electrodes are sandwiching a glass fiber separator and filled with an ion-conducting solid electrolyte as the matrix. The energy is stored through the electric double-layer capacitance effect at the carbon fiber-solid electrolyte interface. In almost all previous studies, the solid electrolytes are made of bi-continuous phase electrolytes (BPEs), which are simply the mixtures of liquid electrolytes and epoxy resins². The BPEs, however, have significant trade-offs between mechanical and

electrochemical performance and poor electrochemical interfaces with electrode materials.

Our recent study demonstrated a solid polymer electrolyte incorporated with hydrates (denoted as SPE-H) that provides promising multifunctionality³. We used polyethylene terephthalate (PET) as the base polymer and melted it together with lithium perchlorate (LiClO_4) to produce an amorphous solid solution. The PET- LiClO_4 electrolyte was then hydrated under controlled humidity to convert the salt to its trihydrate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$). Unlike previous designs of BPEs, we found that the SPE-H provided significant ionic conductivity while retaining the base polymer's stiffness and toughness. Moreover, such electrolytes showed much better electrochemical interfaces with electrodes.

In this research, we present another SPE-H system made from a different base polymer, polylactic acid (PLA), and another salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The new material system is easier to process and form desired shapes through various techniques. One of the compositions achieved a significant ionic conductivity ($3.11 \mu\text{S}/\text{cm}$) with an excellent toughness ($15.4 \text{ MJ}/\text{m}^3$) that is one order higher than the base polymer after proper thermal treatment and controlled hydration. This is the first evidence to show that it is possible to incorporate electrochemical functionality into structural composites while retaining or even enhancing their mechanical functionality. The mechanisms learned in this study can guide the design of better structural energy storage components in the future.

Experiment Details

Sample preparation: In a typical process, 2 grams of PLA and x wt% ($x = 10$ to 50) of LiTFSI were mixed in 40 ml of dimethylformamide (DMF). The mixture was put on the hot plate and stirred vigorously under $110 \text{ }^\circ\text{C}$ for 12 hours overnight to ensure the homogeneity of the solution. Then the solution was cast on a Teflon plate at $120 \text{ }^\circ\text{C}$ for 6 hours. We denote the samples at this stage as "As-cast SE x ", where SE stands for structural electrolyte and x reflects the wt% of the salt. The as prepared SE samples had residual DMF, so the cast film was then put into a convection oven at $165 \text{ }^\circ\text{C}$ for one hour to evaporate the residual solvent as much as possible. The samples are denoted as "Dried SE x " after this step. These dried samples can be melted and shaped through hot press, hot rolling, or injection molding.

The shaped samples were then exposed to air with controlled humidity in an environmental chamber. The samples will absorb water molecules from the air because of the hygroscopic nature of the salt. The amount of water absorbed is self-limiting at fixed temperature (22 °C in our laboratory) and relative humidity, as demonstrated in our previous studies^{3,4}. The samples are denoted as “Hydrated SE x” after this step. Although it seems that the hydrated samples are only the results of replacing the DMF in as-cast samples with water, later tests show that the hydrated samples have both higher ionic conductivities and better mechanical properties than the as-cast ones.

Material characterizations: Fourier transform infrared spectroscopy (FTIR) testing was conducted on an Agilent Cary 630 to detect the presence of chemicals. Electrochemical impedance spectroscopy (EIS) was conducted using a Gamry Interface 1010 potentiostat to obtain the impedance of electrolyte samples for ionic conductivity calculation. Tensile tests were conducted using rectangular samples on an Instron 5569 testing machine to obtain their mechanical properties.

Results and Discussions

FTIR results:

The chemical compositions of the electrolyte samples are confirmed by FTIR analysis, which characterizes chemical bonds through the absorbance peaks of infrared light in resonant frequencies. The FTIR spectra of pure chemicals, including PLA, LiTFSI, DMF, and water are first tested and presented in Figure 1a. Pure PLA is featured by an absorption peak near 1749 cm^{-1} caused by C=O stretching, and many peaks in the range of 1500 cm^{-1} to 1250 cm^{-1} due to C-H stretching and 1250 cm^{-1} to 1000 cm^{-1} due to C-O

stretching⁵. LiTFSI has strong feature peaks between 1500 cm^{-1} and 1000 cm^{-1} , but it is small peaks around 3600 cm^{-1} that distinguish it from other chemicals. DMF shows the strongest feature peak at 1665 cm^{-1} caused by C=O stretching. Liquid water is featured by a broad peak around 3300 cm^{-1} . The FTIR spectra of representative structural electrolyte samples are plotted in Figure 1b. The as-cast SE 40 sample show two feature peaks at 1749 cm^{-1} and 1665 cm^{-1} , respectively, indicating the existence of both PLA and residual DMF. The DMF can be completely removed after the drying process, as the feature peak of DMF disappears in the dried SE 40 sample. The spectrum of the hydrated SE 40 sample, however, shows little difference from the dried sample. The absence of peaks around 3300 cm^{-1} indicates the absence of liquid water. A small rise of absorbance near 3600 cm^{-1} is caused by the interaction between LiTFSI and water.

Ionic conductivity results:

The ionic conductivities of as-cast SE samples with various compositions are first tested and shown in Figure 2a. The values increase by three orders of magnitude from $4.2 \times 10^{-4} \mu\text{S/cm}$ to $8.7 \times 10^{-1} \mu\text{S/cm}$ when the weight ratio of the salt increases from 10% to 50%. The increase of ionic conductivity is partially due to the increased amount of salt ions. More importantly, it is caused by the increased amount of residual DMF that is associated with the salt. When the DMF is completely removed, the ionic conductivity decreases sharply. For example, the ionic conductivity of SE 40 decreases from $4.8 \times 10^{-1} \mu\text{S/cm}$ (as-cast, Figure 2a) to $1.1 \times 10^{-4} \mu\text{S/cm}$ (dried, Figure 2b). The hydration process, on the other hand, will restore the ionic conductivity, as shown in Figure 2b. For SE 40, its ionic conductivity increases to $3.11 \mu\text{S/cm}$ when hydrated at a

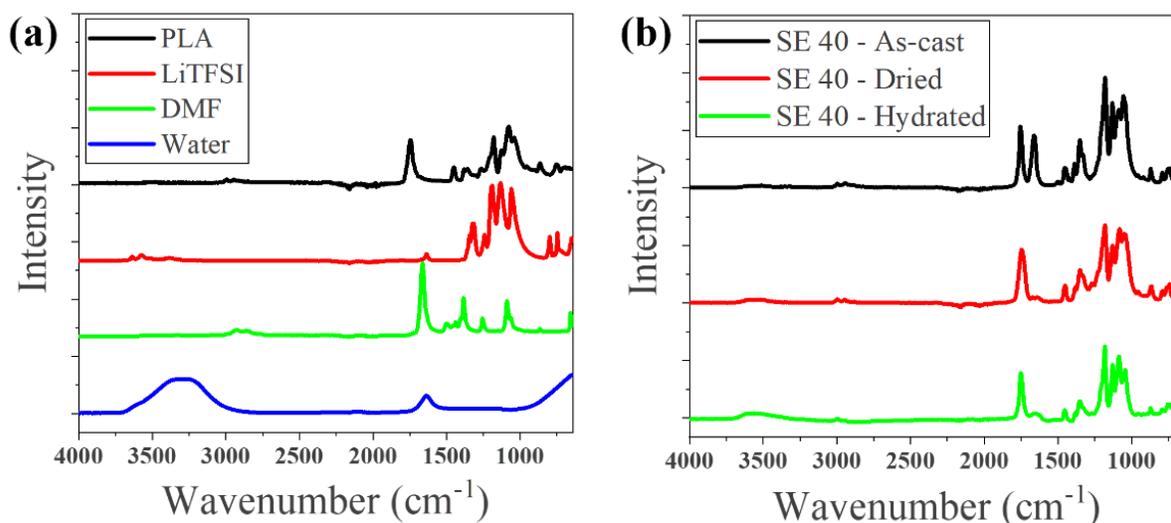


Figure 1. FTIR spectra of (a) pure chemicals used in the preparation of structural electrolyte samples and (b) representative structural electrolyte samples at different stages of processing.

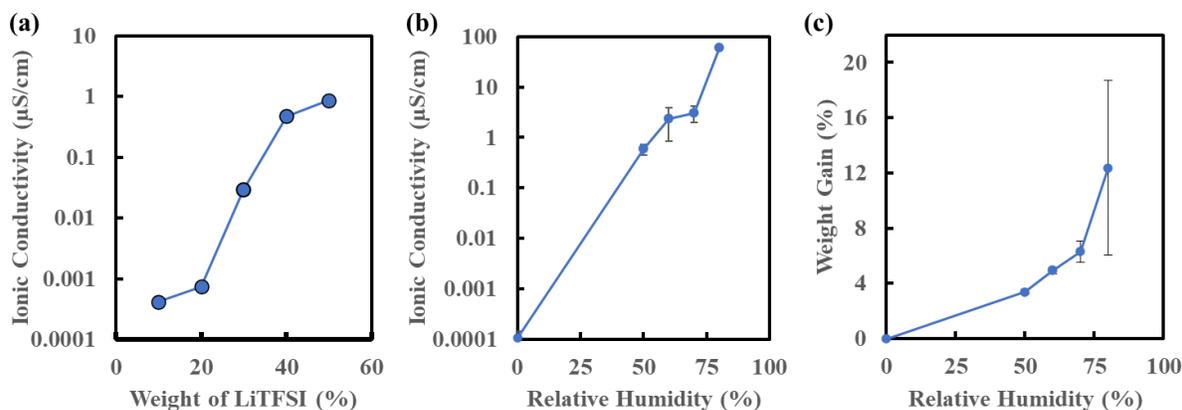


Figure 2. (a) The ionic conductivity of as-cast structural electrolyte samples with various weight ratios of LiTFSI. (b) The ionic conductivity of SE 40 samples hydrated at various relative humidity levels. (c) The weight change of SE 40 samples hydrated at various relative humidity levels.

relative humidity of 70%, and it reaches 59.1 $\mu\text{S/cm}$ when hydrated at 80% humidity. The hydration is self-limiting up to the humidity of 70% as indicated by the controlled weight gain (due to water absorption) measured in Figure 2c. However, the water absorption becomes out of control when the humidity reaches 80%, under which the salt will absorb too much water to form liquid solution. Liquid droplets were detected on samples, and the SE samples became gels with significantly reduced mechanical properties. Therefore, hydration under 70% humidity is considered as the optimized processing condition.

Tensile test results:

The stress-strain curves of as-cast SE samples with various compositions are presented in Figure 3a. As more LiTFSI is added to the polymer matrix, the samples show decreased elastic moduli and tensile strengths. However, the ductility of the samples increases greatly with more salts in them, resulting in very high toughness values as shown in Figure 3b. The significant increase in ductility indicates that the salt, together with the residual DMF, acts as a plasticizer in the material system. The toughness of the base polymer PLA is 1.83 MJ/m^3 , which is comparable to the values reported in the literature⁶. The toughness of as-cast SE 40, however, improves by one order of magnitude and achieves 18.5 MJ/m^3 . Then the mechanical properties of the SE 40 samples at different stages of processing are tested and shown in Figure 3c. The samples become stiffer and stronger after DMF is removed, while most of the ductility is preserved. As a result, the dried SE 40 presents a toughness of 30.0 MJ/m^3 . Hydration of the samples will decrease the elastic modulus and strength again, but they are still stiffer and stronger than the as-cast ones. The hydrated SE 40 (hydrated at 70% humidity) has a toughness of 15.4 MJ/m^3 , which is still one order of magnitude higher than that of pure PLA.

Conclusions

We have demonstrated a solid polymer electrolyte incorporated with hydrates (SPE-H) using hydrated PLA-LiTFSI samples for potential structural energy storage applications. We found that the samples prepared by solution casting method have significant solvent residuals that greatly affect the ionic conductivity and mechanical properties of the electrolyte system. The samples can be processed and shaped through various techniques including hot rolling and injection molding after complete removal of the residual solvent. The final electrolyte prepared through proper hydration of the dried samples achieves a significant ionic conductivity (3.11 $\mu\text{S/cm}$) with an excellent toughness (15.4 MJ/m^3) that is one order higher than the base polymer. Future research will demonstrate the processing of such electrolyte through 3D printing and the combination with electrode materials for high-toughness multifunctional structural energy storage devices.

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References

- Xu, Y., Lu, W., Xu, G. & Chou, T.-W. Structural supercapacitor composites: A review. *Compos. Sci. Technol.* **204**, 108636 (2021).
- Tu, V. *et al.* Performance of bicontinuous structural electrolytes. *Multifunct. Mater.* **3**, 025001 (2020).
- Joyal, N., Chang, Y.-C., Shonar, M., Chalivendra,

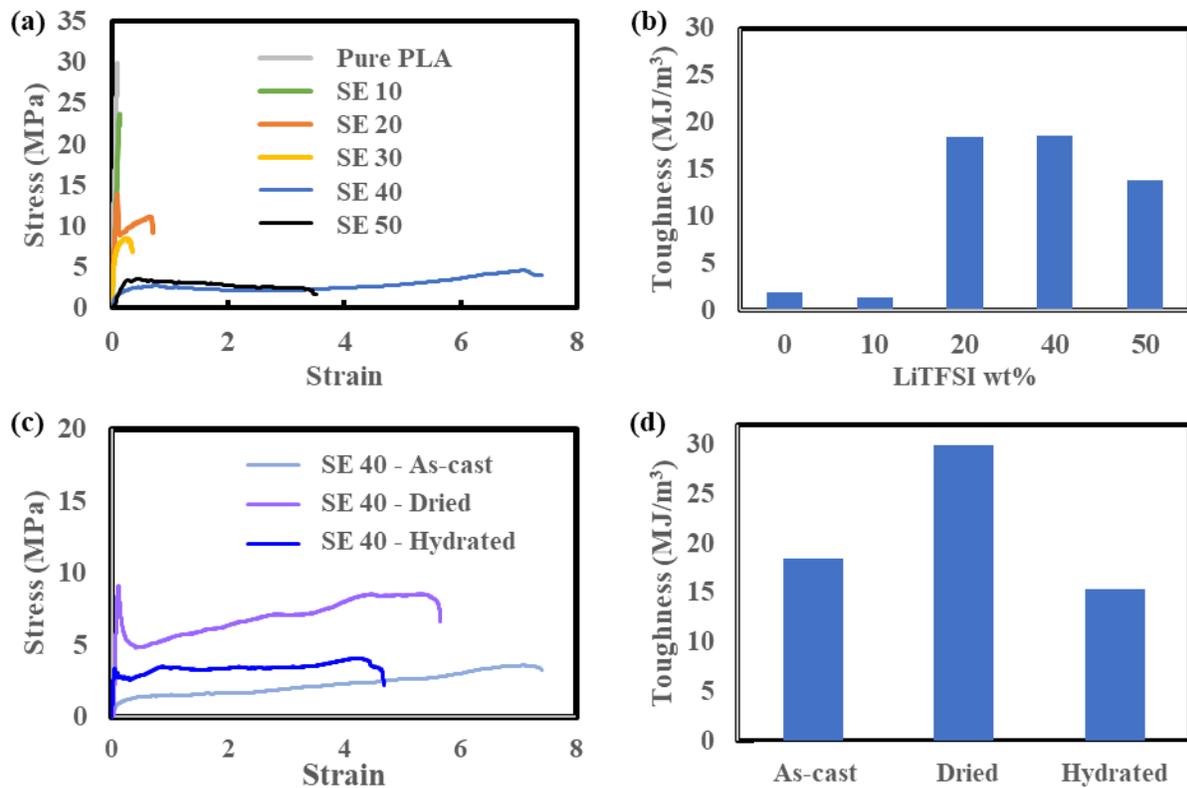


Figure 3. (a) The stress-strain curves of pure PLA and as-cast SE samples with various weight ratios of LiTFSI. (b) The average toughness values of pure PLA and as-cast SE samples with various weight ratios of LiTFSI. (c) The stress-strain curves of SE 40 at different stages of processing. (d) The average toughness values of SE 40 at different stages of processing.

V. & Shen, C. Solid polymer electrolytes with hydrates for structural supercapacitors. *J. Energy Storage* **51**, 104459 (2022).

4. Anjum, N., Joyal, N., Iroegbu, J., Li, D. & Shen, C. Humidity-modulated properties of hydrogel polymer electrolytes for flexible supercapacitors. *J. Power Sources* **499**, 229962 (2021).
5. Li, D. *et al.* Preparation of plasticized poly (lactic acid) and its influence on the properties of composite materials. *PLoS One* **13**, 1–15 (2018).
6. Suttiruengwong, S., Pitak, S., Saedan, M., Wongpornchai, W. & Singho, D. Binary-additives toughened biopolymer for packaging application. *Energy Procedia* **56**, 431–438 (2014).