MULTIFUNCTIONAL STRUCTURAL BATTERIES BASED ON CARBON FIBER REINFORCED PLASTIC COMPOSITES: INVESTIGATION ON MECHANICAL AND ELECTROCHEMICAL PROPERTIES

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ABSTRACT

In this study, the feasibility of multifunctional structural lithium ion batteries (LIBs) based on carbon fiber reinforced plastic (CFRP) composites was investigated. T700S carbon fabrics undertook the roles of both reinforcements and electrode materials in structural batteries. The co-continuous structural electrolytes were prepared by in-situ cure of liquid electrolyte and epoxy resin with the abilities of both load bearing and lithium ion transport. The structural electrolytes were cured with the carbon fabrics to process the CFRP composites. With the increase of liquid electrolyte/epoxy mass ratio, a trade-off relationship was found between the mechanical performance and electrochemical properties of both the structural electrolytes and the corresponding CFRP composites. The CFRP composites based on liquid/epoxy structural electrolytes were proved to have the ability to insert and extract lithium, and can be considered as the potential candidate for the multifunctional structural LIBs. The strategy of functionalizing the LIBs with structural performance via CFRP composites could be helpful for the overall system to provide a mass reduction as well as increase the energy efficiency at a system-level.

1 INTRODUCTION

Nowadays, attention has been shifted to the combination of subsystem functions to achieve the enhancement of overall system performance in many engineering applications. Functionalizing the energy-storage component with structural performance is a promising choice as it decreases the weight as well as increases the energy efficiency at the system-level. [1-3] Thus the concept of structural battery was proposed for the materials able to simultaneously store energy and carry mechanical loads. [4-9] CFRP composites have the potential to realize the energy storage like lithium ion-batteries (LIBs) in view of their composition and structure. [10-17] Both the CFRP composites and the commercial LIBs have the layer-by-layer assembly structures. Moreover, the microstructure of carbon fiber contains the fibrils of graphitic crystallites, which can not only provide the mechanical properties through aligning with the fiber axis, but also realize lithiation and delithiation between the turbostratic folded and interlinked carbon layers. Besides, some polymeric resin in the CFRP composites can sustain load through cross linking (like thermosets) and transport lithium ions through segmental motion (like poly (ethylene oxide)). Therefore, the CFRP composites should be the prospective alternative for achieving the multifunctional goals of the structural batteries.

In this study, the co-continuous structural electrolytes based on liquid electrolyte and epoxy resin were prepared firstly. The effects of liquid electrolyte/epoxy mass ratio of the structural electrolytes on the curing performance, composition, morphology, mechanical properties and conductive properties were discussed. Afterwards, the structural electrolytes were cured with the carbon fabrics to process the CFRP composites, and the charge/discharge capacities, cycle stability and mechanical properties of the CFRP composites were assessed to analyze and optimize the multifunctional performance. Finally, the feasibility of CFRP composites based on liquid electrolyte/epoxy structural electrolytes as
structural batteries were evaluated. The novelty of this work is the successful fabrication of the CFRP composites with the ability of lithium insertion and extraction. In other word, the structural battery which can simultaneously bear loads and store electrical energy is realized.

2 EXPERIMENTAL

2.1 Materials

The epoxy resin systems used in this study were liquid diglycidyl ether of bisphenol A (DGEBA) type epoxy resin E51 from Wuxi Bluestar Resin Co., Ltd and tetrafunctional epoxy resin AG-80 from Shanghai Huayi Resin Co. Ltd. The curing agent JEFFAMINE D400 was polyetheramine bought from Huntsman International LLC. 250 g/m² unidirectional (UD) carbon fabrics (Jiangsu Hongfei Advanced Materials Inc.) composed of 12k tows of T700 carbon fibers with a thickness of 0.21 mm were used as both electrodes and reinforcements. The mixture of 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (EMIM-Tf₂N, 99%, ShangHai Cheng Jie Chemical Co. Ltd.) and propylene carbonate (PC, 99%, Kuer Chemistry Co. Ltd.) with the corresponding lithium salt of lithium bis(trifluoromethanesulphonyl)imide (LiTf₂N, 99.9%, Chinese Special Gases Department of Purification Equipment Research Institute) was utilized as the liquid electrolyte.

2.2 Specimen preparation

The procedure for the preparation of the structural electrolyte and composite specimens is shown in Fig. 1. The liquid electrolyte component was prepared with LiTf₂N dissolved in the mixture of 99 wt% ionic liquid (IL, EMIM-Tf₂N in this study) and 1 wt% PC at the concentration of 2.3 mol/L. E51, AG-80 and the liquid electrolyte were roughly blended following the component ratios listed in Table 1. The blends were preheated in an oven at 55 °C for 5 minutes and mixed by high-shear mixer at 8000 rpm for one hour before the addition of D400. Finally all the components were stirred by power mixer until a uniform solution was obtained.

Table 1 Compositions, thicknesses and fiber volume fractions of structural batteries based on CFRP composites.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Structural phase</th>
<th>Liquid phase</th>
<th>Weight ratio</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E51 (g)</td>
<td>AG-80 (g)</td>
<td>D400 (g)</td>
<td>EMIM-Tf₂N (g)</td>
</tr>
<tr>
<td>1.0EPOXY_0.75IL</td>
<td>70.00</td>
<td>30.00</td>
<td>73.49</td>
<td>128.81</td>
</tr>
<tr>
<td>1.0EPOXY_1.0IL</td>
<td>70.00</td>
<td>30.00</td>
<td>73.49</td>
<td>171.75</td>
</tr>
<tr>
<td>1.0EPOXY_1.25IL</td>
<td>70.00</td>
<td>30.00</td>
<td>73.49</td>
<td>209.69</td>
</tr>
<tr>
<td>1.0EPOXY_1.5IL</td>
<td>70.00</td>
<td>30.00</td>
<td>73.49</td>
<td>257.63</td>
</tr>
</tbody>
</table>

The concentration of LiTf₂N in the liquid phase was kept constant at 30.14 wt%.

In order to characterize the performance of the pure cured structural electrolytes, the resin plaques with the thickness of 2 mm were manufactured using two paralleled glass plates separated by a silicone spacer and clamped by binder clips. After demolding, the plaques were cut into three specimen types: discs (20 mm diameter) for electrochemical impedance spectroscopy and morphology observation, dumbbell specimens for tensile testing, and powders for FT-IR testing. CFRP composites with four different formulations were manufactured using Vacuum Assisted Resin Infusion (VARI) process. The specimens for electrochemical and mechanical tests had the lay-up configurations of [0]₁ and [0]₄, respectively. After inserting vacuum tubes in the bag, resin infusion was carried out by a vacuum created between the mold and the bag, and the structural electrolyte was supplied to the infusion tubes. Both the structural electrolytes and the CFRP composites were cured in the oven in three temperature steps which was determined based on the results in Section 3.1, i.e. 75 °C for 2 h, 110 °C for 2 h and 160 °C for 2 h. All the heating and cooling ramps were carried out at the rate of 2 °C/min.
Fig. 1 Procedure for the preparation of the structural electrolyte and composite specimens.

2.3 Characterization

The cure kinetics and the cure cycles of the polymer electrolytes need to be determined by non-isothermal Differential Scanning Calorimetry (DSC) with different scan rates. For each formulation, DSC measurement was performed from 25 °C to 300 °C on a Mettler Toledo DSC-1 at the rates of 2, 5, 10, 15 and 20 °C/min, respectively.

The specimens for Scanning Electron Microscope (SEM) observation were submerged in ethanol which was changed every 12 hours to extract the liquid phase. After seven days, the specimens were dried in the oven at 75 °C under vacuum until each sample mass was constant. The morphology was observed using the CamScan JEOL 6010.

The Fourier-Transform Infrared Spectroscopy (FT-IR) was conducted on a Nicolet Avatar 360 in order to confirm the chemical compositions. 32 scans at a resolution of ± 4 cm⁻¹ were averaged for each specimen. All the IR measurements were performed in reflection mode with a frequency range of 4000-400 cm⁻¹ at the ambient temperature. The KBr pellets technique (2 or 0.6 mg of sample and 200 mg of KBr) was used. Small pieces were cut off from the sample and added into a mortar. KBr was added and mixed with these pieces afterwards and were grinded to a fine powder.

Polymer tensile tests were conducted for mechanical evaluation according to ASTM D790. The tensile strength and modulus were measured at a crosshead speed of 5 mm/min using Instron 5565 with a 500 N load cell. UD composite tensile tests were performed according to ASTM D3039 using Changchun Kexin-WDW-100 at a crosshead speed of 2 mm/min with a 50 kN load cell. The strain range for modulus measurement was 0.1%-0.3%. All the specimens had linear mechanical behaviors and did not fail at this strain range.

The Electrochemical Impedance Spectroscopy (EIS) was measured for the ionic conductivity of the structural electrolytes using electrochemical workstation (CHI660D, Shanghai Chenhua Device Company, China) in a frequency range of 10-2 to 106 Hz.

The electrochemical properties were evaluated by cycling 2032 coin cells with the composite laminates as the working electrode and lithium metal as the counter/reference electrode. The galvanostatic charge–discharge tests were carried out with an LANHE automatic battery testing equipment at 0.1 C in the voltage range from 0 to 3 V (versus Li/Li+).

3 RESULTS AND DISCUSSION

3.1 Curing performance

The addition of the liquid electrolytes has effects on the epoxy curing performance, so the cure cycle needs to be adjusted for all the structural electrolyte systems. Non-isothermal DSC at different scan rates ranging from 2 to 20 °C/min was utilized to examine the cure behaviors of the structural electrolytes with different liquid electrolyte/epoxy mass ratios in the study. The peak temperature Tpeak, the onset temperature Tonset and the offset temperature Toffset of the DSC thermogram are
shown in Fig. 2 (a). The three characterized temperatures have a linear correlation with the scan rate as shown in Fig. 2(b). The temperatures extrapolating to 0 °C/min can provide an important basis for the determination of the cure cycle. Fig. 2 (c) shows the effects of liquid electrolyte/epoxy mass ratio in the structural polymer electrolytes on Tonset, Toffset and Tpeak at 0 °C/min. A deviation of ±10 °C for each characterized temperatures of pure epoxy was considered insignificant and the corresponding temperature ranges were marked in yellow. Tonset and Tpeak changed little with the increase of the mass ratio, which indicates the initiation of the epoxy cure is not influenced by the introduction of the liquid electrolyte. The epoxy group reacted with the amine group and started crosslinking once the temperature reached about 75 °C. The reaction rate reached its highest value at 110 °C. Toffset almost linearly increased with the increase of the mass ratio, ranging from about 160 °C to 230 °C. As shown in Fig. 2(c), the curing cycle for the structural polymer electrolytes with different liquid electrolyte/epoxy mass ratio were determined as 75 °C for 2 hours, 110 °C for 2 hours and 160 °C for 2 hours.

Fig. 2 Curing performance of the structural polymer electrolytes with different liquid electrolyte/epoxy mass ratios: (a) DSC thermogram with definitions of onset temperature (Tonset), peak temperature (Tpeak) and offset temperature (Toffset), (b) Relationship between the scan rate and the characteristic temperatures, and (c) Relationship between the liquid electrolyte/epoxy mass ratio and the characteristic temperatures at the scan rate of 0 °C/min.

3.2 Composition and morphology

The structural electrolytes containing the distinct structural and conductive phases were successfully prepared according to the process in Fig. 1. FT-IR was utilized for the samples with all the formulations in order to determine the composition of the samples. For the spectrum of liquid electrolyte, the band at 1635 cm\(^{-1}\) was assigned to the in-plane C–C and C–N stretching vibration of the imidazole ring. Besides, the bands from 1578 cm\(^{-1}\) to 1057 cm\(^{-1}\) were assigned to the stretching modes of S–O, S–N and C–F. For the spectrum of pure epoxy, the absence of epoxy band at 915 cm\(^{-1}\) indicates the E51 and AG-80 resins were cured entirely. The bands from 1611 cm\(^{-1}\) to 1457 cm\(^{-1}\) correlated with the C=C stretching vibration of the benzene ring. The C–N stretching vibration was assigned to the band at 1351 cm\(^{-1}\). The characteristic bands of C–C stretching mode, C–O stretching mode and C–H bending mode were corresponded to 1196 cm\(^{-1}\), 1142 cm\(^{-1}\), and 1060 cm\(^{-1}\) in the spectrum of pure epoxy specimen, respectively. [12] The spectra of the structural electrolytes with different liquid electrolyte/epoxy mass ratios in Fig. 3 show almost the same characteristic bands, which suggests there was no difference in the chemical composition between the four samples. Furthermore, the absorbance baseline of these spectra increases with the increase of liquid electrolyte/epoxy mass ratio and leads to the decrease of the peak height. The specific composition of these samples can be analyzed by spectra comparison with pure structural and liquid phase. Like the
spectrum of epoxy, the absence of epoxy band at 915 cm$^{-1}$ indicates the entire cure of epoxy resin. In addition, the S-O band at 1578 cm$^{-1}$ in the liquid electrolyte was overlapped by the bands corresponding to C=C stretching vibration of the benzene ring in pure epoxy. The S-O, S-N and C-F bands from 1350 cm$^{-1}$ to 1057 cm$^{-1}$ in the liquid electrolyte were also covered by the C-C, C-O and C-H bands, respectively. However, the band at 1635 cm$^{-1}$ corresponding to the C-N stretching vibration of the imidazole ring existed in the spectra of all the structural electrolyte samples. This proves the existence of conductive phase, which means all the specimens were co-continuous systems containing both epoxy resin and liquid electrolyte.

The carbon fabrics were comprised of epoxy-sized T700S carbon fibers with a diameter of 7 μm (Fig. 4 (a)). All the structural electrolyte samples exhibited a co-continuous microstructure characteristic with a porous continuous epoxy network in Fig. 4 (b)-(d). In the cross-section of the structural electrolytes, the continuous phase was composed of interconnected epoxy flakes with a dimension of approximately 10 μm and discrete epoxy spheres with a diameter of 1-2 μm. The irregular-shaped holes interconnected with each other had a non-uniform size varying from 2 μm to 4 μm.

![FT-IR spectra of structural electrolytes with different liquid electrolyte/epoxy mass ratios, pure epoxy and liquid electrolyte.](image1)

![SEM micrographs of (a) T700 carbon fiber and (b) structural electrolytes after extraction of the liquid phase.](image2)
3.3 Multifunctional performance

It is well known that the mechanical performance and ionic conductivity are in a trade-off relationship. [3] The former needs the stiffness of polymer chain segments and the undamaged microstructure, while the latter needs a soft chain segments and interpenetrated passageways throughout the epoxy. In order to analyze the relation between the multifunctional performance and liquid electrolyte/epoxy mass ratio, the static tensile test and EIS were conducted on all these structural electrolytes (Fig. 5 (a)). The results show that the tensile modulus of the structural electrolytes decreased substantially from 400 MPa to 1 MPa with the increase of mass ratio from 0.75 to 1.5. However, the ionic conductivity had an opposite tendency compared with mechanical properties, increasing sharply from 0.08 to 0.5 mS/cm. Actually, the increasing liquid electrolyte/epoxy mass ratio means the increasing mass content of liquid electrolyte phase, making the diffusion of the lithium ions easier and the network more open. According to the literature [11][12], a reasonable goal for a structural electrolyte is to achieve both mechanical stiffness and ion conductivity within one order of magnitude of conventional materials. In our study, the structural electrolyte should achieve at least 200 MPa in Young’s modulus and 0.1 mS/em in ionic conductivity. An optimal composition can be chosen from Fig. 5(a) depending on the specific demands on the multifunctional properties, i.e., the structural electrolyte of 1.0EPOXY_1.0IL reaches the goals of load bearing and energy storage simultaneously.

The introduction of carbon fabrics has a great effect on the multifunctional performance. Firstly, the tensile mechanical modulus of the CFRP composite was much higher than the corresponding pure structural electrolyte, but still decreased with the increase of liquid electrolyte/epoxy mass ratio as shown in Fig. 5(b) and (c). The modulus of the UD CFRP composites without liquid electrolytes was 195 GPa. After adding liquid phase to reach a liquid phase/epoxy mass ratio of 0.75, the modulus dropped nearly 15%. However, when the liquid phase/epoxy mass ratio increased to 1.5, the modulus decreased to 33% of CFRP composites without liquid electrolytes with a larger data scatter. This can be attributed to the introduction of liquid phase in the structural electrolytes. The tensile modulus is mainly decided by the carbon fiber modulus and greatly affected by the load transfer of the matrix and interface. As a result, the porous continuous epoxy network plays an important role in the tensile modulus of the composites. For some fibers, the porous epoxy may expose part of the surfaces with the increase of mass ratio, resulting in the poor load transfer between matrix and fibers. Besides, the co-continuous microstructure of the epoxy phase may result in the cracks deviated with the fiber direction on the surface of the composites, which can act as the initiation point of the composite damage and significantly decrease the composite modulus.

![Fig. 5](image_url)

Fig. 5 Effects of liquid electrolyte/epoxy mass ratio on (a) multifunctionality of structural electrolytes, (b) mechanical properties of CFRP composites, (c) tensile stress–strain curves for CFRP composites, (d) charge cycling performance of structural batteries at 0.1C between 3 and 0 V versus Li+/Li, and (e) discharge cycling performance of structural batteries at 0.1C between 3 and 0 V versus
Furthermore, the CFRP composites were found to have the function of energy storage and the potential to be the multifunctional structural LIBs. The electrolyte can be cured together with the carbon fibers as an entirety, without utilizing separators. The CFRP composites were directly attached to the lithium metal and assembled in the 2032 coin cells. The side of the CFRP composites contacting with the cathode can was polished by sandpaper until the fibers in the upper layer were exposed from the resin. It makes the electrons easier to transfer between the can and the carbon fibers. The side contacting with lithium metal had a thin layer of pure electrolyte with a thickness of about 0.04 mm, so the diffusion distance for the lithium ions between the fibers and the lithium metal was significantly reduced compared with the original laminate structural batteries. The galvanostatic charge-discharge tests were performed for the CFRP composites with different formulations at a current density of 0.1C as shown in Fig. 6. They were all found to have the ability to charge and discharge, although the capacity was not satisfactory with the common anode materials. This confirms that the CFRP composites have great potential to be used in the energy field as a handy tool to realize the integration of structural/energy storage functions and the optimization of the overall system performance.

Fig. 6 shows the galvanostatic voltage profiles of the structural batteries at a current density of 0.1C in the voltage range of 0-3 V versus Li/Li+. It is noted that the first discharge capacity for 1.0EPOXY_0.75IL was nearly 12mAh g⁻¹, which was half of the value for other three samples. This indicates that the lithium diffusion is not as active as that with liquid electrolytes. The other three samples had a first discharge capacity ranging from 20 to 25 mAh g⁻¹. This is about 1/10 value of the batteries with liquid electrolytes and the same carbon fiber anode. [3] The large irreversible capacity is due to the rough surface of CFRP composites and the imperfect formation of a solid electrolyte interface (SEI) layer at the interface. The CFRPs have rough surface caused by VARI process. The imperfect formation of SEI is caused by direct contact of CFRPs and lithium metals. The charge/discharge specific capacities of the first three cycles varied a lot, which confirms the SEI layer was not perfectly formed.

Fig. 5(d)-(e) show the cycling performance of the structural batteries with different liquid electrolyte/epoxy mass ratios at 0.1 C. In the first 20 cycles, the discharge specific capacity was higher than the charge specific capacity. With the increase of the cycles, they both decreased gradually to nearly equivalent values. The discharge capacity of 1.0EPOXY_0.75IL dropped from 23 mAh g⁻¹ to 5 mAh g⁻¹, and the charge capacity decreased from 7.7 mAh g⁻¹ to 4 mAh g⁻¹. The charge/discharge capacities of 1.0EPOXY_1.25IL decreased from 22 mAh g⁻¹ and 12 mAh g⁻¹ to 3 mAh g⁻¹. For 1.0EPOXY_1.0IL, the charge and discharge capacities decreased from 25 mAh g⁻¹ and 12 mAh g⁻¹ to 2 mAh g⁻¹. 1.0EPOXY_0.75IL had the lowest capacity, decreasing from 12 mAh g⁻¹ and 7 mAh g⁻¹ to 1.5 mAh g⁻¹ for the discharge and charge capacity respectively. The stable specific capacity increased with the increase of liquid electrolyte content. In terms of the tensile results and the cycling performance in Fig. 5(b)-(e), the trade-off can be also found between the mechanical and electrochemical properties of the CFRP composites.

In addition, the cycling stability of all the samples needs further improvements. It can be attributed to the rough surface of the composites and the poor ability of lithium diffusion. The sizing agent of the carbon fibers which is epoxy for the as-received T700S keeps the lithium ions from diffusing and conducting. There are a great number of ways to further improve the electrochemical properties of the CFRP composites. Desizing, acidizing and alkaline treatments for carbon fabric can increase the specific surface area of the fibers. Modification with high-capacity materials can significantly increase the specific capacity of the CFRP composites. Meanwhile, the manufacturing process can be modified for a better surface quality, such as increasing the cure pressure, and using cover plates.
Fig. 6 Charge-discharge profiles of structural batteries with different liquid electrolyte/epoxy mass ratios: (a) 1.0EPOXY_0.75IL, (b) 1.0EPOXY_1.0IL, (c) 1.0EPOXY_1.25IL, and (d) 1.0EPOXY_1.5IL.

4 CONCLUSIONS

The CFRP composites with liquid electrolyte/epoxy mixture as matrix and T700S carbon fibers as reinforcements are proved to be able to simultaneously carry mechanical loads and store energy in this study. According to the DSC results, the final cure cycle of liquid electrolyte/epoxy polymer systems was determined as 75 °C for 2h, 110 °C for 2h, and 160 °C for 2h. After in-situ cure of the structural electrolytes, the co-continuous microstructure with interconnected epoxy flakes and discrete epoxy spheres was formed. The FT-IR spectra further confirmed the existence of the dual phase microstructure. The mechanical performance and ionic conductivity of the structural electrolytes had a trade-off relationship. With the increase of liquid electrolyte/epoxy mass ratio, the modulus substantially decreased from ~400 MPa to 1 MPa, while the ionic conductivity increased from 0.08 mS/cm to 0.5 mS/cm. An optimal composition of Sample 1.0EPOXY_1.0IL was chosen depending on the specific demands on the multifunctional properties. The carbon fabrics can be cured with the structural electrolytes to form the multifunctional structural LIBs based on CFRP composites. With the increase of liquid electrolyte/epoxy mass ratio, the porous epoxy network interconnected the liquid phase whereas greatly harmed the multifunctional performance. The trade-off also existed between the modulus and specific capacity of the CFRP composites. The first discharge capacity for 1.0EPOXY_0.75IL was nearly 12mAh g⁻¹. The other three samples had a first discharge capacity ranging from 20 to 25 mAh g⁻¹, reaching about 1/10 value of the batteries with liquid electrolytes and the same carbon fiber anode. The battery specific capacity was much lower that the common LIBs owing to the epoxy sizing agent of the carbon fibers and the rough surface of CFRP composites.

Although the cycling stability of all the CFRP composites need improvements, the CFRP composites were found to have the ability to insert and extract lithium, and has the potential to be the structural functionalized LIBs. There are a great number of ways to further improve the electrochemical properties of the CFRP composites, such as fiber activation and grafting. Meanwhile, the manufacturing process can be modified for a better surface quality. The strategy adopted in this work can be useful to provide a mass reduction as well as increase the energy efficiency at a system-level.
REFERENCES