Short communication

Design and fabrication of multifunctional structural batteries

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ABSTRACT

A new design of lithium ion batteries with tunable mechanical properties has been developed. Depending on the material design of the battery components, the battery can range from elastic to structurally rigid. Elastic battery electrodes have been fabricated by utilizing elastic polymer binders in the electrode construction. The design of structural batteries capable of carrying load is based on a fiber reinforced polymer composite structure. The first generation structural battery has been fabricated based on a high molecular weight polyvinylidene fluoride (PVDF) matrix achieving a modulus of 3.1 GPa and an energy density of 35 Wh kg^{-1}. Remaining challenges in fully realizing a multifunctional structural battery are outlined.

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1. Introduction

The continuing demand for lithium ion batteries with higher energy densities is the driving force for the ongoing evolution of battery active materials, new electrode architectures, and improved packaging design [1]. In actual applications, the batteries or battery packs are usually treated as add-on components and are isolated from the rest of the system.

A potentially powerful way of improving system energy storage capability is to view the battery as a functional component of the system. For example, prismatic cells were used as parts of the wing for an unmanned air vehicle which achieved record flight time [2,3]. In this case, the battery served as both the power source and as part of the structure. To achieve this, the mechanical strength of the battery was increased by external reinforcement. An alternative approach is to make the battery itself truly structural by changing the material composition and structure of battery electrodes and separator. This approach is exemplified by the work of Snyder et al. [4]. Both mechanical and electrochemical performance goals were considered in the battery design which dictated the material choices. In regards to the structural battery, great challenges emerged. For example, the electrolyte layer requires high ionic conductivity; however, the ionic conductivity of a material often correlates inversely with its mechanical strength. Nonetheless, this truly multifunctional approach represents a new paradigm in material design and engineering and holds great potential in realizing weight and volume savings on the system level.

The present work reports on our efforts in designing and fabricating multifunctional lithium ion batteries with elastic or potential structural load bearing capabilities. We adopt the true multifunctional approach by redesigning the structure and compositions of the battery components to obtain structural performance. We will discuss our design philosophy, the material choices, and the performance of first generation components and batteries. The remaining challenges in realizing a high performance multifunctional structure will be addressed as well.

2. Experimental

2.1. Structural battery components

The structural battery components were made of composites containing high molecular weight poly(vinylindene fluoride) PVDF (Aldrich, Average M_w ca. 534,000) with a process modified from one previously reported [5]. PVDF was dissolved in *N*-methyl pyrollidone and carbon fiber (CNF, Pyrograf Products, Pyrograf III^{TM} Carbon Fiber, HT grade), carbon black, and LiCoO$_2$ (FMC, Lectro^{TM} Plus 100) were slowly added and mixed. The slurry was cast on a Teflon block and was dried in oven at 110 °C for 5 h. The thickness is typically ∼100 μm. A similar process was used to make structural anodes based on coke (Osaka Gas, MCMB 25-10) with a thickness similar to the cathode. The battery separator was a polymer blend of PVDF–HFP (hexafluoropropene) (Elf Atochem Co., Kynar 2801, Average M_w ca 100,000) and poly(ethylene glycol) dimethacrylate (Aldrich, PEGDMA, Average M_w ca. 330) which forms a high strength polymer gel electrolyte with a electrolyte solution of 1 M LiPF$_6$ in EC + DEC + DMC + PC (4:3:2:1, v/v) (Merck). Coupons of cathode and anode with a dimension of 2.54 cm × 2.54 cm were

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bonded to the copper and aluminum grids by hot pressing at 150 °C. The cathode, separator and anode layers were finally laminated together at 160 °C. The cell was dried for 4 h at 60 °C under vacuum and transferred to Argon filled glove-box where a small amount of electrolyte solution was added, followed by sealing in a metalized plastic bag for electrochemical testing. The tensile properties of the battery components were measured on an Instron Model 5565. Electrochemical testing was performed on an Arbin battery testing system BTS-4000. Both structural and conventional battery cathodes were also tested in a liquid electrolyte cell with lithium as the counter electrode. The electrolyte was the same as that used in the complete structural battery.

2.2. Elastic battery components

Elastic battery electrodes were fabricated with a process similar to previously reported [6,7]. PVDF–tetrafluoroethylene–propylene) (PVDF–TFE–P) dissolved in methyl ethyl ketone (MEK), $LiCoO_2$, and carbon black were combined and mixed, followed by addition of CaO, 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylenetetramine (TETA). The mixture was cast on Teflon sheet and dried in air overnight. The electrode was heated at 110 °C in Argon for 6 h to increase the density of crosslinking. The film thickness was approximately 115 μm.

2.3. Carbon nanofiber reinforcement modification

For the modification of carbon nanofibers, carboxylic groups on carbon fiber surface were produced using diazonium reaction with 4-aminobenzoic acid [8]. Conversion of carboxylic groups to the acid chlorides was achieved by reacting with thionyl chloride. In the final step acid chloride groups were reacted with polyethylene glycol (PEG, Aldrich, Average M_w ca. 10,000) to give the final surface groups of $–Ph-COO-(CH_2CH_2O)_nH$.

2.4. Conventional cathode fabrication

A conventional cathode was fabricated with a process similar to that of the structural cathode, except that the PVDF was Kynar Flex 2801 (Elf Atochem) and no carbon nanofiber was added. After the paste of PVDF, $LiCoO_2$ and conductive carbon was homogenized, propylene carbonate was added as a plasticizer. The paste was cast on a glass substrate and allowed to dry slowly in air before further drying at 110 °C for 6 h. The final electrode composition was $LiCoO_2$:C:PVDF 82:7:11.

3. Results and discussion

3.1. Design considerations for structural battery

Our design starting point is the polymer lithium ion battery previously reported as shown in Fig. 1 [3]. A continuous porous polymer structure is pervasive throughout the battery. In the anode region, carbon particles are held together by the polymer and connected to the copper current collector. Similarly, cathode particles of lithium cobalt oxide and carbon additives are connected to the aluminum current collector. This baseline design was chosen over a traditional three-layer lithium ion battery structure of cathode–polymer separator–anode because it more resembles a polymer composite. The continuous polymer structure effectively eliminates the electrode/separator interface. Finally, organic electrolyte solutions permeate through the whole battery to provide ion conduction.

We can view the polymer lithium ion battery as a very weak composite with regions of the polymer structure filled with oxide or carbon particle fillers. The mechanical property of the battery is largely dependent on the strength of the polymer which is often PVDF. To achieve load bearing capability, we would like to transform the battery structure to resemble that of a conventional fiber reinforced composite. Four major changes are necessary to realize this goal: (1) use a higher molecular weight PVDF; (2) replace all particle fillers with fibers; (3) replace the organic liquid electrolyte with solid-state polymer electrolyte; and (4) reinforce the separator region with non-conducting fibers.

In our ideal design as shown in Fig. 2, the complete solid-state battery can be best viewed as a PVDF-based fiber enforced composite with different fillers. The active materials, for example, $LiCoO_2$ for the cathode and graphite for the anode, are nanofibers of high aspect ratios. In both electrodes, carbon fibers are used as the conducting additive to provide electronic conduction pathways. To build a high strength composite, it is also necessary to eliminate any porosity in the electrodes. Consequently, a solid-state electrolyte has to be used. This electrolyte needs to have high ionic conductivity as well as good chemical and mechanical compatibility with
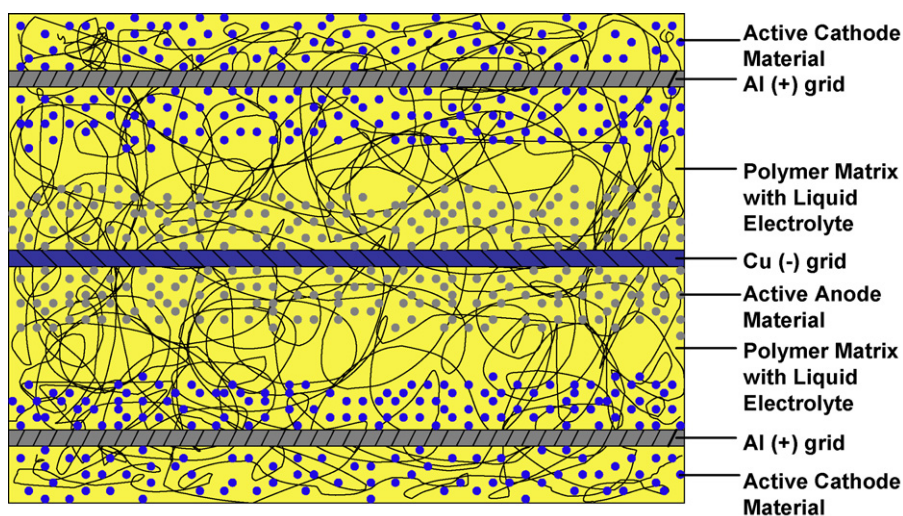

Fig. 1. Struture of a conventional plastic polymer lithium ion batteries. In a polymer matrix with liquid electrolyte, cathode and anode particles fill the two electrode regions and connected to the current collectors by carbon additives [3].
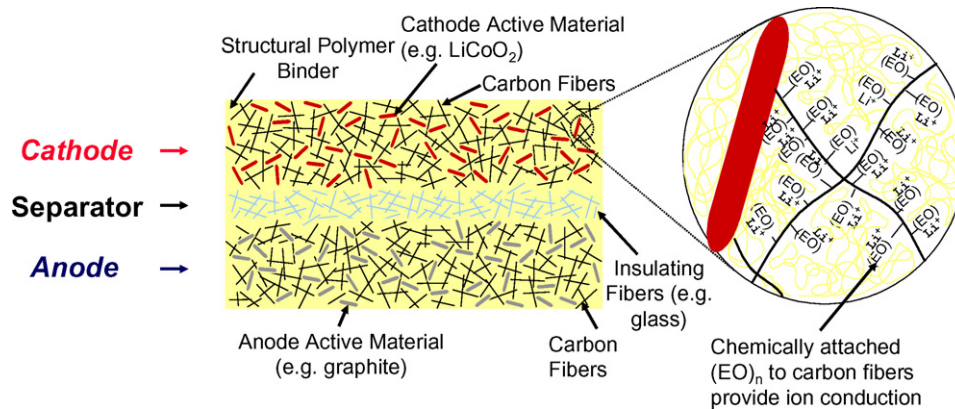
Fig. 2. Design of a structural battery. As compared to Fig. 1, all particulate fillers are replaced by fibers. A high molecular weight polymer serves as the structural polymer binder. On the surface of carbon fibers are polyethylene (PEO) oligomers that facilitate lithium ion transport. Insulating fibers further reinforce the separator region.

PVDF. While polyethylene oxide (PEO) is very compatible with PVDF, PEO-based polymer electrolytes are known to have modest to low conductivities, particularly for PEOs with high enough molecular weights to offer structural integrity [4]. Our design uses a unique modification process to ensure strong interaction between PEO and the carbon fiber surface. They not only provide enhanced ionic conductivity but were also found to improve the mechanical strength of the composite.

3.2. Structural cathode fabrication and testing

Structural cathode was fabricated by using carbon nanofiber as a conducting diluent as well as a structural component. PVDF with a molecular weight of 534,000 was used as the polymer matrix and $LiCoO_2$ was the cathode material. In addition, small amount of carbon black was added to improve conductivity. An example of a structural battery has a final composition of 2% carbon black, 11.5% carbon nanofiber, 35% $LiCoO_2$, and 51.5% PVDF. Fig. 3 compares the stress–strain curves of two structural cathodes to a control sample prepared according to conventional plastic battery fabrication techniques and compositions. The structural electrode fabricated with carbon nanofiber has a tensile modulus of 500 MPa and a maximum tensile strength of 5 MPa before failure. When the structural electrode was fabricated from surface modified carbon nanofibers,

the modulus increased to 650 MPa and the strength improved to 12 MPa. In contrast, the conventional battery electrode has a plastic nature, elongates to a strain of >70% before failure at a stress of <2 MPa. Our data show that the surface modification of the carbon nanofiber not only provides a possibility of surface lithium ion transport, but also serves to enhance the interaction between the carbon nanofiber and the polymer matrix and the mechanical strength of the structural electrode.

The electrochemical performance of the structural cathode was evaluated in a liquid electrolyte cell against metallic lithium as a counter electrode. After being charged to 4.2 V, the electrode was discharged at 0.1 mA cm^{-2} to 3 V (Fig. 4). A specific capacity of 90 mAh g^{-1} for $LiCoO_2$ was obtained as compared to 143 mAh g^{-1} for a conventional electrode. This reduction in capacity is most likely related to the slower kinetics in the structural electrode. However, considering the remarkable improvement in mechanical strength, the reduction in electrode rate capability is deemed acceptable.

3.3. Elastic cathode fabrication and testing

While our main focus of this report is to fabricate battery components with loading bearing capabilities, it is worthwhile to
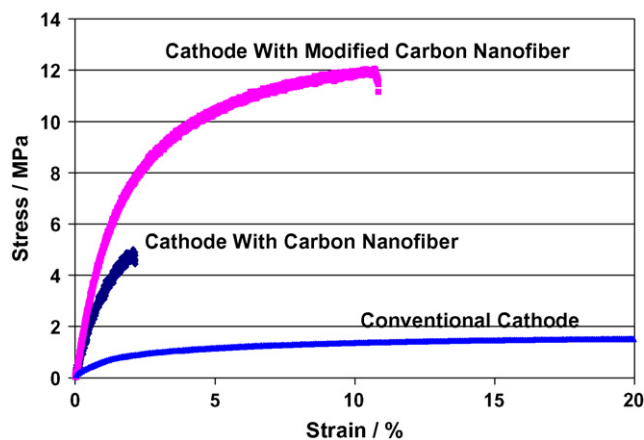

Fig. 3. Stress–strain curves for three cathodes: conventional plastic, carbon nanofiber reinforced, and a modified carbon nanofibers reinforced electrodes. The conventional plastic electrode was fabricated with a process similar to that described previously [5].
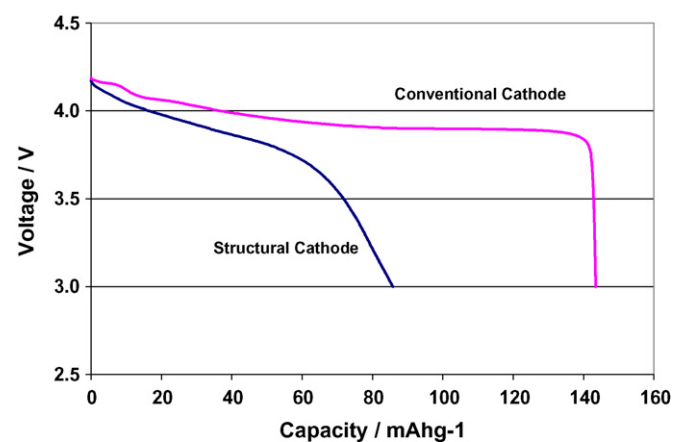

Fig. 4. The discharge voltage profile for the structural electrode made with modified carbon nanofiber as shown in Fig. 3. Shown for comparison is the profile for a conventional electrode without the nanofiber. The current density was 100 μA cm^{-2}. The reported capacities are normalized to the weight of $LiCoO_2$ in the electrodes.
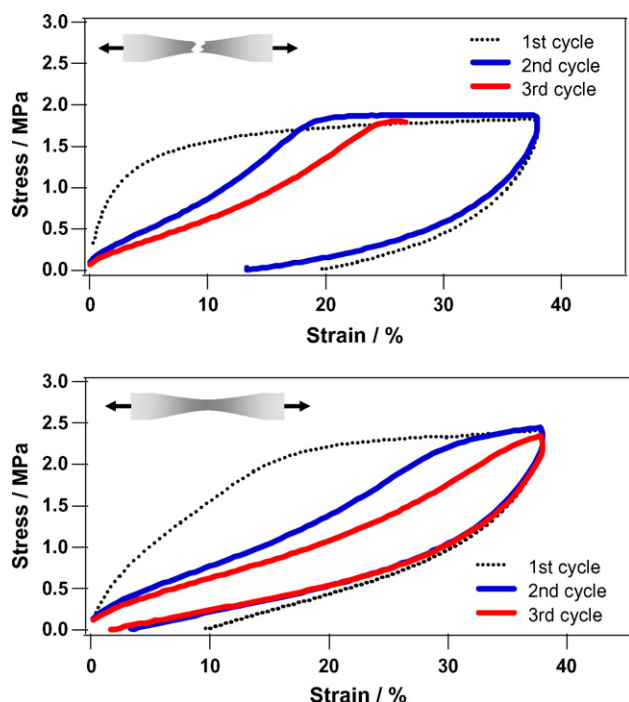
Fig. 5. Stress–strain curves for a conventional electrode (top) and an elastic electrode made with elastic polymer binders (bottom).

show that the composite design can be used to generate battery electrodes of different mechanical properties. We adopt a similar process previously reported to fabricate an elastic cathode [6,9]. Fig. 5 shows the stress–strain curve comparison between an elastic and a conventional electrode. The conventional electrode experienced large irreversible strains for two cycles and failed on the third. In contrast, the elastic electrode can almost recover all of its strain on the 3rd cycle. These results, when combined with those on structural cathodes, show the versatility in tuning the mechanical properties of battery electrodes.

3.4. Structural battery fabrication and testing

We used a similar recipe to prepare a structural anode. Due to a lack of high capacity carbon fiber, we used coke particles as the anode material and relied on the carbon nanofiber to provide structural reinforcement.

Our major challenge turned out to be the fabrication of a structural electrolyte. Our original design is a glass fiber enforced PVDF composite as shown in Fig. 2. The fiber surface is modified with PEO oligomers which when added with LiPF$_6$ are expected to provide ion conduction. Unfortunately, we did not observe conductivities of higher than 10^{-5} S cm^{-1}. Consequently, we used a polymer blend that has good mechanical performance and higher ionic conductivity. PVDF was blended with PEGDMA which forms a polymer gel electrolyte with a LiPF$_6$ solution [10]. The three layers of cathode, anode and the separator were laminated together to form a complete battery structure with Cu and Al grids bond to the anode and the cathode, respectively, to serve as current collectors.

The mechanical property of the complete battery was tested using the three-point bending technique. A tensile modulus of 3.1 GPa was achieved which is sufficient for many modest structural applications. Moreover the structural battery was also found to be electrochemically active. Fig. 6 shows constant-current discharging profiles for the first cycles. An energy density of 35 Wh kg^{-1} was achieved at a C/20 rate.
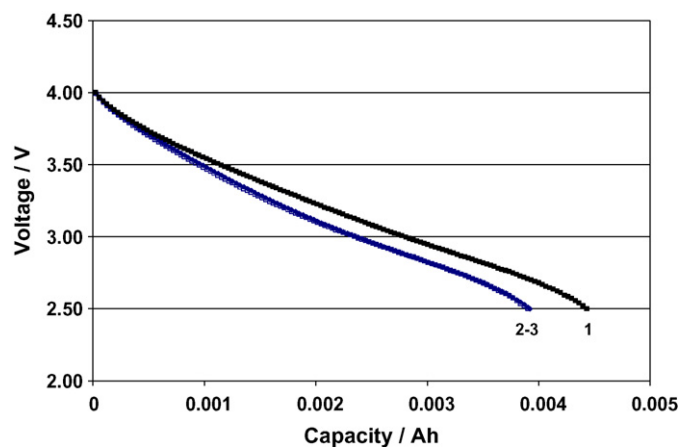

Fig. 6. Constant-current discharge profiles for a structural battery at 40 °C for the first three cycles. The battery was charge at 200 μA to 4.1 V, voltage hold for 24 h, and discharge at 200 μA to 2.5 V. The battery area was 6.45 cm^2.

3.5. Remaining challenges for realizing high performance structural batteries

We have shown in this work a conceptual design for a lithium ion battery with tunable mechanical properties and fabricated a first generation structural battery with promising mechanical properties. The actual material composition of the first generation cell differs from our ideal design in three main aspects: (1) neither the cathode nor the anode was in fiber form; (2) a true solid-state electrolyte with sufficient ionic conductivity was not identified. Instead, the battery relied on robust polymer gel electrolyte; and (3) the polymer gel electrolyte was not reinforced with non-conducting fibers. All these issues would negatively impact the mechanical strength of the structural battery.

Another challenge is that the energy density of the structural battery is low compared to state of the art commercial lithium ion batteries. For a LiCoO$_2$/Coke cell, an energy density of 110 Wh kg^{-1} can be expected with the plastic battery fabrication technique. While certain compromise in energy storage capability is expected and acceptable due to the added benefit of structural properties, further improvement in energy density is necessary to make structural battery a viable solution for applications. The first reason for the low energy density is the lower loading of LiCoO$_2$ in the cathode (35 vs. normally over 70%). This low loading was necessary to achieve the observed improvement in mechanical property since LiCoO$_2$ in fiber form is not yet available. Another likely cause is the dense structure of the electrode which is based on high molecular weight PVDF. Without the porosity which permeates through common lithium ion batteries allowing ion transport, our structural battery relies on very low porosity and the surface ion conduction provided by the ethylene oxide moieties. It is likely that the low ionic conductivity is limiting the power output of the battery. This challenge can be overcome by blending structural polymer electrolytes into the electrode if they become available.

In addition to the need for advancement in component materials, a design optimization will also be necessary to realize the desired structural and energy storage performances for specific applications. An example has been shown by Thomas and Qidwai for a battery with external structural reinforcement [3]. A systematic design optimization for the current approach is needed to quantitatively describe the effect of material properties and ratios on basic parameters of battery components such as ionic conductivities in electrodes and the electrolyte layer as well as tensile

strength of the Young's modulus. All of these parameters will in turn determine the energy and power densities of the battery as well as its mechanical properties.

4. Conclusions

In summary, we have provided a novel design of a battery with tunable mechanical properties. When an elastic polymer matrix is used, the battery electrode becomes elastic and can serve as the starting point for the fabrication of an elastic battery. When a structural polymer matrix is reinforced with fibers, a battery with load bearing capabilities can be designed. A first generation structural battery was fabricated based on a carbon fiber reinforced PVDF composite with good mechanical strength and modest energy storage capabilities. Further advancement in developing polymer electrolytes with robust mechanical properties is nec-

essary to fully realize the potential of multifunctional structural batteries.

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