

# Electrospun Nanofibers for Energy Storage

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## Abstract

Electrospinning technology was used to prepare novel composite nanofiber anodes and cathodes for lithium-ion batteries. Silicon/carbon (Si/C) anode and  $\text{LiFePO}_4$ /carbon ( $\text{LiFePO}_4/\text{C}$ ) cathode composite nanofibers were fabricated. Integration of these nanofibers into lithium-ion batteries was used to achieve high system performance. Anodes made from Si/C nanofibers have the advantages of both carbon (long cycle life) and Si (high lithium-storage capacity). The cathode material,  $\text{LiFePO}_4/\text{C}$  nanofibers, also gave good electrochemical performance, such as satisfactory cycling stability.

## Key Terms

Anode, Batteries, Carbon, Cathode, Electrospinning, Energy, Lithium-ion, Nanofibers, Silicon

## Introduction and Background

Research and development in textiles have gone beyond conventional clothing and furnishing materials applications. The convergence of textiles, nanotechnologies, and energy science opens up opportunities to take on one of the major challenges of the 21st century—energy. For example, electrospun nanofibers are now used in energy storage and conversion systems such as rechargeable lithium-ion batteries (LIBs), proton exchange membrane fuel cells, solar cells, and supercapacitors.<sup>1-5</sup>

Among various existing energy storage and conversion technologies, rechargeable LIBs are considered an effective solution to the increased need for high-energy-density electrochemical power sources. Rechargeable LIBs offer greater energy (2-3 times) and power densities (5-6 times), weigh less, take less space, and deliver more energy than conventional Ni-Cd and Ni-MH batteries.<sup>6-8</sup> In addition, LIBs have other advantages, such as high coulombic efficiency, low self-discharge, high operating voltage, and no “memory effect.”<sup>9</sup>

Each LIB consists of an anode and a cathode separated by an electrolyte containing dissociated lithium salts that enable transfer of lithium ions between the two electrodes (Fig. 1). When the battery is being charged, an external electrical power source injects electrons into the anode. At the same time, the cathode gives up some of its lithium ions, which move through the electrolyte to the anode and remain there. During this process, electricity is stored in the battery in the form of chemical energy. When the battery is discharging, lithium ions move back across the electrolyte to the cathode, enabling the release of electrons to the outer circuit to do the electrical work. Current LIBs were developed mainly for portable applications (such as cell phones and laptops)—they depend on using active powder materials (such as graphite powder in the anode and  $\text{LiCoO}_2$  powder in the cathode) to store energy. However, powder materials have long diffusion paths for lithium ions and slow electrode reaction kinetics. As a result, current LIB performance has not reached its potential.<sup>10</sup> Therefore, new energy-storage materials and electrodes must be developed to obtain advanced LIBs that outperform current technologies and can be used in large-scale systems.

Recent work from this laboratory has focused on developing novel electrospun nanofibers for LIB applications.<sup>8,11,12</sup> Depending on the material choice, these composite nanofibers are used as cathode or anode materials. Compared with active powder materials used in current LIBs, these composite nanofibers have short-diffusion distances and high-lithium diffusion coefficients due to their one-dimensional structure. As a result, LIBs using these

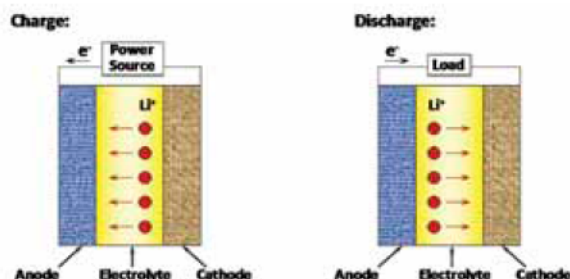


Fig. 1. Charge and discharge diagrams of an LIB.

nanofibers have excellent performance such as large capacity, high charge/discharge rate capability, and extended cycle life.

In this paper, fabrication of silicon/carbon (Si/C) anode and LiFePO<sub>4</sub>/carbon (LiFePO<sub>4</sub>/C) cathode composite nanofibers and the integration of these nanofibers in LIBs to achieve high system performance are presented.

## Experimental

### Chemicals

Carbon source polyacrylonitrile (PAN) (MW = 150,000) and N,N-dimethylformamide (DMF) solvent were purchased from Aldrich. Si nanoparticles (particle size ≥ 70 nm) were purchased from Nanostructured & Amorphous Materials Inc. LiFePO<sub>4</sub> precursors, including ferric acetate (Fe(COOCH<sub>3</sub>)<sub>2</sub>, 95%), lithium acetate dihydrate (LiCOOCH<sub>3</sub>•2H<sub>2</sub>O, 98%), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 99%), were also purchased from Aldrich. Ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were provided by the Ferro Corp. All reagents were used without further purification.

### Nanofiber Preparations

#### Anode

Solutions of DMF/PAN (8 wt%) and DMF/PAN containing 15 wt% Si nanoparticles were prepared by mechanically stirring for 24 h at 60°C. A variable high-voltage power supply (Gamma ES40P-20W/DAM) was used to provide a high voltage (~21 kV) for electrospinning. The flow rate used was 0.75 mL/h and the needle-to-collector distance was 15 cm. Electrospun PAN and Si/PAN composite nanofibers were stabilized in air at 280°C for 5 h (heating rate was 5°C/min) and then carbonized at 700°C for 1 h in a nitrogen atmosphere (heating rate was 2°C/min) to form carbon and Si/C anode nanofibers, respectively.

Several methods can be used to characterize carbon nanofibers and ensure that carbon nanofibers are formed after carbonization.<sup>13-16</sup> In previous work

from this laboratory, X-ray diffraction (XRD) and Raman spectroscopic experiments were performed to characterize Si/C nanofiber structure.<sup>17</sup> XRD results showed that the carbon matrix, derived from the Si/PAN precursor, had a typical non-graphitic structure, whereas Raman spectroscopic results showed that the carbon matrix had a predominantly amorphous/disordered structure.<sup>17</sup> More details on the preparation and characterization of Si/C nanofibers are available in the literature.<sup>18-20</sup>

#### Cathode

LiFePO<sub>4</sub>/C cathode nanofibers were prepared by electrospinning the LiFePO<sub>4</sub> precursor/PAN nanofibers, followed by a calcination/carbonization step. PAN solutions were first prepared at 55°C in DMF by stirring for 24 h. To obtain the LiFePO<sub>4</sub> precursor, Fe(COOCH<sub>3</sub>)<sub>2</sub>, LiCOOCH<sub>3</sub>•2H<sub>2</sub>O, and H<sub>3</sub>PO<sub>4</sub> were mixed in a stoichiometric ratio of 1.02:1.05:1.02 by weight and dissolved in DMF at 55°C for 24 h. The LiFePO<sub>4</sub> precursor solution and PAN solution were then mixed at different weight ratios (Table I) by mechanical stirring. The mixed solutions were then electrospun at 10 kV with a needle tip-to-collector distance of 15 cm. After electrospinning, the LiFePO<sub>4</sub> precursor/PAN nanofibers were stabilized in air at 280°C for 5 h and calcinated/carbonized in argon at 700°C for 24 h to form LiFePO<sub>4</sub>/C nanofibers.

### Nanofiber Characterization

The morphology and diameter of Si/PAN and Si/C nanofibers were investigated using scanning electron microscopy (SEM, JEOL 6400F FESEM at 5 kV). The structure of LiFePO<sub>4</sub> precursor/PAN and LiFePO<sub>4</sub>/C nanofibers was studied using field emission scanning electron microscopy (FESEM, JEOL 6400F).

### Electrochemical Evaluations

Galvanostatic charge-discharge experiments were performed using 2032 coin cells (Fig. 2). Unlike in traditional LIBs, in which both anodes and cathodes are prepared by holding active powder materials using a polymer binder, the anodes and cathodes in

this work were prepared by directly using the flexible Si/C and LiFePO<sub>4</sub>/C nanofiber mats, respectively, without adding any binder. Elimination of non-conductive, inactive polymer binder sig-

**Table I.**  
PAN and LiFePO<sub>4</sub> Precursor Solution Contents and Weight Ratios

|   | LiFePO <sub>4</sub> Precursor Content (wt%) | PAN Content (wt%) | LiFePO <sub>4</sub> Precursor: PAN Weight Ratio |
|---|---|-------------------|---|
| a | 8   | 4                 | 2.0 : 1.0                                       |
| b | 10  | 4                 | 2.5 : 1.0                                       |
| c | 9   | 3                 | 3.0 : 1.0                                       |
| d | 12  | 3                 | 4.0 : 1.0                                       |





Fig. 2. Photograph of 2032 coin cells containing Si/C nanofiber anodes and/or LiFePO<sub>4</sub>/C nanofiber cathodes.

nificantly improved electrode conductivity and promoted lithium-ion transportation in both anodes and cathodes.

Thin, circular, and flexible Si/C nanofibers were attached to a copper current collector for use as the working electrode for performance tests on the anode nanofibers. A lithium ribbon (0.38-mm thick) was used as

the counter electrode. The electrolyte used was 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in 1/1 (v/v) EC/EMC. Coin cells were assembled in a high-purity argon-filled glove box. The charge (Li insertion) and discharge (Li extraction) of cells were conducted using an Arbin automatic battery cyler at several different current densities between cut-off voltages of 0.01 and 2.80 V.

To carry out electrochemical performance tests on the cathode nanofibers, coin cells were assembled by using the LiFePO<sub>4</sub>/C nanofibers placed on an aluminum current collector as the working electrode. The counter electrode and electrolyte used were the same as those in the Si/C nanofiber evaluation. Charge and discharge were conducted using the same instrument between the cut-off voltages of 2.50 and 4.00 V.

## Results and Discussion

### Si/C Anode Nanofibers

#### Morphology and Structure

Carbon (e.g., graphite) is presently the most used anode material for LIBs due to its low and flat working potential, long cycle life, and low cost. However, the most lithium-enriched intercalation compound of graphite only has a stoichiometry of LiC<sub>6</sub>, resulting in a less-than-desirable theoretical charge capacity (370 mAh/g).<sup>21,22</sup> To improve anode capacity, non-carbon materials that can incorporate large amounts of lithium have been developed. Among various non-carbon materials, Si is found to have the highest theoretical capacity of 4,200 mAh/g.<sup>22</sup> However, the high capacity of Si leads to a large

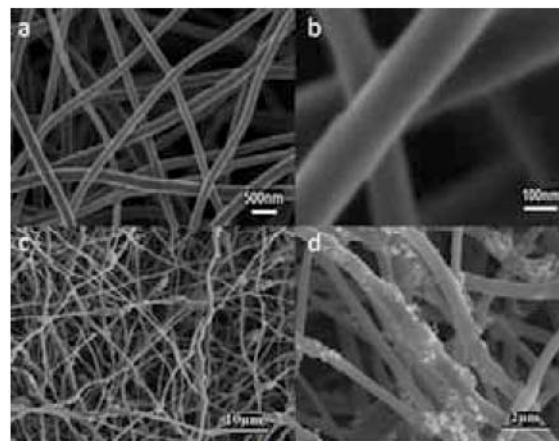


Fig. 3. SEM images of pure PAN (a and b) and Si/PAN (c and d) composite nanofiber precursors. The Si content in Si/PAN composite nanofibers is 15 wt%.

volume change of the anode since a significantly higher amount of lithium is inserted and de-inserted during cycling. As a result, the major problem associated with the use of Si is the mechanical failure of this brittle material brought about by large-volume change during lithium insertion/extraction. Many approaches have been used to reduce this large volume change and therefore obtain better capacity retention and cycle life for Si anodes.<sup>22</sup> The approach used in the present work is to incorporate nano-scale Si particles into carbon nanofibers by carbonizing electrospun Si/PAN nanofibers. In the resultant Si/C nanofibers, the carbon matrix accommodates the large volume change of Si during charge/discharge. As a result, these Si/C nanofibers can have the advantages of both carbon (long cycle life) and Si (large capacity).

Fig. 3 shows SEM images of electrospun PAN and Si/PAN precursor nanofibers. The distribution of Si nanoparticles in the PAN matrix was relatively homogeneous.<sup>8,11,12</sup> SEM images of carbon and Si/C nanofiber prepared from PAN and Si/PAN precursors are shown in Fig. 4. The Si/C nanofibers were less straight than the corresponding Si/PAN precursor nanofibers (Fig. 3). Si/C nanofibers can be obtained by thermal treatment of these electrospun Si/PAN composites.

#### Electrochemical Performance

The electrochemical performance of Si/C nanofiber anodes was investigated by carrying out galvanostatic charge-discharge tests at a constant current density of 50 mA/g between 0.01 and 2.8 V. Figs. 5 and 6 show the charge-discharge curves of the pure Si and the Si/C nanofiber anodes, respectively.

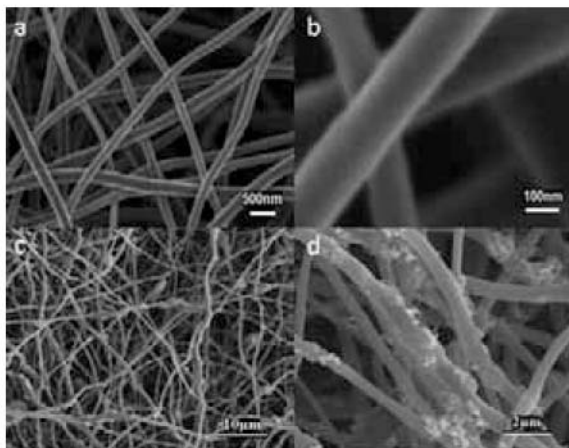


Fig. 4. SEM images of carbon (a and b) and Si/C nanofibers (c and d) made from PAN and Si/PAN precursor nanofibers. The Si content in Si/PAN precursor is 15 wt%.

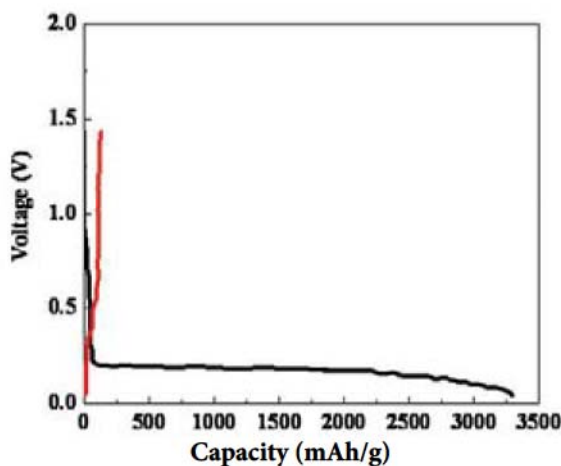


Fig. 5. Charge-discharge curves of Si anode at a constant current density of 50 mA/g.

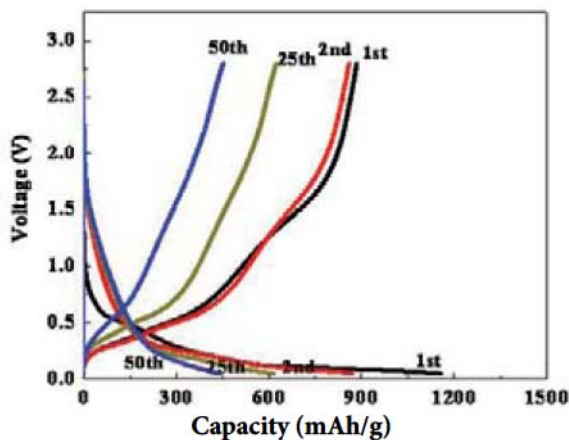


Fig. 6. Charge-discharge curves of Si/C nanofiber anodes at a constant current density of 50 mA/g.

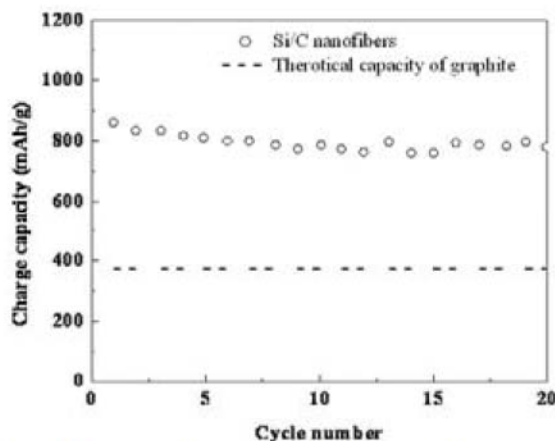


Fig. 7. Charge capacity comparison of carbon nanofibers, prepared from Si/C nanofibers from Si/PAN with 15 wt% Si, with the theoretical capacity of graphite used as LIB anode material. Current density was 50 mA/g.

Si anodes were prepared by using the traditional powder electrode method: mixing 80 wt% Si nanoparticles with 10 wt% polyvinylidene fluoride binder and 10 wt% carbon black conductor.<sup>21</sup> During discharge of Si anodes, a potential plateau appears at ~0.2 V with a charge capacity up to 3,300 mAh/g (Fig. 5). However, the high Li packing density results in a large volume change during the insertion process, which results in anode cracking and therefore a total loss of capacity.<sup>21,23</sup> As a result, the actual charge capacity of the Si anode is only 113 mAh/g, which is less than that of graphite. However, the Si/C nanofiber anodes show relatively good capacity retention during cycling. At the first cycle, the Si/C nanofiber anodes made from 15 wt% Si/PAN precursor gave a specific charge capacity of ~1,157 mAh/g and a discharge capacity of 886 mAh/g, which were significantly greater than the theoretical capacity (370 mAh/g) of graphite. Since Si has a high Li-storage capacity while carbon has a long cycle life, the electrochemical performance of LIB anodes has been improved by embedding Si nanoparticles into carbon nanofibers.

Fig. 7 shows a comparison between the discharge capacities of carbon nanofibers prepared from pure Si/C nanofibers (from Si/PAN with 15 wt% Si) with the theoretical capacity of graphite powder. Graphite is currently used as the anode material in most commercial LIBs. The electrochemical performance of the anodes was improved by incorporating Si into the carbon nanofibers. Compared with the capacities of carbon nanofibers, the capacities of Si/C nanofibers were significantly higher, indicating that Si





Fig. 8. Photograph of industry-standard 18650 cylinder cells containing Si/C nanofiber anodes.

nanoparticles play a significant role in improving the anode capacity. It was also seen that with an increase in cycling number, the capacity of Si/C nanofibers remained relatively constant, indicating that these anode nanofibers have good cycling stability (Fig. 7).

Further experiments are underway to study the detailed effects of Si nanoparticles size and dispersion on the electrochemical performance of anode nanofibers used in LIBs. It is believed that each nanoparticle-polymer solution system behaves very differently. In the present study, no difficulty in dispersing Si nanoparticles in PAN solutions was experienced. Nanofibers can also be formed with these solutions. In previous work, 50 wt% Si was actually dispersed into a PAN matrix and composite nanofibers prepared from it.<sup>21</sup>

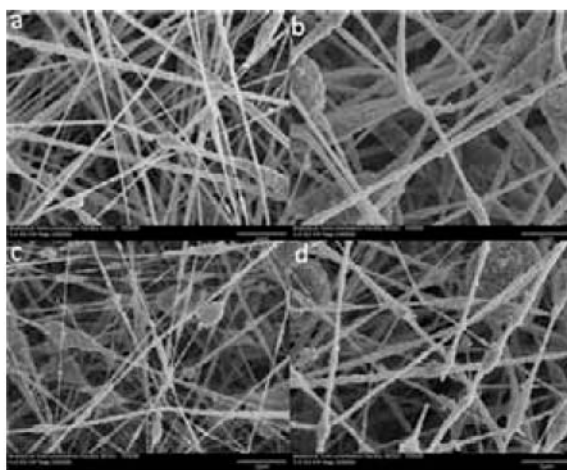


Fig. 9. LiFePO<sub>4</sub> precursor/PAN nanofibers made from solutions at various LiFePO<sub>4</sub> precursor: PAN ratios: (a) 8% LiFePO<sub>4</sub> precursor:4% PAN, (b) 10% LiFePO<sub>4</sub> precursor:4% PAN, (c) 9% LiFePO<sub>4</sub> precursor:3% PAN, and (d) 12% LiFePO<sub>4</sub> precursor:3% PAN.

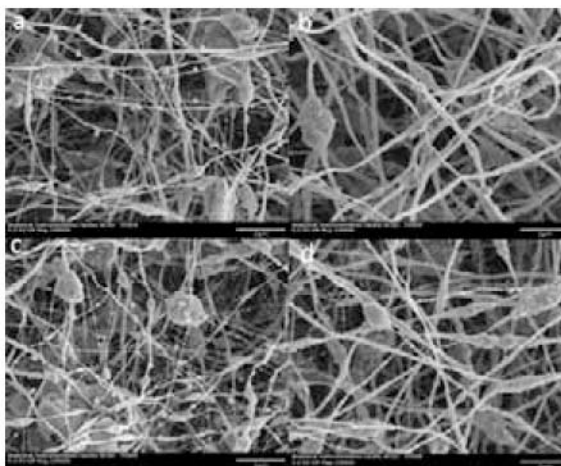


Fig. 10. LiFePO<sub>4</sub>/C nanofibers prepared from the calcination/carbonization of LiFePO<sub>4</sub> precursor/PAN nanofibers at various LiFePO<sub>4</sub> precursor: PAN ratios: (a) 8% LiFePO<sub>4</sub> precursor:4% PAN, (b) 10% LiFePO<sub>4</sub> precursor:4% PAN, (c) 9% LiFePO<sub>4</sub> precursor:3% PAN, and (d) 12% LiFePO<sub>4</sub> precursor:3% PAN.

In addition, these novel Si/C nanofiber anodes have been assembled into industry-standard 18650 cylinder cells (Fig. 8). Their performance is currently being evaluated.

### LiFePO<sub>4</sub> Cathode Nanofibers Morphology and Structure

Among various cathode materials, LiCoO<sub>2</sub> is currently being used in commercial LIBs, however, LiCoO<sub>2</sub> has a low capacity (130 mAh/g) and is too expensive for large-scale applications. On the other hand, lithium iron phosphate (LiFePO<sub>4</sub>) has an olivine structure and is a promising cathode candidate due to its abundant supply. It is environmentally benign, has an acceptable theoretical charge capacity of 170 mAh/g, and has good thermal stability in the fully charged state.<sup>25</sup> One disadvantage of LiFePO<sub>4</sub> is its low-electronic conductivity, which prevents full use of its capacity.<sup>26</sup> To address this problem, LiFePO<sub>4</sub>/C cathode nanofibers were fabricated in which the carbon nanofiber structure provides a continuous electron pathway to significantly improve cathode conductivity and performance.

Fig. 9 shows FESEM images of LiFePO<sub>4</sub> precursor/PAN nanofibers made from solutions with various LiFePO<sub>4</sub> precursor/PAN ratios. The corresponding LiFePO<sub>4</sub>/C nanofiber SEMs are shown in Fig. 10. A slight increase in the fiber diameter with increasing PAN content was observed, but fiber consistency was maintained for all samples. Comparing Figs. 9 and 10, the calcination/carbonization process led

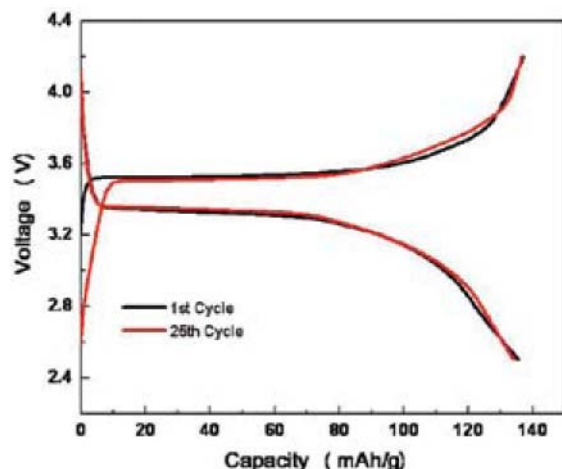


Fig. 11. Charge-discharge curves of LiFePO<sub>4</sub>/C nanofibers prepared from 10% LiFePO<sub>4</sub> precursor:4% PAN solutions.

to a substantial volume contraction and diameter decrease for the resultant LiFePO<sub>4</sub>/C nanofibers. This was due to the removal of some species from the precursors during LiFePO<sub>4</sub> formation and PAN carbonization.

#### Electrochemical Performance

Fig. 11 shows the charge-discharge curves of LiFePO<sub>4</sub>/carbon nanofibers. The cycling performance of LiFePO<sub>4</sub>/C nanofibers is shown in Fig. 12. The LiFePO<sub>4</sub>/C nanofiber cathode had a discharge capacity of 140 mAh/g in the first cycle, with no apparent capacity loss observed during cycling.

Results showed that electrospinning was a promising approach to prepare high-performance LiFePO<sub>4</sub>/C nanofibers with the potential to replace commercial cathodes for LIBs (Figs. 11 and 12). Further work in this laboratory focuses on establishing processing-structure-performance relationships for these novel composite nanofibers. The resulting high-performance LiFePO<sub>4</sub>/C cathode nanofibers can then be used in next-generation LIBs.

## Conclusions

Novel Si/C and LiFePO<sub>4</sub>/C nanofibers were fabricated by electrospinning and subsequent thermal treatments for use as anodes and cathodes, respectively, in LIBs. For Si/C anode nanofibers, Si nanoparticles were dispersed in and on the surface of the carbon matrix. As a result, the high volume change of Si nanoparticles during Li insertion/extraction was accommodated by incorporating

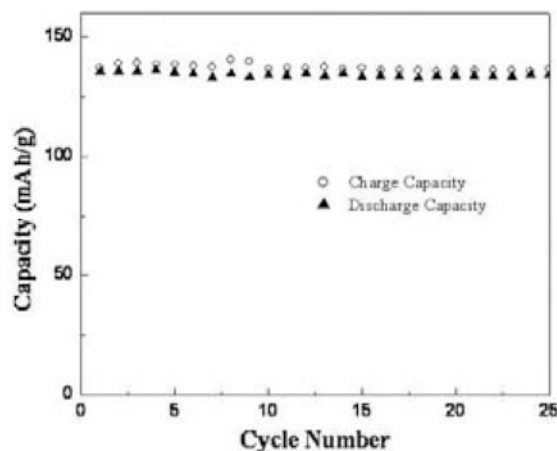


Fig. 12. Cycling performance of LiFePO<sub>4</sub>/C nanofibers prepared from 10% LiFePO<sub>4</sub> precursor:4% PAN solutions.

carbon nanofibers. Hence, the excellent electronic conductivity of carbon and the super-high Li storage of Si nanoparticle provide these composite nanofiber anodes with good electrochemical performance. LiFePO<sub>4</sub>/C cathode nanofibers prepared by the electrospinning method also showed good electrochemical performance, such as satisfactory cycling stability. These results demonstrated that electrospinning was a promising approach to prepare high-performance Si/C and LiFePO<sub>4</sub>/C nanofibers that can replace current commercially-used anodes and cathodes for high-performance next-generation LIBs.

Further work in this laboratory is studying both the relationship between the process, structure, and performance of these novel electrospun composite nanofibers and the structure and performance improvement of nanofiber anodes and cathodes.

## Acknowledgments

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