Electrospun Polymer/Particle Composite Nanofiber Anodes for Li-ion Batteries

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Introduction

Silicon has received considerable attention as an intercalation host for Li-ion battery anodes due to its high theoretical capacity (4,200 mAh/g vs. 372 mAh/g for graphite). However, silicon based anodes typically suffer from rapid capacity fade caused by particle cracking and electronic isolation resulting from large volumetric changes between the lithiated and non-lithiated states. While particle fracture can be eliminated by using nanosized Si domains[1], electronic isolation remains problematic. Another significant obstacle for commercialization of Si in Li-ion batteries is the irreversible consumption of Li^+ in the electrolyte during formation of the solid-electrolyte interface.

Electrospinning has been used previously to create Si-containing carbon fiber anodes for Li-ion batteries.[2, 3] Nanofiber electrospinning has also been used to fabricate high performance polymer/particle cathodes for hydrogen/air fuel cells.[4] Particle/polymer nanofiber electrodes offer two key potential advantages over conventional materials for Li-ion batteries: (1) Sub-micron fiber diameters yield a large surface area and short transport pathways which enhance electronic and ionic conductivities and (2) the flexible/compliant polymer binder and void spaces between fibers can accommodate Si volumetric changes during cycling. This buffering effect maintains the electronic conductivity network and prevents electrode deterioration.

Herein, we present new and preliminary results on a Si-based electrospun nanofiber anode for Li-ion batteries. This system contains Si nanoparticles and conductive carbon powder dispersed in a poly(acrylic acid) polymeric binder. Recent work has focused on correlating anode capacity and cycle life to fiber composition and post-spinning processing steps.

Experimental

An electrospinning ink was prepared by mixing: (a) Si nanoparticles (20-30 nm, US Research Nanomaterials, Inc.), (b) carbon black (Fuel Cell Store, Inc.) and (c) poly(acrylic acid) (M_w=450,000 g/mol, Sigma-Aldrich) in a methanol/isopropanol/butanol solvent (38:50:12 weight ratio). The spinning solution contained 16 wt% solids where the weight ratio of Si:C:PAA was 30:35:35.

The ink was drawn into a 3 mL syringe and electrospun using a 22 gauge stainless steel needle spinneret polarized to +8.0 kV relative to a grounded rotating and oscillating drum collector. The spinneret-to-collector distance was fixed at 8 cm, and the solution flow rate was 1 mL/h. Nanofibers were collected on aluminum foil that was fixed to the drum. Fiber mats were compacted at 1 MPa using a hydraulic press. In some cases, fibers were welded by exposure to methanol vapor for 40 minutes at room temperature.

Electrochemical half-cells were constructed inside a glovebox using an electrospun nanofiber anode and Li metal as the counter/reference electrode. The electrolyte was composed of 1.0 M $LiPF_6$ in a mixed solvent of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1 by volume). All cells contained an electrolyte-soaked Celgard 2500 separator. Cells were cycled galvanostatically between 0.015 – 1.5 V using a 0.1C current. Electrochemical capacities were calculated with respect to anode delithiation.

Results

As an example of the performance of nanofiber anode mats, the effect of interfiber welding on anode performance is shown in Figure 1. Exposing the mat to methanol vapor welded fiber intersections while maintaining the interfiber voids. The performance of anodes containing welded fibers and untreated fibers were compared. As can be seen, both anodes attain initial capacities exceeding 1,000 mAh/g. However, while the untreated system exhibits significant capacity fade, the welded fiber anode retains a stable capacity over 7 cycles. The coulombic efficiency of the welded fibers exceeds 97% while that of the untreated fibers is below 95%, indicating better retention of the electronic conductivity network and access to Si sites for the welded morphology.

A more detailed description of the electrospinning process and additional experimental results showing anode cycle life and rate capabilities will be presented.

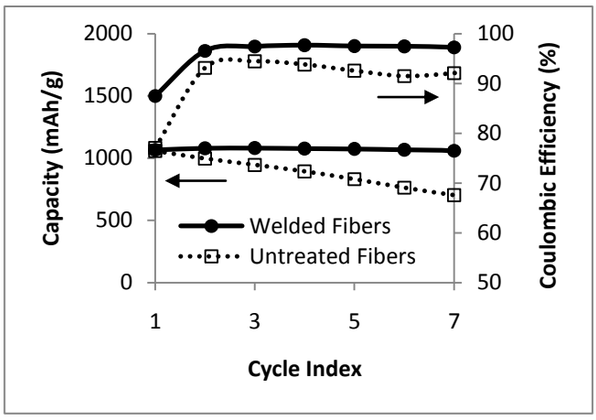

Figure 1. Electrochemical performance of Si based nanofiber anodes with and without a post-spinning welding treatment.

Acknowledgements

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