COMPARATIVE STUDY OF THERMALLY TREATED SILICON ANODE NANOSTRUCTURES BASED ON POLYACRYLIC ACID AND POLYANILINE FOR LITHIUM ION BATTERY APPLICATION

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ABSTRACT

A comparative study between a nonconductive thermoplastic, polyacrylic acid (PAA), and an electronic-conducting polymer, polyaniline (PANI), has been conducted related to their function as binders for Silicon Nanoparticle (SiNP)-based anodes in Li-ion battery application. SEM analysis was used to understand the morphological differences associated with dispersion of PAA/PANI with SiNPs. Further, thermogravimetric analysis was conducted in order to understand the thermal degradation and to choose their associated heat-treatment temperatures of 400 °C (PAA) and 300 °C (PANI). The electrochemical performance of the resultant silicon-based electrodes assembled in Lithium-half-cell configuration was evaluated in terms of their specific capacitance and cycle-stability. The results indicated that PANI-based SiNP anodes heat-treated at 300 °C demonstrate the highest specific capacitance and the lowest capacity loss over 10 cycles, which could be attributed to higher electrical conductivity and improved adhesion.

INTRODUCTION

Silicon has attracted substantial attention in lithium ion battery (LIB) research due to its exceptional theoretical specific specific capacitance (4200 mAhg⁻¹) which is the highest among any known material. However, Si undergoes a 300-400% volume expansion during the lithiation process which causes mechanical deterioration of the silicon macrostructure and loss of LIB performance. Furthermore, loss of electrical conductivity of silicon particles during delithiation implies that the conductivity factor should be considered at nanoscale. Finally, the solid electrolyte interface (SEI) layer (Kawamura, Okada, & Yamaki, 2006) formed on the anode surface and within the anode interior introduces additional challenges,
such as reduced Li-ion transport, separation of silicon nanoparticles from the conductive carbon and/or polymer phase, and anode delamination from the Cu support. These challenges can be addressed by (1) using silicon nanostructures (<50 nm) that sustain their mechanical integrity during lithiation-delithiation and (2) choosing an appropriate binder with sufficient electric conductivity, high elastic modulus, and mechanical strength to keep Si-nanoparticles in intimate contact with the conducting phase. Conventional binders, such as polyvinylidene fluoride (PVDF), carboxymethyl cellulose (CMC), sodium salts of CMC, combinations of Na-CMC with butadiene block copolymers, and polyacrylic acid (PAA) (Magasinski et al. 2010) partially eliminate the problems and improves LIB performance and cycling behavior. Conductive polymers such as polyaniline (Li et al. 2014; Wang et al. 2013) and poly(3,4-ethylenedioxythiophene) (Kim et al. 2014) were applied for both LIB cathode and anode materials to improve conductivity and provide mixed ion-electronic pathways for Li cations and electron transport. SiNP-PANi half cells (Wu et al. 2013) with 1600 mAhg⁻¹ capacity at high currents (up to 6 Ag⁻¹) demonstrated close to zero capacity loss after 1000 cycles. However, the SiNP-PANI half-cell specific capacitance (1600 g⁻¹) was significantly lower than Si-nanotubes (Cui et al. 2009) (3200 mAhg⁻¹) or nanowires (4277 mAhg⁻¹). Earlier it was shown that thermal treatment of PANI, PAA, and PANI/PAA blends (Lu et al. 2003) can significantly change their electrical conductivity (3.2 mS·cm⁻¹ for polyacrylic acid/graphite nano-platelet (Tang et al. 2009) and PANI ~10³ -10² mS·cm⁻¹).

The purpose of this study was to identify the effects of heat-treatment on the SiNP based anodes prepared with two binders, specifically PAA and PANI, and characterize the effects in terms of electrochemistry. The chemistries involved with heat treatment of PAA and PANI are starkly different. Heat treatment of PAA results in the partial dehydration and in some cases decarboxylation of the carboxylic acid groups. Heat treatment of PANI, specifically the PANI-phytic acid hydrogel previously introduced (Wu et al. 2013), results in the oxidation of phosphate groups found on phytic acid and the evolution of water. In both cases, the eliminated functional groups are acidic in nature, which, in an electrochemical cell, can result in the activation of organic carbonates used as electrolyte solvents. This increases the likelihood of electrolyte reduction and the deposition of insoluble products (SEI) onto the anode surface. It is our hypothesis that elimination of acidic functional groups by heat treatment may have a beneficial effect on cell performance by minimizing electrode-electrolyte interaction.

METHODS

The SiNP-based anode slurries with PAA as a binder were synthesized by homogenization of 0.2 g SiNP (US Research Nanomaterials) with 5 mL of distilled water (2 hr) followed by addition of a 2.5 g of graphitized carbon and exfoliated carbon in 1:1 weight ratio under stirring conditions (2 hr). An aqueous solution of PAA from Alfa Aesar (Av. M.W. 240,000) in distilled water was prepared and added to the initial SiNP-water mixture under stirring conditions resulting in an SiNP-PAA slurry. The SiNP-PANi nanocomposites were processed in three steps.
First, 0.08 g of SiNP (US Research Nanomaterials) were homogenized with distilled water. Then, 0.00837 g of the aniline monomer (Sigma-Aldrich) and 0.01782 g aqueous phytic acid solution (50% by wt., Sigma-Aldrich) were added to the SiNP-water suspension and sonicated. Finally, 0.00856 g of ammonium persulfate (Sigma-Aldrich) was added to initiate radical polymerization of the oxidized aniline. After about 3 minutes of continuous stirring, we observed a color change from brown to green indicating formation of an electrically conductive emeraldine. The slurries were deposited onto carbon coated Cu foil (MTI) using a Systematic Automation screen printer and allowed to dry under ambient conditions for 1 hour. Once dried, the PANI electrodes were soaked in deionized water for 1 hour to remove excess phytic acid. The electrodes were heated in a vacuum oven at various temperatures and constant pressure covered with Teflon and a stainless steel plate. The electrodes were cut into disks (active area 0.907 cm²) and degassed overnight in a vacuum. CR2023 stainless steel coin cells with a K1640 Celgard polyethylene membrane (16 µm thick) were assembled in an argon glove box with O₂ and H₂O concentrations < 1 ppm. Lithium foil reference electrodes (Alfa Aesar) were used with SiNP-PANi and SiNP-PAA working electrodes. During the half-cell assembly, 30 µL of an electrolyte solution from Solvionic containing 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate: dimethyl carbonate with 2% wt. vinylene carbonate was deposited on both sides of the separation membrane.

Thermogravimetric analysis was performed using an SDT Q600 (TA Instruments). Impedance spectroscopy data were obtained from PARStat 2273 (Princeton Applied Research). Galvanostatic charge/discharge cycling and cyclic voltammetry measurements were performed using 580 Battery (Scribner Associates). The images of the electrode surfaces and nanocomposites were taken using a Supra 40VP (Zeiss) field emission scanning microscope equipped with EDX.

RESULTS AND DISCUSSION

Morphological characterization—The SEM images for SiNP-PAA and SiNP-PANI (Figure 1) indicate satisfactory coverage of the Cu support and an even distribution of the silicon nanoparticles with a mean diameter of about 50 nm within the anode layer. The “in-situ” PANI impregnation resulted in higher dispersion and better distribution than the simple stirring process used for PAA. The SiNPs-C-PAA nanocomposite revealed “islands” of PAA indicated by the circle in Figure 1.

Thermogravimetric analysis (TGA) and dynamic scanning calorimetry (DSC) were performed on SiNP-PAA and SiNP-PANI composites to elucidate the temperatures at which their acidic groups evolve. The results of TGA/DSC are presented in Figure 2. In the case of PANI, the significant weight loss below 100 °C corresponds to the evaporation of moisture and ambient monoatomic molecules. The steady weight loss between 100 and 300 °C corresponds to the decomposition/evaporation of synthesis byproducts (e.g. ammonium persulfate, ammonia, sulfuric acid, and aniline). The massive drop in weight percent between 300 and 400 °C which parallels the DSC peak at 362 °C most likely corresponds to the
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Figure 1. FESEM images for non-heat treated (A) SiNPs-C-PAA and (B) SiNP-PANI deposited on copper support. Islands of PAA are enclosed within the oval in A.

thermal dehydration of phytic acid, which coincides with the recent study by Daneluti and Matos 2013. The slight drop in weight percent between 500 and 600 °C corresponds to the partial pyrolysis of phytic acid. Based on these results, the chosen heat-treatment temperature for SiNP-PANI was 300 °C. Upfield shifts in the DSC peaks were assumed to be present due to the 10 °C per minute scan rate. Because of this, 300 °C was chosen as there should be sufficient energy to initiate the dehydration of phytic acid, yet avoid the side reaction seen at 475 °C where the weight percent slightly increases, suggesting oxidation of silicon. In the case of SiNP-PAA anodes, the heat treatment temperature was chosen to be 400 °C to parallel the strong DSC peak which most likely represents the dehydration/decarboxylation of the PAA. Heat treated anodes were compared to a control group of non-heat treated SiNP-PAA and SiNP-PANI anodes. We hypothesized that degradation of these acidic groups may improve cell performance by decreasing the amount of electrolyte decomposition and SEI formation.

**Electrochemical characterization**—Heat treated and non-heat treated SiNP-PAA and SiNP-PANI half cells were galvanostatically charged and discharged at 0.1 Ag⁻¹ from 0.1 to 1 V. The specific capacitance values as well as coulombic efficiency can be seen for the first 10 cycles in Figure 3. For all cells, heat treated and non-heat treated, the initial specific capacitance was approximately 2000 mAhg⁻¹.
with the exception of non-heat treated SiNP-PANI which was approximately 2300 mAhg⁻¹. However, initial specific capacitance values can be misleading since a fraction of that value is contributed by the reduction of the organic electrolyte solvent by the Li reference electrode to form SEI. From an engineering perspective, minimizing capacitance loss after the first cycle is more important for anode performance than striving to achieve exceedingly high specific capacitance values. The demand for batteries that exhibit greater stability and cycle life greatly outweighs the demand for higher specific capacitance, especially since cathodes, not anodes, are the capacitance defining electrodes in a full cell. In all of our cells, the original specific capacitance values drop after the first cycle. This difference can be accounted for by electron exchange between the reference electrode and the electrolyte solvent. For all non-heat treated cells, the capacity continues to drop even after the first cycle and every cycle thereafter. We hypothesize that this continual drop in capacitance is due to the catalyzation of further electrolyte reduction by the acidic groups in the binder. Greater amounts of insoluble SEI products deposited on the surface of the working electrode accelerates the rate at which the open circuit potential of the cell drops during the lithiation process. Therefore, the potential for Li insertion into the bulk of the SiNP diminishes as well. In the case of SiNP-PAA, carboxylic acid groups in polyacrylic acid donate a proton to activate the organic carbonates found in the electrolyte solvent. In the case of SiNP-PANI, it is the phosphate groups found in phytic acid that donate protons. It was expected that heat treatment would weaken this catalytic effect. However, it is apparent that for heat treated SiNP-PAA cells, the specific capacitance violently drops after every cycle and approaches zero. This poor performance is due most likely to the loss of ion-conductivity throughout the electrode. The ion conductivity of PAA is directly dependent on cation exchange through the carboxylic acid group. When Li ions cannot conduct through the interior of the electrode, the cell voltage quickly drops before maximum capacity is reached. Therefore, heat treatment of PAA does not improve the performance of the SiNP-PAA electrode. For heat treated SiNP-PANI cells, the ion conductivity of polyaniline is not dependent on the acidic groups found in phytic acid. Therefore, Li cations can still make their way into the interior of the Si bulk. The flat line specific capacitance following the first cycle shows that a limited amount of Li is irreversibly consumed and the open circuit potential does not change from cycle to cycle.

Another hypothesis is that the composites undergo morphological changes when subjected to heat treatments. PAA has a glass transition temperature of 106 °C and PANI has a glass transition of 160-300 °C (Qi et al. 2009) depending on the doping level, anion, chain length, and crosslinking. Heat treatment of the polymer binders may cause nanostructure changes, such as the amount of surface contact between the SiNP and the polymer. This may impact the ion and electron transport processes in these electrodes. In the case of SiNP-PAA, this effect would be harmful, because PAA covering the SiNP surface would block ion and electron transport. In the case of SiNP-PANI, this effect may be beneficial as it would improve electron transport to the SiNP.

The improved performance of SiNP-PANI can also be explained by the in-situ synthesis process which promotes a high level of homogenization and thorough
dispersion of polyaniline throughout the electrode interior. The same level of homogenization cannot be achieved by simply mixing silicon nanoparticles with a polymer, such as is the case with polyacrylic acid. This distinction is clearly visible in SEM images, where islands of polyacrylic acid are found remotely from the SiNP. Furthermore, phytic acid has the ability to oxidize multiple polyaniline chains, therefore crosslinking (Figure 4) them and creating a three-dimensional “caged” nanostructure that confines each silicon nanoparticle to a limited volume (Pan et al. 2012; Wu et al. 2013). The caged nanostructure helps control volume expansion by inhibiting outward growth and, in turn, minimizing discontinuity caused by fracture and pulverization. The homogenous nature of the polymer network ensures that there is Si-polymer interface throughout the electrode interior, promoting stable electron/ion pathways to each Si nanoparticle in the structure.

Additional evidence for the advantages of PANI- vs. PAA-based systems was obtained from the cyclic voltammetry (CV) data (Figure 5A and Figure 5B, respectively) that provided valuable information about the morphological changes within silicon-lithium alloy upon lithiation and delithiation, ionic and electronic transport at the interface of SiNP and solid electrolyte interface (SEI), and an indication of the ionic and electronic transport at the interface of SiNP and the binding polymer.
In the case of PAA (Figure 5A), a small anodic peak at 0.25 V corresponds to delithiation of the carbon phase and the flow of electrons into the SiNPs-C-PAA working electrode. It is necessary to emphasize that this peak is visible from the very beginning (Cycle 1), representing high reactivity for Li-ion insertion into the carbon phase as opposed to the silicon phase, which does not present a peak until Cycle 5 at 0.52 V. However, with the growing number of cycles, the second anodic Si peak at 0.38 V becomes clearly visible. The existence of two Si peaks indicates that with time more pronounced gradual phase transformation takes place. In this case, two steps corresponding to different energies and crystal structural modifications of silicon –lithium Li,Si, alloy in the presence of PAA and carbon are assumed.

Regarding the PANI-based electrode (Figure 5B), a very different electrochemical picture is observed. Since the PANI-based electrode does not contain carbon, the first peak in the lower voltage range is absent. However, two silicon peaks are
present from the very beginning (Cycle 1), suggesting that a better electronic and ionic transport takes place at the interface with SiNPs in the presence of PANi, making Li exchange more favorable. The second “high energy” peak (0.48V) disappears with cycling, suggesting that the system reaches an equilibrium and that the delithiation process requires less energy consumption. Furthermore, comparison of the major silicon peaks after multiple cycles in SiNP-PAA (0.52V) and SiNP-PANI (0.33V) show that more energy is required for delithiation of PAA- vs. PANI-based electrodes.

Based on our observation, the stability of the PANI-based electrodes can be explained by the improved ratio of the ionic and electronic conductivity at the interface between the PANi and SiNPs.

CONCLUSIONS

The superior performance of PANI as a conductive binder for Li-ion battery anode has been demonstrated in comparison to PAA. The effects of heat treatment were investigated for both materials, indicating that that heat treatment of PAA is detrimental to electrode performance, while the heat treatment of PANI greatly improves cycle stability. It is assumed that the heat treatment decreases the acidity of both polymer binders, therefore reducing the presence of parasitic SEI forming reactions. In comparison to the PAA, SiNP-PANI-based electrodes demonstrate the most stable cyclic stability with almost zero capacity loss between cycles. However, heat treatment negatively affected the conductivity of PAA, and ultimately decreases its performance. The results confirmed by the CV analysis indicate that PANi is superior to PAA as a binder due to its electrically conductive properties and that the electrode performance can be optimized with heat treatment.

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LITERATURE CITED


