A comparative study on the performance of binary SnO₂/NiO/C and Sn/C composite nanofibers as alternative anode materials for lithium ion batteries

Victor A, Agubra, Luis Zuniga, David Flores, Howard Campos, Jahaziel Villarreal and Mataz Alcoutlabi*

Department of Mechanical Engineering, University of Texas, Rio Grande Valley, Edinburg, TX 78539

* *Corresponding Author*. Tel: 956-665-8945. Email: mataz.alcoutlabi@utrgv.edu

Abstract

The development of alternative anode materials out of flexible composite nanofibers has seen a growing interest. In this paper, binary carbon nanofiber electrodes of SnO₂/NiO and Sn nanoparticles are produced using a scalable technique, Forcespinning (FS), and subsequent thermal treatment (carbonization). The Sn/C composite nanofibers were porous and flexible, while the SnO₂/NiO composite nanofibers had “hairy-like” particles and pores on the fiber strands. The nanofiber preparation process involved the FS of Sn/PAN and SnO₂/NiO/PAN solution precursors into nanofibers and subsequent stabilization in air at 280°C and calcination at 800°C under an inert atmosphere. The flexible composite nanofibers were directly used as working electrodes in lithium-ion batteries without a current collector, conducting additives, or binder. The electrochemical performance of the SnO₂/NiO/C and Sn/C composite fiber anodes showed a comparable cycle performance of about 675 mAhg⁻¹ after 100 cycles. However, the SnO₂/NiO/C electrode exhibited a better rate performance than the Sn/C composite anode and was able to recover its capacity after charging with a higher current density. A postmortem analysis of the composite nanofiber electrode after the aging process revealed a heavily passivated electrode from the electrolyte decomposition by-products. The synthesis and

processing methods used to produce these composite nanofibers clearly were a factor for the high rate capability and excellent cycle performance of these binary composite electrodes, largely on the account of the unique structure and properties of the composite nanofibers.

1.0 Introduction

The use of nanostructured materials for energy storage devices has been the trend in recent years. Nanostructured fibers made from metals, metal oxides, ceramics, and composites have been developed for use in various energy storage devices. The popularity of these nanostructured fibrous materials stem from their many attributes: controllable fiber diameter, high surface area-to-volume ratio, low density, and high pore volume [1, 2]. These properties make the nanofiber structure advantageous compared to their powder, crystal, nanowire, thin film, etc. counterparts [3, 4], when used as electrodes in lithium ion batteries (LIB). These nano fibrous metal/metal oxides and ceramic composite electrodes deliver a comparable electrochemical performance including: a stable cycle performance, enhanced capacity, and superior low temperature performance [5, 6]. These improved properties/performances of composite nanofibers are often attributed to the non-woven structure that gives the nanofibers its high labyrinth-like porous structure, good high surface and interfacial areas resulting in a short-diffusion distance of Li-ions (Li^+) during the charge/discharge cycles. These physical characteristics lead to the creation of more reactive sites while the porous structure provides the buffering effect to accommodate the large volume changes often associated with the alloying/de-alloying of lithium with these metal/metal oxide and ceramic composite compounds [7, 8].

Tin (Sn)-based derivatives such as tin oxides, tin sulfides, and stannates have become attractive anode materials for LIBs [9-11]. The popularity of these Sn-based lithium alloys stem from their properties that include the ability to inhibit solvent co-intercalation and significant improvement in electrochemical performance over the commercial graphite anode in LIBs [12, 13]. In addition, these Sn-based/carbon nanofiber composites are easy to process and exhibit a lower potential hysteresis compared to other transition metal oxides [14, 15]. The crystal structure of Sn has the ability to host a higher amount of lithium ions, i.e. about four (4) atoms (i.e. Li_xSn , $0 < x \leq 4.4$) compared to carbonaceous anode (i.e. Li_xC_6 , $0 < x \leq 1$) thereby giving Sn-based/C composite nanofibers a higher lithium storage capacity. Typically, the Sn-based/C nanofiber composite electrodes show a reversible capacity between 800mAhg^{-1} and 600mAhg^{-1} even at a higher current density of 200mA g^{-1} to 1Ag^{-1} [8, 16]. The electrochemical performance has been found to largely depend on the carbonization temperature which tends to have a direct impact on the fiber morphology, structure, and the pore distribution [8] .

Ternary composites of Sn/CNFs containing other metals and their oxides have been investigated and shown to further improve the conductivity and the cyclic and rate performance of the composite electrode. Tin-based ternary composites such as SnO_2/ZnO heterogeneous nanofibers [17, 18], Nitrogen doped CNFs with Sn quantum dots [19], Co-Sn alloy carbon nanofibers [20], and $\text{Fe}_3\text{O}_4/\text{SnO}_2$ coaxial nanofibers [21] have been reported to enhance the electrochemical performance when used as anodes in LIBs. For instance, the N-doped Sn/CNF's, provides fast and versatile electrolyte transport and can act as efficient electron transport pathways and stable mechanical supports to keep the structural integrity of the electrodes during cycling [19]. On the other hand, the Cobalt in Sn/CNFs reduces the volume expansion and enhances the electrical conductivity of the electrode [2]. In this paper, we compare the electrochemical performance of

Sn-particles/carbon composite nanofibers with that of SnO₂-NiO binary carbon composite nanofibers. These composite nanofibers are considered potential alternative anodes for LIBs. The composite nanofibers were prepared using a facile technique known as Forcespinning® (FS) that was recently developed at UTPA [22]. Several methods can be used to produce nanofibers such as electrospinning[23], liquid shearing method[24], centrifugal and/or rotary jet-spinning[25, 26], electrospray[27], touch-brush spinning[28] and reactive magnetospinning [29]. The FS method is the trade name of the centrifugal spinning method that has been recently used to produce fibers for energy storage [30-34] and biomedical applications[35]. The centrifugal spinning process was originally developed and used by Hopper in 1924 to produce artificial silk threads from viscose or equivalent substances by applying centrifugal forces to a viscous material[36] and was extensively used to produce fibers in nano/micro range[37]. The centrifugal spinning method has been recently used to produce polymer nanofibers after the pioneer work reported by Weitz et al. on the unexpected formation of nanofibers, with diameters in the nanometer range, from polymer solution using a standard spin-coating process[38]. This process was named as Nozzle-Free Centrifugal Spinning.

The FS method has several features such as: capability for dual material feed that allows continuous material feed, an almost 100% yield and solvent-free processing for melt spinning with melt temperatures up to 350°C, and requires less solvent or no solvent at all, thereby making it a more cost effective method and better safety of operation compared to other nanofiber making techniques such as electrospinning, melt-blowing, and the in-house built centrifugal system [39]. In this paper, the FS method is used to produce Sn/PAN and SnO₂/NiO/PAN nanofibers from solution precursors. The collected fibrous mats were subjected

to different thermal treatments to produce uniform and flexible Sn/C and SnO₂/NiO/C nanofibers with hairy-like morphology of the dispersed SnO₂/ NiO particles on the porous fiber strands.

2.0 Experimental

2.1 Materials

Poly(acrylonitrile) with average Mw 150,000 used as the carbon precursor was purchased from Sigma Aldrich USA, while solvent N,N-dimethyl Formamide (DMF) was obtained from Fisher Scientific USA. The commercial lithium foil, lithium hexafluorophosphate (LiPF₆), ethylene carbonate (EC), dimethyl carbonate (DMC) were purchased from MTI corp. USA. A Whatman glass microfiber from GE healthcare was used as a separator. The nano powder (Sn, 99.9%, 60-80 nm) was purchased from US research Nanomaterials while that of the Tin (II) 2-ethylhexanoate and Nickel (II) acetate tetrahydrate (98%) were purchased from Sigma Aldrich USA and used as received.

2.2 The Production of Sn/ PAN and SnO₂/NiO/PAN fiber Mats

The Sn/PAN nanofiber mats were prepared by adding 15 wt% of Tin (Sn) nanoparticles of the base polymer polyacrylonitrile (PAN) and dissolved in DMF. The DMF/Sn suspension was then sonicated in a water bath for 30 min to obtain a homogenous dispersion of Sn particles in the solvent. The base polymer, PAN (12wt%) was then added to the DMF/Sn suspension and mechanically mixed using magnetic stirring for 24 hours at room temperature. For the SnO₂/NiO/PAN precursor the weight percentages of the Tin (II) 2-ethylhexanoate and Nickel (II) acetate tetrahydrate were 15 wt% and 10 wt%, respectively, and for the baseline sample, the CNFs were forcespun from the PAN with concentration of 12 wt% of the solution (i.e.

PAN/DMF). Forcespinning was used to produce the nano fibrous mats from PAN, Sn/PAN and SnO₂/NiO/PAN solution precursors. A thin fiber spun-bond was used on a fan box as the substrate for the deposition of fibers. In the FS technique, centrifugal forces are used to extrude polymer solutions or melts through the spinneret. An amount of 2 mL of the precursor solution was injected into the needle-based spinneret equipped with 30 gauge half-inch regular bevel needles. The rotational speed of the spinneret was kept at 8,000 rpm. The substrate was rotated 90° after each run and the needles were changed after each run. The Sn/PAN and SnO₂/NiO/PAN fibrous mats were removed from the substrate drum and dried at 120°C under vacuum for 24 hours prior to being carbonized. The forcespun nanofibers mats were then further stabilized in air at 280°C for 5 h, and then calcined at 800°C for 2 h in an argon atmosphere to obtain the Sn/Carbon and SnO₂/NiO/carbon composite nanofiber mat (heating rate was 3°C min⁻¹).

The structure, morphology, and elemental composition of the Sn/C and SnO₂/NiO/C composite nanofiber mats were analyzed using scanning transmission electron microscopy (STEM/EDAX) from Sigma VP Carl Zeiss. The crystal structure and the surface analysis were evaluated using X-ray powder diffraction and XPS from Bruker and Thermo Scientific, respectively. The thermal and residual weight of carbon in the Sn/PAN and SnO₂/NiO/PAN matrix was carried out using Thermo-Gravimetric analyzer (TGA) from TA Instruments (QA 600). The temperature was ramped up from 24°C to 700°C using a heating rate of 10°C/min in nitrogen gas. The surface area, pore volume and pore size were evaluated from the Brunauer, Emmett and Teller (BET) analysis using micromeritics ASAP 2020. For the postmortem analysis of the aged electrode, the cell was discharged to 0.01V and transferred into the glovebox. The cell was then disassembled and the harvested electrode was washed in DMC solvent and dried in vacuum.

2.3 Sn/C NFs and (SnO₂-NiO)/C half-cell assembly

Electrochemical experiments were performed using coin-type (2032) half cells containing Sn/C and SnO₂/NiO/C composite nanofibers as the working electrode. The cell preparation was performed in a glove box (Mbraun, USA) filled with high purity Argon with oxygen and moisture content <0.5ppm. The Sn/C and SnO₂/NiO/C electrodes formed flexible free-standing nanofibers, which were punched directly and used as binder-free electrodes without any additives. The average electrode thickness was around 2mm, and the average weight was in the range of 2-4mg. Lithium metal was used as the counter electrode and a Whatman glass microfiber membrane as the separator. The electrolyte used was a 1M LiPF₆ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v). The electrochemical performance was evaluated by carrying out galvanostatic charge–discharge tests at a current density of 100 mA/g and between 0.05 and 3.0V, with a 10 minute rest at the end of each discharge cycle. The rate capabilities for both electrodes were evaluated at different current densities: 50mA/g, 100 mA/g, 200 mA/g, 400 mA/g, and 500 mA/g. The specific charge/discharge capacities were calculated based on the mass of the flexible nanofiber anodes. The cyclic voltammetry and impedance experiments were evaluated using an electrochemical impedance spectroscope (Autolab 128N) with a scan rate of 0.5mV/s between 0 and 3V and frequency of 0.1 Hz and 1 kHz, respectively.

The impedance for the fresh (uncycled) Sn/C cells and the aged cells after cycling was carried out using an electrochemical impedance spectroscope (Autolab 128 N) at frequencies of 0.1 Hz and 1 kHz. The measured impedances of the batteries were fit using the equivalent circuit model shown in Fig. 14a (insert) to determine parameters such as the SEI film resistance, the Ohmic

resistance, charge transfer resistance, double layer capacitance, and the Warburg impedance of the battery. In the model, R_0 presents the Ohmic resistance caused by the electrolyte, deposit layer, separator, current collector, and the electrode, which equals to the left intercept between impedance spectrum and the x-axis at high frequency (~ 1 kHz), R_{sei} and C1 indicate SEI resistance and constant phase element (CPE) at the anode, which dominates the shape of the first semi-circle in high frequency domain from 1 kHz to several Hz. While R_c and C2 indicate charge transfer resistance and double layer capacitance, respectively. They affect the shape of the second semi-circle, which is less obvious in the lower frequency range (several Hz to several mHz). On the other hand, W_a is the Warburg admittance, which represents ion diffusion in the solid electrode. The Warburg admittance dominates the impedance spectrum in the low frequency region ($< \text{several mHz}$). To extract these parameters, the EIS-ECM was fitted to the impedance spectrum measured by EIS using a simplex algorithm.

3.0 Results and Discussion

3.1 Surface Morphology and Elemental Analysis

The SEM micrographs of the Sn/CNFs and $\text{SnO}_2/\text{NiO}/\text{CNFs}$ composite nanofibers are shown in Figure 1a and Figure 1b, respectively. After carbonization at 800°C in an inert environment for 2h the Sn/PAN and $\text{SnO}_2\text{-NiO}/\text{PAN}$ precursor nanofibers were transformed to Sn/C and $\text{SnO}_2/\text{NiO}/\text{C}$ composite nanofibers. The average diameters of the nanofibers from the SEM images ranged from 100–300 nm. The Sn nanoparticles can be clearly seen on the surface of both Sn/C and $\text{SnO}_2/\text{NiO}/\text{C}$ composite nanofibers. The SnO_2 and NiO particles in the $\text{SnO}_2/\text{NiO}/\text{C}$ composite nanofibers were “hairy-like” on the fiber strands (Fig. 1b). Another feature of these fibers was the presence of many pores in the fiber strands that were evenly

distributed. In particular, the pores on the Sn(nanoparticle)/C fibers had a pore volume of 0.305 cm³/g which is larger than that for the SnO₂/NiO/C composite nanofibers (i.e. 0.136 cm³/g), as illustrated in Table 1, although the pore size for the SnO₂/NiO/C was much larger. These pores contributed to the buffering effect that provided the accommodation for the volume change during the alloying and de-alloying process of Sn and SnO₂/NiO with lithium. The pores on the composite nanofiber anode were created during the calcination process via the passage and interaction of the inert gas molecules with the nanofibers.

Table 1: The average pore size, pore volume, and BET surface area of the various composite fibers

Microstructure.

Sample	Pores Size (Å)	Pores Volume (cm ³ /g)	Surface Area (cm ² /g)
Sn₂ONiO/ CNFs	31.84	0.136	171.24
Sn/CNFs	21.89	0.305	575.28
CNFs	19.98	0.151	301.71

The elemental mapping analysis (i.e. EDAX) of the composite Sn/C and SnO₂/NiO/C nanofibers (Fig. 2) clearly shows that these composite nanofibers consist predominantly of Sn and carbon for the Sn/C composite anode and Sn, Ni, and carbon for the SnO₂/NiO/C anode. The EDAX area mapping for the composite nanofibers showed the heterogeneous distribution of the composite electrode constituents in the carbon matrix. The area mapping clearly shows that the composite electrode predominantly consists of carbon. The actual content of carbon and the cations in the composite nanofibers were determined by TGA analysis (Fig. 3). It can be seen in

Fig. 3 that up to 92°C, a minor weight reduction of ~3% which corresponds to the removal of physically absorbed water from the fibers, was observed for both composite electrodes. At temperatures between 290°C and 410°C, there is a multistage decomposition that could be attributed to the polymer (polyacrylonitrile), which recorded a weight loss of ~38% for the Sn/C composite electrode. For the SnO₂/NiO composite nanofiber, the multistage decomposition was observed at temperatures 320°C and 410°C. The oxidation of carbon for both Sn/C and SnO₂/NiO/C was observed above 450°C, and beyond 530°C while the weight loss remained steady. The TGA results indicate that the composite nanofibers contained ~64wt% and ~58wt% of carbon for the Sn/C and SnO₂/NiO/C fibers, respectively.

3.2 Analysis of the Crystal structure of the composite electrodes

X-ray diffraction (XRD) analysis of the as-synthesized Sn/PAN and SnO₂/NiO nanofiber precursors along with their respective composite nanofiber electrodes was carried out to evaluate the crystal structure of the composite nanofiber electrodes. In Figure 4a, the XRD pattern of Sn/C composite electrode showed the tetragonal rutile structure (JCPDS 41-1445) of the space group $P4_2/mnm$. The peak at the 18° followed by a broad peak is attributed to the un-stabilized PAN polymer in the Sn/PAN nanofiber precursor (Fig. 4a). This small peak disappears after carbonization but the broad amorphous peak still remains after the carbonization process. The broad peak in the calcined Sn/C could indicate the presence of hard carbon or non-graphitized carbon in the carbon fibers. During the carbonization process of Sn/PAN nanofibers at 800°C in an inert atmosphere, the PAN polymer is converted into carbon fibers, while the Sn could have been oxidized to SnO₂ during the stabilization process at 280°C and back to the metallic phase at

800°C during the carbonization process in the inert environment. However, it is expected that some amount of the oxide will still exist in the final product of Sn/C composite electrode. The peak pattern obtained in the X-ray shows a small amount of SnO₂ [40] and metallic Sn. The peaks of the metallic Sn were observed as doublet at 43° in the as-forcespun Sn/PAN fibers. The carbonization process completely separates the shoulder of the peak of the metallic Sn in the forcespun Sn/PAN nanofibers into two distinct peaks indexed as (220) and (211). Additionally, there was a shift of the (200) and the (101) peaks to a lower 2θ relative to the baseline, which is indicative of an improvement in the interplanar layer spacing in the Sn/C crystal structure. Another difference in the XRD patterns is the relative intensity ratio of XRD peaks of the as-spun Sn/PAN nanofibers and that of the Sn/C composite electrode which is attributed to the difference in crystallinity and crystal size. For the SnO₂/NiO/C composite electrode and SnO₂/NiO/PAN precursor fiber, the XRD pattern in Figure 4b shows several broad peaks of low intensity for both the precursor fiber and the carbonized fibers. These broad peaks are attributed to the low crystallinity level on these fibers. The broad peaks at 26° and 43° indexed to (101) and (211) are identified as the planes of tetragonal rutile SnO₂ (JCPDS41-1445), while the cubic NiO are indexed at (200) plane (JCPDS71-1179). However, the NiO peak was not obvious on the SnO₂-NiO/PAN fiber XRD pattern. The carbon peak pattern was not observed, which could be attributed to the amorphous structure of carbon in these nanofibers. The lack of distinct peaks for the SnO₂ and that of the NiO in the carbonized fibers are indication of the amorphous nature of these compounds in the carbon fiber matrix.

3.3 Surface Analysis (XPS)

To evaluate the composition of the surface compounds on the Sn/C nanofibers and that of the carbonized SnO₂/NiO/C composite nanofibers, a high resolution XPS analysis was carried out. The XPS results shows the survey spectra in Figure 5a as well as those for the C1s, O1s, and the Sn 3d peaks for the composite electrode of Sn/C. The C1s peak for both the Sn/C and SnO₂/NiO nanofibers show a broad peak, which was de-convoluted into two peaks at 284.6 eV and 285.6 eV. Typically, the binding energy with the peak at 284.6 eV is often associated with the C-C bonds and attributed with the amorphous carbon phase or from adventitious carbon, while the peak at 285.6 eV was characteristic of the combination of C-O or the carboxyl (i.e. O-C=O) groups that could have served as the nucleation point for the SnO₂ [41, 42]. The spectra for the Sn 3d revealed the spin-orbit components (3d_{3/2} and 3d_{5/2}) of the Sn 3d peaks at binding energies ~ 495.3 and ~486.7 eV for both as shown in Figure 5a for the Sn/C and SnO₂/NiO/C composite nanofibers in Figure 5b. In the SnO₂/NiO Sn 3d spectra, there were two shoulder peaks on the 3d_{3/2} and 3d_{5/2} that were absent in the Sn/C nanofibers, these shoulder peaks could not be immediately explained. However, the splitting of the 3d doublet of Sn at 8.6 eV, indicates a probable valence state of Sn to be +4[43](i.e. Sn⁴⁺ in the SnO₂). For the Sn/C nanofibers, this phenomenon further enforces the formation of small amounts of SnO₂ nanoparticles as part of the Sn/C composite electrode structure. The XPS spectra for the O1s scan in both composite nanofibers showed one peak at binding energy 530.6eV and assigned to the O in the SnO₂. These results thus point to a heterogeneous structure from the composite nanofibers comprising SnO₂ nanoparticles embedded in the carbon nanofibers for the Sn/C and SnO₂/NiO composite anodes. In the SnO₂/NiO nanofibers, the main Ni2p_{3/2} peak at 856.62eV, its satellite peaks at 862.96eV, 874.86 eV, and 881.28eV shown in Fig. 5b are attributed to NiO [44] and there were not

attributable to Ni metal in the spectra, suggesting that the residual Ni in the fibers was insignificant.

3.4 Electrochemical Performance

3.4.1 Cyclic voltammogram for the Sn/C composite NF anode

Cyclic voltammetry (CV) test was carried out on the Sn/C and SnO₂-NiO composite nanofiber electrodes to evaluate the Lithium storage properties. A half-cell configuration of these electrodes was constructed and the CV test was performed between 0.0-3.0V vs. Li/Li⁺ at slow scan rate of 0.2 mV s⁻¹. The CV curves for the SnO₂/NiO and Sn/C electrodes are shown in Figure 6a and Figure 6b, respectively. During the first cathodic scan, the test Sn/C cells exhibited a broad and sharp peak potential at ~0.38 V vs. Li/Li⁺, which is attributable to the structural destruction of Sn/SnO₂ and associated initial electrolyte decomposition [45].

The decomposition reaction of the electrolyte solution with Li leads to the formation of a solid electrolyte interface (SEI) on the composite nanofiber anodes/electrolyte interface. In this case, the SEI layer will mainly consist of lithium carbonate and lithium alkyl species. The structural destruction of SnO₂ species in the SnO₂/NiO/C composite electrode leads to the formation of amorphous Li₂O according to the partially reversible equilibrium equation;

The formation of Li₂O on the electrode was confirmed from the CV curve of the SnO₂/NiO/C nanofiber electrode and exhibited at potential 1.2V vs Li/Li⁺[46], which continues to increase after each scan. However, for the Sn/C composite electrode, the Li₂O peak was absent during the cathodic sweep, therefore reaction (1) could not have occurred in the case of Sn/C composite electrode. Therefore the amount of SnO₂ in the electrode was considered insignificant in the Sn/C nanofibers.

The presence of a peak potential at ~0.23 V vs. Li/Li⁺ for both electrodes is associated with the reversible alloying formation process between the Sn and lithium according to the following reaction;

Again during the anodic sweep, the peak potential of ~0.82 V vs. Li/Li⁺ corresponds to the de-alloying reaction according to the reduction reaction above. During this de-alloying process, it is possible that electrochemically formed Sn nanoparticles could aggregate to form large clusters in order to reduce surface free energy. It is the formation of such large clusters that normally lead to the cracking of the electrodes and the eventual increase in the cell's internal resistance.

The storage/cycling performance of the Sn/C composite anode was investigated at room temperature. The charge/discharge curves for the Sn/C and that of the SnO₂/NiO/C composite

nanofibers electrode, for the first 100 cycles were obtained at a voltage between 0.05V and 3.0V and at a current density of 100mA/g. The presence of SnO₂ in SnO₂-NiO/C and small amounts for the composite Sn/C electrode initiates the general electrochemical reactions in Equations 1-3 and presented schematically in Figure 7. This reaction gave a first initial specific discharge capacity of 589 mAhg⁻¹ for the baseline CNFs electrode (Fig. 8a), 2586 mAhg⁻¹ for the Sn/C composite anode (Fig. 8c), and 1885 mAhg⁻¹ for the SnO₂-NiO/C composite electrode (Fig. 8b). A current density of 100 mA g⁻¹ was used for the first discharge step to allow greater amount of Li⁺ into the composite electrode structure. These capacities are remarkably higher than those reported in various literatures [47, 48] on the Sn/C or SnO₂/C composite nanofiber electrodes. There was a steady drop in the discharge capacity for all electrode; SnO₂/NiO/C, Sn/C as well the baseline CNFs composite anodes from the 1st to the 10th cycles, which are consistent with results reported in literature [8, 49, 50].

The drastic drop in capacity is often associated with inevitable irreversible loss of lithium ions for the formation of the solid electrolyte interface layer. Unlike in many other battery chemistries such as the over lithiated cathodes; Li_{x+1}FePO₄ and Li_xMn_{1-x}NiCoO₄ where extra lithium is provided for in the electrode to compensate for amount of lithium used for the SEI layer formation, the composite nanofiber electrode do not have that extra Li⁺ for this purpose. Interestingly, for the SnO₂/NiO/C electrode (Fig. 8b), the capacity fade existed from the 1st through to the 10th cycle and the specific capacity steadily increased. A similar trend was also observed for the Sn/C composite electrode (Fig. 8b). The steady rise of the specific discharge capacity continued the 50th and 100th cycle, with the discharge capacity almost equal to that of the 2nd discharge capacity (i.e. ~85% capacity recovery) for the SnO₂/NiO/ composite electrode.

On the other hand, the Sn/C composite electrode had a steady recovery of the faded capacity after 10th cycle up to the 50th cycle, which had a discharge capacity significantly greater than that at the 10th cycle. However, there was a significant second capacity fade that was observed after 50th cycle, i.e. from 714 mA^g⁻¹ to 677mA^g⁻¹ at the 100th cycle. The second capacity fade was not observed in the SnO₂/NiO/C composite electrode. The Sn/C composite anode on the other hand, showed less irreversible capacity loss at the second cycle than that for SnO₂/NiO/C composite nanofibers electrode, with the SnO₂/NiO/C losing almost half of the 1st discharge capacity on the 2nd cycle. This is often attributed to SnO₂ content in SnO₂/NiO/C anode, the oxygen-containing functional groups on the SnO₂/NiO fibers react with Li⁺ resulting in the irreversible loss of recyclable lithium ions [51, 52]. The electrochemical performance for the baseline progressively decreased from the 1st to the 50th cycle, thereafter it remained steady at 124 mA^hg⁻¹ at the end of the 100th cycle. When the contribution of carbon nanofiber in the composite electrode (i.e. 124 mA^hg⁻¹) is taken out, the Sn and the SnO₂/NiO would have specific capacities of 509 mA^hg⁻¹ and 551 mA^hg⁻¹ respectively for the 100 cycles, which is significantly impressive.

The cycling performance for both composite electrodes is shown in Figure 9. The results shown in Fig. 9 indicate that the Sn/C composite nanofibers, which had a much higher initial discharge capacity compared to the SnO₂/NiO/C composite electrode cell, maintained a steady capacity of 675 mA^g⁻¹ compared to 633 mA^g⁻¹ for the SnO₂/NiO/C composite electrode. The slight difference in capacity between the two electrodes was not that significant after the 100th cycle, considering that fact, the addition of NiO to the SnO₂ was aimed at improving the conductivity. This notwithstanding, the Sn/C composite nanofiber electrode appeared to have a little improved capacity retention over the SnO₂/NiO/C binary composite electrode. Statistically, the subtle

difference between the specific capacities of the two composite electrodes was the same. Furthermore, even after 100 deep charge/discharge cycles, both cells maintained a Coulombic efficiency > 95% as shown in Figure 9. The relatively higher capacity of these composite nanofiber electrodes is most importantly due to the quality of the nanofiber produced using the Forcespinning method, which produced fibers with unique microstructures that include pores and hairy-like microstructure, capable of buffering the volume change associated with Sn/C and SnO₂/NiO/C electrode during the alloying/de-alloying process. The porous structure of these composite nanofibers also contributed to improving their cycle performance. Most reported literature using binder free electrodes from electrospinning and centrifugal spinning show [48, 53] lower discharge capacities ranging from 400 to 650 mAhg⁻¹ after 50 cycles.

A postmortem (tear-down) analysis was carried out on the cycled cells after undergoing 100 cycles to elucidate any changes in the materials structure and morphology. The morphology of the aged SnO₂/NiO/C electrode as shown in Figure 10, consisted of a heavily passivated layer on the surface of the fiber strands.

The formation of the passivation layer on the fiber strands could be explained as follows; in the electrolyte solvent mixture of EC and DMC, the high polarity and dielectric constant of ethylene carbonate compared to the DMC, will position it to preferably undergo a reduction reaction[54]. The reduction of EC involves a two-electron transfer to one mole EC and reaction with Li⁺ to produce Li₂CO₃ and C₂H₄ gas (Equation 1).

Subsequently, the species $(\text{CH}_2\text{OCO}_2\text{Li})_2$ in Eq.1 on the composite carbon SnO_2 -NiO electrode surface, can readily react with traces of H_2O either in the solution or in the working environment (i.e. glovebox) to produce Li_2CO_3 , $(\text{CH}_2\text{OH})_2$ and CO_2 gas (Eq. 2) [55].

The reaction with H_2O could therefore compound the amount of gases produced in the cell leading to cell venting. It is therefore imperative to keep the H_2O content in the glovebox to minimal levels ($<0.5\text{ppm}$).

The formation of these species form part of the solid electrolyte interface (SEI) on the composite electrode surface. However, after prolong cycling, the SEI layer structure may be distorted, thus exposing the composite electrode surface to more electrolyte decomposition reaction. In particular, the decomposition species of POF_3 and PF_6^- - from the unstable lithium salt, LiPF_6 undergoes a reduction reaction with EC to produce various species (Eq. 3 &4);

The salt dissociates into LiF and the Lewis acid PF_5 (Eq. 3);

which can dissociate further to form an additional anion in solution (Eq.5)

Which can initiate an autocatalytic process to perpetuate the decomposition reaction [34].

The surface species PF₅ was identified as a possible compound on the aged SnO₂/NiO/C and Sn/C composite electrodes as evident in qualitative analysis (EDS) of the aged electrode in Figure 10d.

The crystal structure analysis of the aged SnO₂/NiO/C and that of the Sn/C electrode were again analyzed after the aging process (Fig. 11). The X-ray pattern for the aged vs the fresh electrode of SnO₂/NiO/C (Fig.11a) shows a general reduction in the amorphous peak at lower 2 θ , a shift of the peaks to higher 2 θ , broadening of the peaks, and emergence of two new phases for the aged electrode. The broadening and peak shift was indicative of lithium residing in the host electrode, although the cell was discharged to 0.01 V, it is expected that some amount of lithium will remain in the crystal structure of the electrode. The two new phases on the aged SnO₂/NiO/C electrode were identified to belong to the electrolyte species of LiF and possibly PF₅, which correlates the qualitative results from the EDS analysis in Figure 10d. For the aged Sn/C electrode, there was neither a peak shift nor peak broadening observed relative to its fresh electrode x-ray diffraction pattern. However, four new phases, two observed at 32° and 38° and similar to those found in the aged SnO₂/NiO/C electrode were also attributed to the presence of the electrolyte species LiF and PF₅. The other two phases were observed at lower 2 θ i.e. at 22° and 24°, the sharp peak at 22° was identified as that of graphite peak indexed (002), the appearance of the graphite peak along with that at 22° on the aged Sn/C electrode could not readily be explained. These electrolyte decomposition species, in particular LiF form a resistive layer on the fiber surface, which negatively affected the Li⁺ transfer. This was manifested amply in the impedance for both SnO₂/NiO/C and Sn/C aged electrode in Figure 14 (a and b) where there was an increase in the impedance of their respective aged electrode relative to the baseline.

The suitability of these alternative nanofiber composite electrodes was further evaluated by performing a rate capability test at different current densities: 50, 100, 200, 400, and 500 mA g^{-1} and cycling for just 10 cycles as shown in Figure 12. In all these rate capability tests, the $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode exhibited a much higher discharge specific capacity compared to the Sn/C composite electrode cells. Another observed phenomenon was the steady stabilization of the capacity fade of the Sn/C composite electrode at 50 mA g^{-1} , 100 mA g^{-1} , 200 mA g^{-1} , and even at 500 mA g^{-1} compared to a steep loss and slower stabilization of the $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode. At the 400 mA g^{-1} cycling, however, the $\text{SnO}_2/\text{NiO}/\text{C}$ capacity was nearly stable while that of the Sn/C had a steep drop in the capacity that showed no steadiness over the 10 cycles, much like capacity fade behavior of the $\text{SnO}_2/\text{NiO}/\text{C}$ electrode observed at the 500 mA g^{-1} region. The good performance in terms of capacity stability of the Sn/C composite electrode is attributed to the large and evenly distributed pores on the fibers, which offered a much more buffering to accommodate the volume change during the alloying/de-alloying process. On the other hand, the recorded higher capacity of the binary $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode was attributed to the presence of NiO . The NiO provided the needed structural stability of the electrode that prevented it from pulverization, while at the same time enhanced the electrical conductivity of the electrode [2, 20, 56].

The capacity recovery after applying a cyclic current was evaluated. In this test, the cells were cycled at 500 mA g^{-1} for 10 cycles and the cell rested an hour to achieve electrochemical stability and then charge/discharge tests were performed for 10 cycles at a low current density of 50 mA g^{-1} . The electrochemical performance of the Sn/C and $\text{SnO}_2/\text{NiO}/\text{C}$ composite fiber anodes subjected to this current cyclic test is shown in Figure 13. In this capacity recovery test, the Sn/C

electrode had a gradual capacity fade during the 500 mA g^{-1} cycle compared to an initial dip follow by a gradual steady stabilization of the capacity observed from the $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode. When the cycling current was ramped down to 50 mA g^{-1} , as expected, the capacities of both electrodes increased dramatically. The $\text{SnO}_2/\text{NiO}/\text{C}$ electrode capacity became steady and recorded a capacity comparable to that recorded in Figure 12 for 50 mA g^{-1} rate performance. However, a rather continual capacity fade was observed for the Sn/C electrode for the 50 mA g^{-1} region. From these studies, it is observed that the $\text{SnO}_2/\text{NiO}/\text{C}$ electrode has a better cycling and rate performance than that for the Sn/C electrode, although the Sn/C electrode has a slight edge over it in terms of long cycle performance stability.

3.4.2 Impedance analysis

Impedance test was carried out on the freshly assembled cells of Sn/C (Fig. 14a) and $\text{SnO}_2/\text{NiO}/\text{C}$ (Fig 14b) composite electrode and subsequently after the cells were cycled 100 times. The various components of the impedance were extracted using the equivalent circuit model (Fig. 14a insert) to the simulated impedance. The impedance test was carried out to elucidate the associated electrochemical performance. The depressed semicircles in the region of the high to middle frequency range, which represents the initial interfacial resistance and charge-transfer resistance, clearly showed a large variation between the fresh and the cycled cells for both electrodes. While the baseline (fresh) cell of the $\text{SnO}_2/\text{NiO}/\text{C}$ (Fig. 14b insert) had a relative low impedance compared to that for the fresh cell Sn/C (Fig. 14a), both cell had similar impedance after aging for 100 cycles. The extracted resistances from the simulated impedance from the equivalent circuit (Table 2) showed a drastic increase in the cell ohmic resistance after

cycling. There was also a corresponding increase in the SEI layer resistance as well as the charge transfer resistance in the cell after the 100 cycles.

Table 2: Extracted resistances of the aged and fresh cell of Sn/C from the equivalent circuit model (Fig. 14a insert).

		Ohmic (R_1)(Ω)	SEI (R_o)(Ω)	Charge Transfer (R_2) (Ω)
Sn/C	Fresh Cell	0.53	7.72	38.42
	Aged Cell	7.91	10.3	47.11
SnO ₂ /NiO/C	Fresh Cell	2.16	2.51	6.08
	Aged Cell	8.68	8.35	54.9

The increase in charge transfer and the SEI resistance at the electrode/electrolyte interface affected the lithium ion kinetics at the interface. This correlated the steady loss of capacity of the cell during the initial cycles. The electrochemical performance of the Sn/C and SnO₂/NiO/C composite electrode does not differ significantly. For the Sn/C electrode the uniform dispersion of Sn particles in the carbon nanofibers provided a large number of active sites for Li ion storage and shorter lithium ion transfer distance, while the pores in the fibers provided a pathway for ion and electron transport without the need for a current collector. All these attributes contributed immensely to the improved cycling and performance of the Sn/C nanofiber composite electrode produced by Forcespinning. .

4.0 Conclusion

The unique morphology and structure of the composite SnO₂/NiO/C and Sn/C electrode provided a large surface area for an easy ion transport. The pores, in combination with the NiO for the

SnO₂/NiO/C, provided the needed structural stability of the electrode that prevented pulverization, and enhanced the electrical conductivity of the electrode. These two factors played a key role in the improved cycle and rate performance of the binary electrode. The Sn/C nanofiber electrode, on the other hand, showed a better cycle performance and capacity retention relative to the SnO₂/NiO/C electrode. The improved cycling and rate performance of these binary nanofiber electrodes were relatively better compared to those prepared by electrospinning and centrifugal spinning system.

5.0 Acknowledgement

This research was supported by NSF PREM award DMR-1523577: UTRGV-UMN Partnership for Fostering Innovation by Bridging Excellence in Research and Student Success. Partial funding was also received from the following agencies: the USDA, the National Institute of Food and Agriculture, and the Integrating Food Science/Engineering and Education Network (IFSEEN) with award number: 2015-38422-24059.

Figures

Figure 1: SEM images of solid carbon fiber (a,b), Sn/CNFs composite fibers (c,d) with nanoparticles of the Sn attached to the fibers strands and pores distributed evenly. SnO₂-NiO/CNFs composite fibers at different magnification showing uniform fiber mat (e,f), and fiber strands with nanoparticles of the SnO₂ and NiO attached to the fibers strands in a hair-like structure with pores distributed evenly.

Figure 2: EDAX area mapping of $\text{SnO}_2/\text{NiO}/\text{C}$ composite nanofibers (a) and that of the Sn/C composite nanofibers (b) the $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode shows the distribution of the Sn, Ni, and C on the composite fiber mat.

Figure 3: TGA analysis of the $\text{SnO}_2/\text{NiO}/\text{C}$ and Sn/C composite fibers showing the actual carbon content in the electrodes.

Figure 4: XRD pattern of Sn/PAN precursor nanofibers and that of Sn/C composite nanofibers prepared from 15 wt.% Sn/PAN precursors at 800°C (a) and that for the $\text{SnO}_2/\text{NiO}/\text{PAN}$ precursor and $\text{SnO}_2/\text{NiO}/\text{carbon}$ fibers(b).

Figure 5a: XPS spectra of C 1s, O1s, and Sn3d for Sn/C composite nanofibers

Figure 5b: XPS spectra showing a survey spectra, the spectra of C1s, O1s, Sn3d, and Ni1s for the SnO₂/NiO composite nanofibers. With the Sn3d and Ni1s showing distinct peaks with shoulders compared to that observed in the Forcespun SnO₂/NiO nanofibers

Figure 6a: Cyclic voltammogram (CV) of Sn/C composite NFs in half-cell configuration between 0.005-3V vs. Li at scan rate of 0.2 mVs⁻¹.

Figure 6b: Cyclic voltammogram (CV) of carbonized $\text{SnO}_2/\text{NiO}/\text{C}$ composite nanofibers in half-cell configuration between 0.005-3V vs. Li at scan rate of 0.2 mVs^{-1} .

Figure 7: Schematic of Lithium insertion/Lithium de-insertion process that occurs within the half-cell upon cycling.

Figure 8a: Galvanostatic charge/discharge curves of carbon nanofiber (CNF) electrode made from PAN precursor at a current density of 100 mA g^{-1} with a voltage window of 0.05-3.0V.

Figure 8b: Galvanostatic charge/discharge curves $\text{SnO}_2/\text{NiO}/\text{C}$ composite electrode made from $\text{SnO}_2/\text{NiO}/\text{PAN}$ precursor nanofibers at a current density of 100 mA g^{-1} with a voltage window of 0.05-3.0V.

Figure 8c: Galvanostatic charge/discharge curves Sn/C composite electrode made from Sn/PAN precursor nanofibers at current density of 100 mA g^{-1} with a voltage window of 0.05-3.0V.

Figure 9: A comparison of the cycle performance of the $\text{SnO}_2/\text{NiO}/\text{CNFs}$ and Sn/CNFs composite electrodes at 100 cycles cycled between 0.05V-3.0V potential.

Figure 10: SEM images of aged Sn/C (a) $\text{SnO}_2\text{-NiO/C}$ (b) and electrode after 100 cycles. EDS micrograph with corresponding spectra of elements (d) on the surface of the aged $\text{SnO}_2\text{-NiO/C}$ electrode.

Figure 11: XRD pattern of the aged (a) $\text{SnO}_2\text{-NiO/C}$ and Sn/C (b) composite electrode after undergoing 100 cycles.

Figure 12: Rate performance of the SnO₂/NiO/C and Sn/C composite electrode at various current densities from 50 mA/g to 500 mA/g over 10 cycles between 0.05-3.0V

Figure 13: Capacity recovery after cyclic current performance for the Sn/C and SnO₂-NiO/C composite electrodes.

Figure 14a: Nyquist plots for the experimental and simulated impedance plots of the fresh and aged Sn/C electrode batteries after 100 cycles.

Figure 14b: Nyquist plots for the experimental and simulated impedance plots of the fresh (insert) and aged $\text{SnO}_2/\text{NiO}/\text{C}$ electrode batteries after 100 cycles.

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