Microstructural Characterization of Nanocrystalline Sn-Coated Carbon Fibre Electrodes Cycled in Li-Ion Cells

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The mechanisms of electrochemical capacity retention and eventual degradation in composite anodes prepared by electrodepositing nanocrystalline Sn coating on carbon fibres (CF), Sn-CF, were studied using in situ optical microscopy, high-resolution scanning and transmission electron microscopy. Specific capacity changes of Sn-CF anodes (vs Li/Li^+) were observed to take place in three stages: during the first two galvanostatic cycles, a rapid capacity decrease (from 1045 to 930 mAh g^{-1}) occurred, which was followed by a steady-state stage where the capacity remained constant at $922 \pm 22 \text{ mAh g}^{-1}$. The fast capacity drop of Sn-CF in the first cycle was attributed to the partial decohesion of Sn from CFs although the carbon substrate remained unaffected due to formation of a layer from the solid electrolyte reduction products. The pure Sn electrode with a higher initial specific capacity than the Sn-CF displayed a rapid decrease in the same range, whereas the specific capacity of the uncoated CF was already much lower as the fibres were severely damaged in the first cycle.

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I. INTRODUCTION

GRAPHITE is a commonly used anode material in rechargeable Li-ion batteries^[1,2] and has a theoretical capacity of 372 mAh g^{-1} ,^[3] which is calculated by considering that the intercalation of Li-ions between the graphene layers would lead to the formation of LiC_6 . Electrochemical tests have revealed that the capacity of graphite decreases abruptly and irreversibly during the initial electrochemical cycles.^[4] This phenomenon, sometimes referred to as electrochemical shock,^[5,6] is a result of intense graphite surface damage that occurs by fragmentation of graphite particles.^[7] Once a solid electrolyte interphase (SEI) layer^[8] forms, the severity of graphite degradation decreases^[7] leading to a more gradual decline of capacity.^[9,10] A recent study^[11] observed that a uniform and continuous SEI (with a tubular morphology) that was formed during low scan rate tests (0.05 mV s^{-1}) was effective in reducing the graphite damage. At high scan rates ($>3.00 \text{ mV s}^{-1}$), delamination of graphite layers by the formation and propagation of interlayer cracks adjacent to SEI/graphite interfaces occurred due to the diffusion of

co-intercalation products (Li_2CO_3 , LiC_6) at the crack tips during the subsequent cycles.^[12]

Electrode surface modification is a common focus of the attempts made in order to improve the electrochemical performance.^[13–19] For example, heating Li-ion cells containing graphite electrodes at 333 K (60 °C) in an EC-based electrolyte was found to generate a Li_2CO_3 -enriched SEI on graphite surface, which in turn ensued a 28 pct increase in the battery capacity when subsequently tested at 298 K (25 °C).^[13] In another study, Li_2CO_3 particles were pre-deposited on the surfaces of electrodes prior to cycling.^[14] The SEI that was formed on the Li_2CO_3 pre-treated electrodes improved the capacity retention of Li-ion batteries during long-term cycling, and this effect was attributed to enhanced Li-ion diffusion. The chemical composition of graphite surfaces and their morphological features could be altered by mechanical milling of natural graphite particles in oxygen and nitrogen. It was observed that the reversible lithium intercalation capacity increased with the amount of disorder induced in the milled samples by these treatments.^[15] Application of carbon coatings by thermal vapour decomposition treatment at 1273 K (1000 °C)^[16] and heat-treatment of graphite/PVC mixtures at 1073 K (800 °C)-1273 K (1000 °C) in Ar ^[17] showed that the irreversible capacity decreased while the Coulombic efficiency increased with an increase in the coating thickness. Another surface modification method for graphite anodes was developed by encapsulating polyacrylonitrile (PAN)^[18] on the surface of natural graphite particles *via* radiation-initiated polymerization. It was suggested that the PAN coating could reduce the co-intercalation of solvated lithium ions and contribute to the capacity improvement during cycling in a PC-based electrolyte. Graphite

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modified by adsorption/adhesion of polydimethylsiloxane (PDMS)^[19] reduced the magnitude of the first cycle capacity drop and also improved the cycling performance of the graphite electrode. In all these cases, application of coatings was suggested to modify the electro-active locations on the graphite surfaces that could in turn reduce the rate of solvent molecule intercalation during SEI formation and improve cyclability.

Sn-based anodes are potentially important alternatives to graphite because of their high theoretical capacity of 992 mAh g^{-1} .^[20] However, large volume changes in the order of 300 pct are known to occur and cause fragmentation of electrodes made of pure Sn during cycling in the Li-ion cells.^[20,21] Although the degradation mechanisms are not extensively studied, Li-ion insertion in Sn-based anodes may lead to the formation of a broad range of Li-Sn intermetallic compounds^[21] that would contribute to volume expansion and fragmentation. In order to reduce the propensity of Li-ion-induced electrode disintegration, several approaches have been taken including manufacturing of anodes consisting of Sn-based intermetallics notably Cu_6Sn_5 ,^[22–24] CoSn_3 ,^[25] and Ni_3Sn_4 .^[26–28] The main hypothesis that motivated fabrication of these intermetallic electrodes was that Cu, Co or Ni would form an “inactive matrix” that could buffer volume changes during Li_xSn formation. Some of these electrodes provided higher capacity retentions that ranged between 20 and 80 pct (for ≥ 40 cycles) compared to anodes made of pure Sn.^[23,29] Yet they had lower specific capacities that varied between 200 and 500 mAh g^{-1} . An alternative strategy to improve the capacity retention consisted of the development of anodes made of composite materials that incorporated oxides^[30] and carbonaceous phases^[31–33] dispersed in a Sn matrix. The oxide and carbon phases could be expected to accommodate the cycling-induced volume changes that occur in the Sn matrix. Some of these composite anodes have shown high reversible capacity and good capacity retention (520 to 850 mAh g^{-1} for 50 cycles^[30–33]), but their manufacturing involved intricate multi-step processes that impeded their commercialization prospects.^[34]

Surface engineered electrodes, namely micro- and nano-scale textured Sn coatings with a large surface-to-volume ratio such as Sn-plated nanopillar-textured surfaces^[35] may improve electrode's tolerance to the volume changes. Enhancements in chemical reactivity with the electrolyte, and the electronic contact with the current collector were noted for 3-dimensional electrodes.^[36–38] The use of metallic foams^[39–41] could serve the similar purpose as they were shown to improve the cycling performance of anodes in Li-ion cells. Another surface engineering method applied to the electrode material design makes use of Sn coatings on carbon fibre (CF) paper. CF paper is a light material normally made of PAN-based CFs with large surface area and good electrical conductivity. As such it can be used as both the current collector^[42] and as an active component in the electrode construction. For the current study, CF paper was selected as a substrate

material for the electrodeposition of Sn coating considering that the resulting material could provide higher capacity retention than its individual components. Electrochemical tests were performed on the new electrode made by coating CF with Sn, designated as the Sn-CF anode, consisting of a Sn coating with a thickness of $500 \pm 100 \text{ nm}$ and a grain size of $350 \pm 50 \text{ nm}$ as described previously by Shafiei and Alpas.^[43] Sn-CF retained 50 pct of its initial capacity after 20 cycles compared to the 23 pct for a pure Sn coating deposited on a Cu foil.^[43] A fundamental understanding of the electrochemical damage mechanisms responsible for capacity changes can be obtained by determining the microstructural variations that occur in Sn-CF electrodes.

The focus of this paper is on the delineation of the micromechanisms responsible for the delay in electrochemical degradation of the Sn-CF electrodes. Microscopical changes that took place during electrochemical cycling of Sn-CF anodes were studied using cross-sectional focused-ion beam, FIB, and high-resolution (HR) transmission electron microscopy, TEM. The experimental investigations were used to rationalize the effect of the electrode damage mechanisms on the electrochemical performance of Sn-CF in comparison to those observed in case of the electrode's individual components, Sn and CF. The resulting knowledge can be used for designing more robust anodes with prolonged cycling performances.

II. EXPERIMENTAL

A. Description of Carbon Fibres (CF) and Sn Coating

A $370\text{-}\mu\text{m}$ -thick sheet of Toray CF paper consisting of PAN-type CFs with an average diameter of $7.5 \pm 1.5 \text{ }\mu\text{m}$ was used as the base anode material. The Sn coatings were electrodeposited on the randomly oriented fibres of the CF papers. The fibres had a tensile strength of 24 MPa, and flexural modulus of 10 GPa. A secondary electron image displaying the morphology of the individual CFs, examined by scanning electron microscope, SEM, prior to the Sn deposition process, is shown in Figure 1(a). The CF surface exhibited a morphology comprising continuous bands oriented parallel to the fibre axis, which is the typical surface morphology of PAN-based CFs. A higher magnification SEM image of the CF surface shown in Figure 1(b) reveals that the bands in Figure 1(a) consisted of bundles of graphite nodules, each of about 200 to 500 nm in width corresponding to the spacing between the bands. The Sn coatings electrodeposited on the CFs had a mass loading of $3.2 \pm 0.2 \text{ mg cm}^{-2}$. The electrode preparation procedures were described previously by Shafiei and Alpas.^[43] The electrodeposition process coated all fibres on the top of the CF paper, as well as most fibres to a depth of $65 \pm 5 \text{ }\mu\text{m}$. Figure 1(c) shows the morphology of Sn coatings deposited on the CFs. A high-magnification image of the Sn coating shown in Figure 1(d) indicates that the average size (width) of the Sn grains was $350 \pm 50 \text{ nm}$.

Fig. 1—Secondary electron SEM images of (a) uncoated carbon fibres (CF); (b) the region marked as (b) in (a) showing the fibre's surface texture at high magnification; (c) Sn-coated carbon fibres (Sn-CF); (d) the equi-axed Sn grains present in the region marked as (d) in (c). Images were obtained prior to conducting electrochemical tests.

A cross-sectional scanning transmission electron microscope (STEM) image of Sn grains obtained by examining a section of Sn-coated CFs prepared by FIB milling (see Section II-C) is shown in Figure 2(a), which indicates that the as-deposited coating consisted of a single layer of Sn grains. The coating on the CF was continuous, indicating good adhesion between the substrate and Sn. The average thickness of the Sn coating on the CFs was 500 ± 100 nm. A HR-TEM image obtained from a location adjacent to the Sn/CF interface marked as (b) in Figure 2(a) is shown in Figure 2(b). Using fast Fourier transform, FFT-derived diffraction patterns, a d -spacing of 0.29 nm was measured corresponding to the (200) planes of Sn. A d -spacing of 0.34 nm was measured for C which corresponded to the (002) planes of C. Sn coatings with a mass loading of 1.6 ± 0.2 mg cm⁻² were also deposited on commercially pure 25-μm-thick Cu substrates with flat surfaces using the same electrodeposition bath for comparison of their electrochemical properties with those of Sn-CF electrodes. The thickness of the Sn coating deposited on Cu was 2.2 ± 0.2 μm.

B. Assembly of Li-Ion Cells and Electrochemical Tests

1. Galvanostatic charge–discharge cycling tests

Galvanostatic experiments were conducted to achieve fully charged and discharged capacity for Sn-CF and

study the changes in its specific capacity with cycling. Charge–discharge cycling tests, with a voltage cut-off window of 0.02 to 1.50 V vs Li/Li⁺, were conducted on the Sn-CF anodes, as well as on uncoated CF, and Sn-coated Cu electrodes. Due to the high capacity retention of Sn-CF anodes (as seen in Figure 4), a large current density of 1.50 mA cm⁻² was applied. As application of a current density of 1.50 mA cm⁻² would have prevented complete charging of Sn and CF anodes, a current density of 0.75 mA cm⁻² was used in these experiments. The electrodes were placed inside a CR2032-type coin cell with a Li counter electrode, a polypropylene membrane (Celgard 2400) separator and an electrolyte composed of 1 M LiPF₆ in a mixture of ethylene carbonate (EC), dimethyl carbonate and diethyl carbonate (1:1:1 by vol.). Cells were assembled and sealed in an Ar-filled MBraun LABstar workstation where H₂O and O₂ levels were maintained below 1 ppm.

2. Cyclic voltammetry tests

For monitoring *in situ* surface changes that occurred on Sn-CF anodes in the first two cycles, cyclic voltammetry (CV) experiments were carried out. The electrodes were placed at the centre of an electrochemical cell constructed from polytetrafluoroethylene (PTFE). The top surface of the anode was observed using a Keyence VHX-600 digital microscope. Detailed description of the experimental setup used for CV tests was provided by

Fig. 2—(a) Cross-sectional STEM image of a single layer of Sn grains across the coating thickness; (b) HR-TEM image obtained from a location (marked as (b) in (a)) at the fibre/Sn interface. Images were obtained prior to conducting electrochemical tests.

Bhattacharya *et al.* in Reference 12. A 99.99 pct pure Li wire with a resistivity of $9.446 \mu\Omega \text{ cm}$ [at 293 K (20 °C)] was used for both counter and reference electrodes. The electrolyte was 1 M LiClO_4 in a 1:1 (by vol.) mixture of EC and 1,2-dimethoxy ethane. CV experiments were conducted starting from $V = 3.00$ to 0.02 V (vs Li/Li^+) at a constant scan rate of 2.0 mV s^{-1} . Both galvanostatic and CV electrochemical experiments were performed using a Solartron Analytical Modulab system.

C. SEM and TEM Investigations of Coated and Uncoated CF

An FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with an EDAX energy-dispersive

X-ray spectrometer (EDS) was used to study the elemental compositions of the Sn-CF electrodes before and after the galvanostatic cycling. EDS maps depicting distributions of C and Sn and other elements on the electrode surfaces were acquired using a voltage of 15 kV, and sixteen scanning frames were used for each measurement. An FEI Magellan 400 SEM with sub-nanometer resolution operated at 1 to 5 kV was used to study the surface morphologies of both the coated and uncoated electrodes before and after the electrochemical experiments.

TEM studies were carried out on the Sn-CF electrodes using cross sections excised by means of FIB milling. A Zeiss NVision 40 cross-beam instrument comprised a FIB milling apparatus and a Schottky Field Emission Gun (FEG) filament SEM (dual beam FIB/SEM system) was employed for micro-machining of site-specific trenches on the CFs. Cross-sectional TEM samples were prepared in a direction parallel to the fibre diameter. These samples were sectioned and removed from their original locations using the FIB lift-out technique that consisted of ion-milling a trench on each side of the sample to obtain a $1\text{-}\mu\text{m}$ -thick plate using a Ga-ion beam current of 13 nA at a voltage of 30 kV. The final milling was conducted using an ion-beam current of 700 pA at a voltage of 5 to 10 kV. The surface of the sample was protected from ion damage by a Pt layer deposited prior to FIB cutting. The thickness of the plate was reduced to about 100 nm using low ion beam current (10 pA) polishing. The samples, prepared in this way, were examined by an FEI Titan 80-300 TEM operated at 300 kV.

III. RESULTS

A. Charge–Discharge Profiles and Specific Capacity of Sn-CF During Electrochemical Cycling

The galvanostatic charge–discharge profiles of the Sn-CF electrodes recorded for the 1st, 2nd, 12th and 20th cycles are shown in Figure 3. During the first charge, the lithiation of the Sn coating on the CFs in the Sn-CF electrode manifested itself by the formation of a long plateau at approximately 0.30 V, followed by the lithiation of the fibres that generated a positive potential curvature below 0.20 V. During the first discharge, the delithiation process of the Sn-CF started above 0.25 V, as evidenced from the gradual increase in potential from 0.25 to 0.60 V, followed by a large delithiation plateau that occurred between 0.60 and 0.80 V. The large plateau suggested that both intercalation and alloying mechanisms^[20,21] were active in the Sn-CF electrodes. With the progress in cycling, the length of the plateaus observed during charging and discharging decreased as can be seen in the 2nd, 12th and 20th cycles indicating a decrease in the amount of cyclic intercalation and alloying processes.

Using the results of the galvanostatic charge–discharge cycling tests shown in Figure 3, the change in the specific capacity of Sn-CF with the number of cycles is plotted in Figure 4. Specific capacities of pure Sn and

uncoated CFs electrodes are also shown in Figure 4. The first cycle specific capacity of the Sn-CF anodes was 1045 mAh g^{-1} , whereas the capacity of the pure Sn was 1200 mAh g^{-1} and that of the uncoated CF was 236 mAh g^{-1} . The initial enhancement in the capacity of Sn-CF was attributed to the high capacity of Sn. The percentage of irreversible capacity loss of the Sn-CF anodes was lower than the other two electrodes tested. While the specific capacity of Sn-CF dropped to 930 mAh g^{-1} at the end of the second cycle, the capacity of pure Sn decreased to 1025 mAh g^{-1} and that of the uncoated CF electrodes to 54 mAh g^{-1} . Thus, the Sn coating on the CF increased the specific capacity of uncoated CF by 876 mAh g^{-1} as shown in Figure 4. The specific capacities of Sn and uncoated CF continued to decrease during the subsequent cycles. In contrast, following the initial drop, the capacity of Sn-CF ceased to decay further and remained almost constant at $922 \pm 22 \text{ mAh g}^{-1}$ for the next 10 cycles. Thus, Sn-CF exhibited practically a steady-state capacity plateau during this period. Eventually, a gradual decrease in capacity followed the steady-state plateau to 505 mAh g^{-1} at 20 cycles.

Fig. 3—Galvanostatic charge-discharge voltage profiles obtained during the 1st, 2nd, 12th and 20th cycles for the Sn-CF electrode.

Fig. 4—Variation of specific capacities of the Sn-CF composite, pure Sn and the CF electrodes with number of cycles.

The capacity retention plateau that was observed for the Sn-CF electrode between the 2nd and 12th cycles was the most salient observation arising from Figure 4, while a rapid decrease occurred in the specific capacity of the pure Sn anodes in the same period. At the end of the galvanostatic charge-discharge cycling tests, a cumulative capacity loss of 50 pct was recorded for Sn-CF (evaluated at 20th cycle), which compared favourably to that of the Sn that showed a 79 pct decrease for the same number of cycles.

B. Microstructural Characterization of Sn-CF During the First Two CV Cycles

As stated in Section III-A, a rapid drop in the capacity of Sn-CF was observed during the first two cycles. The microscopical changes that occurred on the surfaces of Sn-coated CFs were examined by conducting CV tests. *In situ* observations made using an optical microscope on the electrode surface, while conducting the CV tests, allowed characterization of the damage mechanisms that occurred during the first and second cycles. The CV tests were conducted in such a way that initially a high voltage of 3.00 V was applied and then the voltage was decreased while maintaining a constant scan rate of 2.00 mV s^{-1} to a minimum of 0.02 V , i.e., $V = 3.00 \text{ V} \rightarrow 0.02 \text{ V}$ (vs Li/Li^+) as shown in Figure 5. For the first cycle, two current peaks were identified; the first occurred when the voltage dropped to 1.05 V and the second at $V = 0.40 \text{ V}$ as marked on the current density vs voltage (vs Li/Li^+) curve in Figure 5. The occurrence of the peak at 1.05 V can be considered to coincide with the reduction of Sn oxides to metallic Sn.^[21,44–47] These reactions are considered to be

Fig. 5—Cyclic voltammograms obtained during the cycling of Sn-CF electrodes using a voltage scan rate of 2.00 mV s^{-1} .

irreversible and expected to occur only in the first cycle. The peak at 0.40 V can be attributed to the Li-Sn alloy formation, Li_xSn .^[44,45] During the reverse sweep, while the voltage was increased from 0.02 to 3.00 V, two additional current peaks were observed at 0.56 and 0.85 V that were attributed to the de-alloying of the Li_xSn . The decrease in the intensity of the first peak observed in the second cycle when voltage was reduced from 3.00 to 0.02 V can be attributed to damage and disintegration of Sn. (Cross-sectional investigations revealed formation of a layer at 1.20 V on the surfaces of the CFs that were exposed as a result of the disintegration of the Sn coating as will be discussed later in this section). During the reverse sweep of the second cycle (from 0.02 to 3.00 V), peaks were observed at 0.63 and 0.95 V when the de-alloying of Li_xSn occurred.

Simultaneously, in situ optical microscopy was conducted on Sn-CF anodes to reveal the damage features and the sequence of events is shown in Figures 6(a) through (d). The initial surface morphology of Sn-CF electrode immersed in the electrolyte as observed through the glass observation window of the

electrochemical cell at the onset of the CV test is shown in Figure 6(a). The Sn coating that provided continuous coverage to all fibres on the top surface of the fibres can be seen. During the CV tests, as the voltage decreased to 2.50 V, damage to the Sn-CFs became apparent as parts of the Sn coating were detached and removed from the Sn-CF surfaces [Figure 6(b)]. Coating removal continued to occur at other parts of the Sn-CF surface as the voltage was further decreased as shown in an image taken at 0.50 V, Figure 6(c). The microstructure of the Sn-CF electrode surface, displaying the extent of damage to Sn-coated fibres at the end of the 2nd cycle, is shown in Figure 6(d). Sn coating removal and detachment from CF surface can be attributed to the large volume changes (~259 pct) that the Sn electrode becomes subjected to during the lithiation/de-lithiation cycles.^[48–50] However, many parts of Sn coating still remained intact on the CFs. Another observation, made during the in situ microscopy tests, was that the diameter of the coated fibres increased by about 30 pct. A fibre of diameter $9.00 \pm 0.26 \mu\text{m}$ before cycling marked on [Figure 6(a)] for example appeared to have a larger size of $11.60 \pm 0.35 \mu\text{m}$ at the end of the

Fig. 6—Optical micrographs obtained in situ at $\times 1000$ during the CV test (shown in Fig. 5) with Sn-CF electrodes: (a) at the onset of the test, (b) at 2.5 V, (c) at 0.5 V, and (d) at the end of the second cycle. Arrows indicate locations of exposed CF after removal of sections of Sn coating.

second cycle [Figure 6(d)]. This was attributed to the combined effects of the volume expansion of Sn and (may be more importantly) partial decohesion of parts of Sn coating that were not entirely removed. The TEM observations in Section IV-A revealed this aspect of damage clearly. The damage events, examined in more detail by SEM and TEM, are described in the following paragraphs.

Cross-sectional microstructures of Sn-coated CFs observed by SEM provided details of the decohesion of the Sn coating at the Sn/CF interface in the first cycle [Figure 7(a)]. Interfacial cracks between the Sn coating and the CF could be detected on this and other cross-sectional images examined. It also became clear that the CF at the core was unaffected and remained damage-free. A layer was formed around the outer surface of Sn. As shown in Figure 7(a), the morphology of the layer consisted of porous regions as well as regions with featureless morphology. The layer thickness varied from a few nanometers to more than 1 μm . However, as the Sn coating started to delaminate soon

after the CV test initiated [Figure 7(b)], the Sn coating became detached from the CF and the layer was removed. Figure 7(b) shows the cross-sectional microstructure of a CF after the second CV cycle. Accordingly, at the end of the second cycle, the Sn coating was almost completely detached from the CF and only a small section of the Sn coating separated from the CF remained intact at the lower part of the CF in Figure 7(b). A solid layer was observed on the exposed surfaces of the CF. Formation of this layer was attributed to electrochemical reduction of the electrolyte causing further irreversible charge consumption. The morphology of this layer was not different from the layer on Sn shown in Figure 7(a). It was porous and had a non-uniform morphology. The layer can be observed at the interface between Sn coating and the carbon (left part of Figure 7(b)) and a closer inspection indicates that it was attached to the CF surface rather than the surface of the Sn coating. Some sections of the layer were as thin as 10 nm but mostly its thickness varied between 1.0 and 2.5 μm . Formation of a thick layer could be attributed to a large surface area of the CF that prompted high irreversible charge consumption. The CFs were not subjected to the same degree of volume expansion as Sn^[48–50] and for this reason the layer formed on the CF could have remained intact for several cycles. Stable layers formed on graphite electrodes are known to protect these electrodes from electrochemical damage^[7,11] and it is possible that a similar role was played by the solid layer generated on the CF. Microstructures of Sn-CF anodes obtained after prolonged cycling are examined in Section III-C.

C. Microstructural and Compositional Characterization of Sn-CF After 20 Galvanostatic Cycles

As indicated previously, the surfaces of CF were covered uniformly by the Sn coating, which was confirmed by the low-magnification secondary electron SEM image (Figure 8(a)) and the corresponding EDS maps of Sn and C (Figure 8(b)) of the Sn-CF electrode taken before cycling. A back-scattered electron SEM image of the Sn-CF electrode examined after 20 charge–discharge cycles [Figure 8(c)] revealed that solid electrolyte deposits were formed between the CFs. The EDS maps of the solid electrolyte deposits generated between the CFs were rich in F and P as expected indicating that they were formed as a result of the reduction of the electrolyte [Figures 8(d) through (f)]. The Sn coating fragments that were removed from the surfaces of the CF were mixed with F and P as they filled the space between the CFs. Accumulation of the solid electrolyte reduction products possibly contributed to the capacity decline after the 12th cycle as observed in Figures 3 and 4.

Further evidence for fragmentation of the Sn coating was provided by higher magnification SEM images of individual CFs taken after 20 galvanostatic cycles [Figure 9(a)] which revealed that parts of the CF surfaces were stripped of the coating but the CFs themselves remained undamaged. The coating's damage features are similar to those described in Figure 7(b).

Fig. 7—Secondary electron SEM images showing cross-sectional microstructures of a Sn-coated CF observed at the end of the (a) first, and (b) second cycles of the CV test shown in Fig. 5.

Fig. 8—(a) Secondary electron SEM image of the Sn-CF electrode in as-prepared condition. (b) EDS map of the area shown in (a) with C shown as yellow and Sn shown as purple. (c) Back-scattered electron SEM image of the Sn-CF electrode microstructure after 20 galvanostatic cycles. EDS maps of (d) C and Sn, (e) F (blue) and (f) P (green) obtained from the area shown in (c) (Color figure online).

Hence, after the initial damage to the Sn coating, the CFs remained almost damage-free until the end of the tests and were possibly protected by the layer formed from the electrolyte reduction products as described earlier. When the microstructures of the uncoated CFs were examined after 20 galvanostatic cycles at the same magnification, extensive damage was observed on their surfaces. The CFs were exfoliated as shown in Figure 9(b) where several exfoliated plates of flakes that were partially detached from the CF surfaces could be identified. This damage feature is consistent with those

reported in the literature for carbon electrodes.^[11,12,51–53] It is likely that most damage to the uncoated CFs occurred prior to the establishment of the solid electrolyte layer.^[7,8]

IV. DISCUSSION

The Sn coating along with the carbon core contributed to the higher performance of the Sn-CF composite anodes cycled in the Li-ion cell compared to

Fig. 9—Back-scattered electron SEM images showing (a) Sn-coated and (b) uncoated CF after 20 galvanostatic cycles.

its individual components (Figure 4). The initial lithiation/de-lithiation cycles had an adverse effect on the Sn coating. The coating partially separated from the CF surfaces by the end of the first cycle but the fact that the CFs continued to remain almost damage-free during subsequent cycles revealed the positive effect of having an initial Sn coating on their surface. In this section, the cross sections of the cycled CFs of Sn-CF were examined by high-resolution TEM that shed light on the possible reasons of eventual capacity loss of the Sn-CF electrodes described in Section IV-A. The role of ionic and solvent intercalation on CF lattice spacing are considered in Section IV-B. The mechanisms of capacity retention of the Sn-coated CFs are discussed in Section IV-C.

A. TEM Analyses of Electrochemically Cycled Sn-CF

A STEM image of the cross section of an initially Sn-coated CF after 20 galvanostatic cycles is shown in Figure 10(a), which once more indicates that the damage to the Sn coatings was extensive, in agreement with observations noted in Sections III-B and III-C. Additional details emerge from Figure 10(a) as it indicates that the Sn coating after being removed from the fibre surface became fragmented into very fine particles

Fig. 10—(a) A cross-sectional STEM image of Sn-coated CF after 20 galvanostatic cycles showing clustered and isolated Sn particles scattered in a porous matrix between the CFs. (b) HR-TEM image of disintegrated Sn nanoparticles in the amorphous matrix. Sn nano-particles with (200) and (220) planes could be identified. Inset shows a FFT-derived diffraction pattern indicating the co-existence of Sn and Li_2CO_3 .

(nano-particles) of sizes <100 nm. In some regions, the fragmented Sn particles were agglomerated to form clusters of 0.5 to 2.0 μm in diameter. The distribution of

fractured Sn nano-particles and clusters that were mixed with the solid electrolyte reduction products surrounding the CFs is shown in Figure 10(a). A high-resolution TEM image of the fragmented Sn nano-particles obtained from a region marked as (b) in Figure 10(a) is shown in Figure 10(b). Two distinct features of the solid electrolyte reduction products can be identified: an amorphous matrix and regions with crystalline lattice structures. FFT analyses of the crystalline region shown in Figure 10(b) determined a lattice spacing that corresponded to the {200} planes of Sn with an inter-planar distance of 0.30 nm. This particular Sn nano-particle had a diameter of ~16 nm. In another region, a particle with a diameter of ~6 nm, with an inter-planar spacing of 0.21 nm corresponding to the {220} planes of Sn was detected. FFT-derived diffraction pattern (inset) of the region marked (with a rectangular box) in Figure 10(b) indicated {002} planes of Li_2CO_3 that was formed during the reduction of the EC-containing electrolyte.^[54]

B. Ionic and Solvent Intercalation in Coated and Uncoated CFs

Analyses of HR-TEM images obtained from surface and near-surface regions of Sn-coated and uncoated CFs revealed small but consistent differences in the d -spacing values of the crystallographic planes. For these measurements, the FFT patterns of two CFs from each sample were examined, and nine d -spacing measurements were carried out on each CF. The d -spacings of the carbon (002) planes ($d_{(002)}$) measured after 20 galvanostatic cycles were larger than the initial $d_{(002)}$ values of pristine CFs (Figure 11). At a depth of $0.75\ \mu\text{m}$ underneath the surface, the $d_{(002)}$ of the uncoated CFs was $0.347 \pm 0.002\ \text{nm}$ when measured prior to the electrochemical test, and increased to $0.355 \pm 0.001\ \text{nm}$ after electrochemical cycling (averages were based on three measurements at each location). The $d_{(002)}$ value for carbon planes measured at the same depth in Sn-CFs subjected to the electrochemical cycling was $0.354 \pm 0.001\ \text{nm}$. The increase in the carbon inter-planar spacing can be attributed to the solvent co-intercalation and Li-ion diffusion between the planes.^[55,56] The $d_{(002)}$ -spacing of carbon in Sn-CFs decreased to $0.345 \pm 0.002\ \text{nm}$ at a depth of $3.75\ \mu\text{m}$, presumably due to lesser amount of co-intercalation products reaching at these depths. A larger $d_{(002)}$ -spacing of $0.350 \pm 0.002\ \text{nm}$ was measured in CFs without an Sn coating, which could be attributed to facilitated diffusion of solvent molecules into the carbon lattice structure.

C. Micromechanics of Damage in Electrochemically Cycled Sn-CF

The damage mechanisms that occurred during electrochemical cycling of Sn-CF composite anodes and uncoated CF anodes in Li-ion cells are summarized in

Fig. 11—The d -spacing values of the carbon (002) planes in the fibres of the uncoated CF and the Sn-CF anodes measured along the radius of the fibres before cycling and after 20 galvanostatic cycles.

the form of a schematic diagram shown in Figure 12. The Sn coating provided an initial high capacity to the Li-ion cells. However, the Sn coating partially delaminated from the CFs causing capacity decrease. A solid electrolyte layer formed on the exposed CFs as a result of reduction of the cell electrolyte that protected the CFs from exfoliation. The high capacity retention of Sn-CF electrode between the 2nd and the 12th cycle was attributed to the high capacity of the Sn remaining on the CFs, and the mechanically stable CF that also acted as a conductive agent. CFs that were not initially coated with Sn showed severe delamination damage during the first cycle. After the 12th cycle, delamination of the entire Sn coating led to the capacity decline of Sn-CF. Another factor that possibly contributed to the capacity decline between the 12th and 20th cycles was due to the electrolyte reduction products filling the voids between the CFs and forming a continuous solid layer (Figure 8). At the end of the 20th cycle, the Sn-coating had disintegrated into nano-sized fragments and clusters that were mixed with the solid electrolyte reduction products. If the Sn-CF anodes were subjected to further electrochemical cycling longer than 20 cycles, the specific capacity of Sn-CF anodes would have approached that of the uncoated CFs.

It can be suggested that an Sn coating with small grain size may be beneficial since the small grain size would reduce propensity of fracture and hence delay coating delamination compared to a coating with a

	Sn-coated carbon fibre (Sn-CF)	Uncoated carbon fibre (CF)
Before test	CFs uniformly coated with nanocrystalline Sn	PAN-type carbon fibres
After cycle 1	Partial detachment of Sn coating	Initiation of exfoliation damage in CFs
After cycle 20	Sn coating almost completely removed from the fibres	Exfoliated fibre surfaces

Fig. 12—Schematic showing the damage mechanisms that occurred in the Sn-coated and uncoated CFs during electrochemical cycling in Li-ion cells.

larger grain size^[20,34] resulting in a stable anode with high capacity and long cycle life.

V. CONCLUSIONS

The electrochemical degradation mechanisms of a Sn-carbon fibre (Sn-CF) anode, which was fabricated by electrodepositing a 500 ± 100 nm thick nanocrystalline Sn coating on carbon fibres (CF), were studied by cycling the Sn-CF anodes in a Li-ion cell and comparing their performance with those of pure Sn and uncoated CF electrodes using SEM/EDS and high-resolution TEM. The main conclusions arising from this work can be summarized as follows:

1. A decrease occurred in the initial specific capacity of Sn-CF electrodes for the first two galvanostatic cycles followed by a steady state stage (between the 2nd and 12th cycles) where the capacity was retained. Over the same range the pure Sn and the uncoated CF anodes continued to show capacity decreases.
2. The initial capacity drop of Sn-CF was attributed to partial removal of the coating from CFs. However, a solid layer formed due to electrolytic reduction protected the surfaces of the CFs.
3. Preservation of the capacity of Sn-CF at 922 ± 22 mAh g⁻¹ for several cycles, after the initial decrease, was attributed to the high capacity of the Sn-coating supported by mechanically

stable CFs, whereas the CFs that were not initially coated with Sn showed delamination damage.

4. At the end of the charge–discharge cycling tests, a cumulative capacity loss of 50 pct was recorded due to disintegration of the Sn coating and accumulation of solid electrolyte reduction products, but the high capacity retention capability of Sn-CF compared favourably to that of the pure Sn that showed a 77 pct decrease for the same number of cycles.

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