Graphical Abstract

Thermal Stability of Active/Inactive Nanocomposite Anodes based on Cu_2Sb in Lithium-ion Batteries

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Abstract

Various active/inactive nanocomposites of $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$, $\text{Cu}_2\text{Sb}-\text{TiC}$, and $\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$ have been synthesized by high energy mechanical milling and investigated by differential scanning calorimetry (DSC) to determine the lithiated phase stability and heat generation arising from these electrodes. The milling process reduces the Li_3Sb phase stability, relative to the un-milled samples, to below $\sim 200^\circ\text{C}$. However, the incorporation of the reinforcing, inactive phases Al_2O_3 , TiC , and carbon black offer a slight improvement. DSC curves also show that the low-temperature heat generation in the SEI-layer reaction range is not noticeably altered by either the milling process or the addition of the inactive phases. A strong exothermic peak is observed at $\sim 200^\circ\text{C}$ for the 0 % state of charge electrodes of $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$ and $\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$ that was caused by the incorporation of carbon black into the composite. This peak was not present in the electrodes of milled Cu_2Sb or $\text{Cu}_2\text{Sb}-\text{TiC}$, suggesting that efforts to extend the cycle life of alloy anodes should avoid carbon black due to its destabilizing effects on delithiated electrodes. Fourier Transform infrared spectroscopy analysis indicates that the reaction arising from the incorporation of carbon black is tied to a low-temperature breakdown of the lithium salt LiPF_6 .

Keywords: lithium-ion battery, alloy anodes, antimony alloys, composites, thermal stability

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Introduction

Enhanced safety and improved understanding of the mechanisms of failure in lithium-ion batteries is imperative to the continued expansion of the lithium-ion technology into new realms of application such as electric vehicles and stationary storage. Lithium-ion batteries possess a number of characteristics and components that make them inherent safety concerns: (i) the battery electrodes are highly oxidizing /reducing when in the fully charged state and kept in very close proximity to one another, (ii) highly flammable electrolytes are necessary to ensure stable cycling over large voltage windows and in the fully charged state the anode surface still typically necessitates the formation of a passivating SEI-layer to prevent continuous reaction with the electrolyte, and (iii) many compounds in the battery are reactive to ambient air. These issues have not prevented the proliferation of lithium-ion batteries into small-scale portable electronics, but a history of product recalls, battery fires/explosions, and restrictions on the transportation of lithium-ion batteries is a testament to the risks they still pose.[1]Improvements in manufacturing and the development of a wide range of external safety controls and mechanisms (*e.g.* improved cell monitoring, gas venting, current interrupt devices, *etc.*) have greatly reduced the rate of incidence and the consequences of failure in lithium-ion batteries.[1]However, in larger scale applications with more individual cells and more energy stored, the statistical likelihood of failure increases and the potential consequences of a failure event become much more severe. Therefore, it is imperative that efforts are made to investigate the safety characteristics of new materials developed for lithium-ion batteries to allow for greater inherent safety of the cells beyond the application of additional external controls.

The most dangerous event that can occur with lithium-ion batteries is known as thermal runaway, in which uncontrolled heat generating reactions within the cell become self-sustaining

and lead to a rapid increase in cell temperature that usually ends with cell rupture or explosion. This process is most heavily controlled by reactions involving the cathode and the electrolyte, but is only initiated at temperatures $>180\text{ }^{\circ}\text{C}$. [2–5] At lower temperatures leading up to the initiation of thermal runaway, the vast majority of heat generating reactions (estimated at $>95\%$ for typical LiCoO_2 / graphite cells) arise from the anode. [6] These anode reactions are strongly associated with the passivating SEI-layer on the anode surface. At temperatures $>60 - 70\text{ }^{\circ}\text{C}$, the metastable components within the SEI-layer begin exothermically reacting to form more stable compounds. [6–10] If temperatures increase to above $150\text{ }^{\circ}\text{C}$, then the SEI-layer begins to lose its passivating effects on the anode surface and the electrolyte starts to react directly with the lithiated electrode. This reaction typically continues until the onset of thermal runaway, but if higher temperatures are reached then the polyvinylidene fluoride (PVDF) binder reacts exothermically with any remaining lithium in the electrode. This reaction usually does not initiate until the temperatures reach well above $300\text{ }^{\circ}\text{C}$. [3,4,11–13] Efforts to improve battery safety via new electrode materials typically focus on (i) cathodes with higher temperature stability to reduce the chance of thermal runaway, (ii) cathodes with less heat generation upon thermal degradation to reduce the consequences of thermal runaway, or (iii) anodes with less heat generation at low temperatures to reduce the chance of inducing thermal runaway. [2,6, 14–16] This study focuses upon the third route and is an expansion upon a previous study on thermal stability of antimony active material anodes. [17]

Antimony is an alloying anode, similar to silicon or tin, which forms the compound Li_3Sb upon lithiation to yield a theoretical capacity of 660 mAh g^{-1} . It has a reaction potential of approximately $\sim 0.9\text{ V}$ versus lithium and like all other alloy anode materials, it suffers from a short cycle life due to the large volume change of $\sim 137\%$ that occurs during the

lithiation/delithiation reaction.[18,19] Therefore, in order to attain a useful electrode with antimony as the active material, mitigation techniques such as incorporating the antimony into intermetallics or composites must be employed. A number of reports have investigated such methods and are capable of attaining attractive electrode properties.[20–28]In addition, the higher operating potential of antimony is expected to contribute to an enhanced thermal stability of its lithiated phase and greater charge tolerance to protect against lithium plating.[29]However, there is a scarcity of actual data on the thermal stability of antimony and of the effect of its incorporation into an intermetallic or composite structure to improve cycling performance.[17] We focus here upon thermal stability testing of a Cu_2Sb intermetallic, which is a well-studied electrode material and known to undergo lithiation/delithiation via the two step mechanism shown in reaction 1. As an electrode material it has demonstrated both enhanced cycling relative to pure lithium as well as effective incorporation into composite structures.[20,21,28]

The composite structures to be tested are all synthesized with a high energy mechanical milling method to achieve nano-scale phase mixing and high final electrode density.[21,24,30,31]The composite components that are combined with Cu_2Sb are Al_2O_3 , TiC, and carbon black. All three of these composite structures have been well-tested and shown to effectively extend the cycle life of alloying anode materials and yield attractive final electrodes in terms of overall performance.[21,24–26,32,33]Figure 1 demonstrates this enhancement with a comparison of the cycle life of pure Cu_2Sb to the composite electrodes of $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$, $\text{Cu}_2\text{Sb}-\text{TiC}$, and $\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$ that are being investigated in this study.

When incorporating the Cu_2Sb intermetallic into the composite structures, there are two key changes to the material: (i) the actual addition of the reinforcing composite phase and (ii) the

physical effects of the milling process on the material particle size and morphology. Because electrode particle size and surface area have been shown to affect the thermal stability performance of anode materials in certain cases, it is essential to separate these effects from those of the composite phases.[8,34] In order to properly analyze the effects of each, milled Cu_2Sb is used as the baseline electrode material and analyzed relative to the results for un-milled Cu_2Sb from the previous study by our group and relative to the composite structures under investigation here.[17] The thermal performance of the materials are tested via both differential scanning calorimetry (DSC) and *ex situ* x-ray diffraction of heated electrodes to observe the heat generation arising from the materials as well as the phase change reactions they undergo during these degradation reactions. In addition, exothermic peaks identified in DSC are subjected to further analysis using Fourier Transform infrared spectroscopy (FTIR) to identify reactions that are not observable via XRD because they may not necessarily involve alterations of the bulk crystalline structures.

Experimental

The electrode materials used in this study are a milled Cu_2Sb intermetallic, $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$ composite (66 : 14 : 20 respective mass content), $\text{Cu}_2\text{Sb}-\text{TiC}$ composite (70 : 30 respective mass content), and $\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$ composite (55 : 30 : 15 respective mass content). The Cu_2Sb intermetallic powder was initially synthesized by mixing metallic powders of antimony and copper (Acros Organics, 99 %, 45 μm) in a 1 : 2 atomic ratio and heating the mixture to 450 °C for 12 h in an alumina crucible under flowing reducing gas (5 vol. % H_2 / Argon). The resulting intermetallic powder was then subjected to high-energy mechanical milling (HEMM) under an argon atmosphere with a Fritsch Pulverisette 6 at 500 RPM for 6 cycles consisting of 1 h milling followed by 1 h of rest. The synthesis method for $\text{Cu}_2\text{Sb}-$

$\text{Al}_2\text{O}_3@\text{C}$ involves HEMM of metallic powders of copper, aluminum (Alfa Aesar, 99 %, 17 – 30 μm), Sb_2O_3 (Alfa Aesar, 99.6 %, 1.1 – 1.8 μm), and acetylene black carbon (Alfa Aesar, 99.99 %, -200 mesh) and was carried out as described by our group before.[21] The synthesis of $\text{Cu}_2\text{Sb-TiC}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$ was carried out with metallic powders of copper, antimony, titanium (Alfa Aesar, 99.5 %, -325 mesh), and carbon black in which, initially, the powders of copper, antimony, and titanium were mixed to yield a Cu : Sb atomic ratio of 2 : 1 and with calculated Ti content to yield a final composition with 30 wt. % TiC. This mixture was heated in an alumina crucible under flowing argon to 500 °C for 10 h. After heating, the mixture was combined with a stoichiometric amount of carbon to fully convert the Ti in the mixture to TiC (in the case of $\text{Cu}_2\text{Sb-TiC}$) or with 15 wt. % excess carbon to the stoichiometric amount (in the case of $\text{Cu}_2\text{Sb-TiC}@\text{C}$) and then subjected to HEMM. A more detailed description of this synthesis process can be found for a similar antimony intermetallic in our previous report.[24]

The as-synthesized electrode powders were subjected to XRD phase analysis with a Rigaku Miniflex 600 with Cu-K α radiation. The powder morphology was observed via scanning electron microscopy (SEM) with a JEOL JSM-5610 microscope. Brunauer-Emmett-Teller (BET) surface area measurements were carried out with a Quantachrom Autosorb iQ2 instrument. Tap densities were measured with a Quantachrom AT-4 Autotap equipment.

To acquire *ex situ* XRD measurements, the prepared electrode powders were incorporated into pellet electrodes. The pellet electrodes were prepared by first mixing slurries of 80 wt. % electrode material of interest, 10 wt. % Super P conductive carbon, and 10 wt. % PVDF binder with N-methyl pyrrolidinone (NMP) as the solvent. The slurries were mixed overnight and subsequently dried for 48 h in a vacuum oven at ~ 100 °C. The dried slurries were then ground with a mortar and pestle and pressed at 2300 psi into pellet electrodes with an

approximate mass of 40 – 60 mg active material. The pellet electrodes were pressed to copper mesh current collector and assembled into CR 2032 coin cells inside an argon filled glovebox with a half-cell configuration with lithium foil, Celgard polypropylene separator, and an electrolyte of 1 M LiPF₆ dissolved in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cells were placed in an electrical short condition for at least one week to fully lithiate the pellet electrodes, which were then extracted from the cells inside an argon filled glovebox. The extracted electrodes were either immediately analyzed with XRD or subjected to heating as described below and then analyzed with XRD. This *ex situ* XRD measurement was carried out with a Rigaku air-sensitive sample holder under the same measurement settings as for the as-synthesized electrode powders.

Heating of pellet electrodes was carried out by first sealing the electrode inside of a copper foil pouch under an argon environment and then further sealing that copper pouch inside of a stainless steel bag from McMaster-Carr. This served to protect the electrode from the ambient atmosphere as it was heated at 10 °C min⁻¹ to either 200 °C or 300 °C in a box furnace and held at those temperatures for 5 min prior to cooling to room temperature. The sealed bag was then returned to the glovebox where the pellet was extracted for *ex situ* XRD analysis as described above.

Cast electrodes of the materials of interest were prepared for DSC and FTIR measurements. The cast electrodes were prepared by mixing overnight a slurry of 80 wt. % active material, 10 wt. % Super P, and 10 wt. % PVDF with NMP solvent. The mixed slurries were cast onto a copper foil current collector with the doctor blade method and dried under vacuum at 120 °C for at approximately 12 h. Individual electrodes were punched from the cast sheets and assembled into CR 2032 coin cells in a half-cell configuration as described above for the pellet electrodes.

DSC analysis was carried out on extracted cast electrodes in three different conditions: open-circuit voltage (OCV), 0 % state of charge (SOC), and 100 % SOC. OCV electrodes were extracted from the cell without subjecting it to any cycling conditions. Electrodes at 0 % SOC were subjected to 2 conditioning cycles from 0 – 2 V vs. lithium at C/20 rate and then held potentiostatically at 2.0 V (full delithiation) until the applied current dropped below $\sim 10\text{mA g}^{-1}$. Electrodes at 100 % SOC were also subjected to 2 conditioning cycles and then discharged to 0.0 V (full lithiation) where they were held potentiostatically until the applied current dropped below $\sim 10\text{mA g}^{-1}$. After preparation, the extracted electrodes were dried and sealed with 15 μL of added electrolyte (1 M LiPF_6 in EC:DEC) inside of a stainless steel DSC crucible with a perforated lid and gold foil seal. The DSC tests were carried out with a Netzsch STA 449 F3 Jupiter thermogravimetric analyzer (TGA)/DSC at a heating rate of $2\text{ }^\circ\text{C min}^{-1}$ up to $400\text{ }^\circ\text{C}$. The test chamber was evacuated twice prior to analysis and purged with high purity nitrogen as the test environment.

FTIR analysis was carried out on OCV electrodes as well as 0 % and 100 % SOC electrodes that had been heating under DSC conditions to a desired temperature. The DSC heating was stopped at the temperature of interest and the heated electrode was removed from the sealed crucible for FTIR analysis with a Thermo Scientific Nicolet iS5 FTIR spectrometer. The electrode undergoing FTIR analysis was held under inert argon gas until immediately prior to testing in order to minimize contamination from the ambient environment.

Results and Discussion

After synthesis, the composite electrode powders were analyzed with XRD for phase identification. Figure 2 shows the resulting XRD patterns of (a) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (b) $\text{Cu}_2\text{Sb-TiC}$, and (c) $\text{Cu}_2\text{Sb-TiC}@\text{C}$. For all composite materials the crystalline peaks are relatively weak but the primary peaks observed are associated with the Cu_2Sb phase cuprostibite (JCPDS File: 01-071-3333). The TiC containing materials of $\text{Cu}_2\text{Sb-TiC}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$ also show peaks associated with the crystalline rocksalt TiC phase (JCPDS File: 03-065-8805). While the reinforcing Al_2O_3 is not observable by XRD in the $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ material, it has been shown previously by our group that the Al_2O_3 is present in the system as an amorphous mixture of Al_2O_3 and carbon.[21] In all three composite materials, the carbon black is well incorporated into the composite structure by the milling process and is not merely present as a surface coating.[21,24] The synthesized Cu_2Sb intermetallic is also shown in Figure S1 to be phase-pure cuprostibite phase both before and after it underwent HEMM. The basic morphology of the electrode powders is shown Figure 2d-f in the form of SEM micrographs. All three powders have relatively similar morphologies of roughly spherical particle shapes with particle sizes ranging from several microns down to the sub-micron range. The primary morphological difference observed is that the $\text{Cu}_2\text{Sb-TiC}$ material has smoother particle surfaces and less fine particles because unlike the other two composite electrodes, it does not contain the small particle carbon black component.

A summary of the properties of the electrodes is shown in Table 1. The data here supports the observation from the SEM micrographs in Figure 2d-f that $\text{Cu}_2\text{Sb-TiC}$ has smoother particle surfaces with fewer very fine particles as its measured BET surface area is only $1.02 \text{ m}^2 \text{ g}^{-1}$, lower than the measured surface area of the other two composite powders. The larger BET surface areas of $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$ can be attributed to carbon black being a

final component of their composite makeup as the measured BET surface area of the acetylene black carbon precursor material is extremely high at $73.43 \text{ m}^2 \text{ g}^{-1}$. Both of these composite powders are also shown to possess much lower tap densities than milled Cu_2Sb and $\text{Cu}_2\text{Sb-TiC}$, again as a result of the carbon black inclusion. The observed reversible capacities of the composite electrodes are shown in Table 1 as well, and counterintuitively they are all higher than that for the pure Cu_2Sb . This is a result of the conductive materials incorporated into the composite structure that allow for greater active material usage and the participation of the carbon material in the structure in lithium storage.[24]

For all three composite electrodes studied, the primary active material is Cu_2Sb , which is anticipated to undergo reaction 1 upon lithiation to yield a final product of cubic Li_3Sb and metallic copper.[20,21,28] Figure 3 shows the observed *ex situ* XRD patterns for each composite electrode material that confirms these reaction products for all materials. The metallic copper peaks overlap with those of the steel sample holder, but the strength of the primary copper peak at ~ 43 degrees relative to the secondary sample holder peak at ~ 44 degrees suggests that there is indeed metallic copper present. The reinforcing TiC phase is also present for both $\text{Cu}_2\text{Sb-TiC}$ and $\text{Cu}_2\text{Sb-TiC@C}$, which is expected as it is largely electrochemically inert.[24,26,33] The same reaction products of Li_3Sb and metallic copper are observed for the lithiation of milled Cu_2Sb as shown in Figure S2.

Electrodes are subjected to heating under an inert environment in the presence of electrolyte in order to observe the phase stability of the lithiated electrode materials upon heating as well as the thermal degradation products upon heating. In previous studies of pure antimony and un-milled Cu_2Sb , it was shown that the lithiated Li_3Sb phase was thermally stable to higher temperatures than the baseline lithiated graphite electrode with evidence of strong Li_3Sb peaks up

to 300 °C and remaining peaks of partially lithiated phases up to 350 °C. However, the process of milling the Cu₂Sb sample for 6 h in preparation for this study was shown to drastically reduce the high temperature persistence of the lithiated Li₃Sb phase with Figure S2 showing that by even 200 °C for milled Cu₂Sb the lithiated phase has reverted back to the delithiated Cu₂Sb phase. Figure 4 shows the *ex situ* XRD pattern of the heated composite electrodes and for the most part, the same trends as observed for milled Cu₂Sb are seen for all three materials, with significant evidence of delithiation occurring by 200 °C. However, the composite materials appear to have a somewhat higher phase stability of the lithiated compounds relative to pure milled Cu₂Sb as all three materials still show evidence of partial lithiation remaining in the form of weak Li₃Sb peaks. By 300 °C, Figure 4a shows that Cu₂Sb-Al₂O₃@ has largely reverted to the delithiated phase, although there are still weak peaks from Li₃Sb observed, suggesting that the delithiation reaction is still ongoing at these high temperatures. However, at this temperature, both Cu₂Sb-TiC and Cu₂Sb-TiC@C have completely delithiated as the only observed peaks are for Cu₂Sb and TiC.

As demonstrated by the decreased phase stability of lithiated Cu₂Sb after milling, the simple process of milling the active electrode material can alter its thermal performance. Figure S1 shows that the effect of milling is purely physical as the Cu₂Sb phase is not altered by the milling process, with the only change being a broadening of the diffraction peaks. This observed broadening is used to calculate the change in the crystalline domain size with milling by using the Scherrer equation, shown in equation 2 below, in which τ is the average crystalline domain size, K is a shape factor (assigned a value of 0.9), λ is the x-ray wavelength, β is the full width at half maximum of the diffraction peak, and 2θ is the peak Bragg angle.

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Figure S3 shows the trend of decreasing domain size as Cu₂Sb is milled for longer times with a stabilization of the domain size when the milling time reaches 6 h. A corresponding increase in BET surface area is also observed for the milling of Cu₂Sb. After 6 h the intermetallic powder shows a surface area of 5.21 m² g⁻¹ relative to a value of 3.25 m² g⁻¹ measured for the un-milled Cu₂Sb. This physical alteration of the Cu₂Sb can be visualized by the comparative SEM images in Figure S4, which show a dramatic decrease in particle size with milling, in agreement with both the Scherrer and BET data. Because all of the electrode composites being studied here are synthesized by HEMM, it is important to differentiate between the effects from milling and the effects from the additional composite phases on the thermal performance of the Cu₂Sb active material. As such, Figure 5 shows the DSC curves for milled Cu₂Sb as a baseline for what will be observed for the composite electrodes. Overall, the reactions for the milled Cu₂Sb do not vary strongly from those analyzed in our previous study on pure Sb and un-milled Cu₂Sb.[17] There are three clear reaction regimes: the low temperature SEI-layer peaks, the mid-range temperature active material delithiation peaks, and high temperature electrolyte decomposition reactions.[7,11,12,35] These three reaction peaks are labelled in Figure 5, respectively, as 1, 2, and 3. The previously mentioned decrease in the high-temperature stability of the lithiated phase of milled Cu₂Sb manifests in a more pronounced peak for reaction 2 in the 100 % SOC sample as the electrolyte more rapidly reacts with and delithiates the electrode. **In addition, a quantitative heat generation analysis, as shown in Table 2, shows that the heat generation for the milled Cu₂Sb below 150 °C is higher than that of the unmilled Cu₂Sb from our previous study with respective values of 0.72 J mAh⁻¹ and 0.48 J mAh⁻¹.**

In addition to the effects of milling on the composite Cu_2Sb electrodes, the potential contributions from the reinforcing materials on the thermal performance of electrode materials must also be identified. DSC testing is carried out on samples of pure Al_2O_3 , TiC , and carbon black and shown in Figure 6. With the exception of carbon black, these materials are largely electrochemically inert and are, therefore, tested in the OCV condition. Carbon black was also tested in a 0 % and 100 % SOC condition but showed virtually no variation in thermal performance with the exception of the SEI-layer peaks so the OCV curve is shown here. Endothermic reactions associated with the electrolyte and identified as region 1 are observed for both Al_2O_3 and TiC at high temperatures.[36,37] The reaction curve for Al_2O_3 also shows a small exothermic peak at approximately 100 °C, identified in region 2. There are no observed exothermic reaction for the TiC material, but a small additional endothermic peak is present at ~ 180 °C in region 3. The peak in region 4 for the acetylene black is the only strong exothermic reaction observed for these reinforcing phase material, and once again it is most likely associated with the electrolyte degradation. However, this reaction is noteworthy for both how exothermic it is and for how low the peak temperature is relative to typically observed electrolyte degradation peaks. Carbonaceous electrodes in the OCV state have been shown on occasion to react exothermically with 1M LiPF_6 in EC:DEC electrolytes and the intensity and early onset observed in region 4 of Figure 6c could be a result of the previously mentioned extremely high surface area of carbon black ($73.43 \text{ m}^2 \text{ g}^{-1}$).[7,17]

From the observations thus far made, it can be hypothesized that the Cu_2Sb composite electrodes will exhibit variations from un-milled and pure Cu_2Sb in the following ways: the milling process will result in a stronger exothermic reaction peak around 180 °C associated with the electrode delithiation; the inclusion of Al_2O_3 could lead to an additional exothermic peak at

low temperatures; the inclusion of TiC could result in an endothermic peak at $\sim 180\text{ }^{\circ}\text{C}$; the incorporation of carbon black could lead to a stronger and lower temperature reaction with the electrolyte.

Figure 7 shows the experimental DSC curves for $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, $\text{Cu}_2\text{Sb-TiC}$, and $\text{Cu}_2\text{Sb-TiC}@\text{C}$. The materials were tested in OCV condition as well as in both 0 % SOC at 2 V vs. Li and 100 % SOC at 0 V vs. Li. The cycling data for the preparation of these cells can be seen in Figure S5, showing that the 0 % SOC cells are fully charged and the 100 % SOC cells are fully discharged prior to testing. For the most part, the observed curves are very similar to the milled Cu_2Sb sample from Figure 5 with a few notable exceptions. Region 1 shows that as predicted, there is a low temperature exothermic peak for $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ that occurs with the addition of the reinforcing phase. However, this peak is unexpectedly present in both other composites as well. Fortunately this peak is only present in the OCV materials and does not appear to affect the low temperature performance of the electrodes once they have been cycled and an SEI-layer has formed. Another rather unusual observation is the exothermic reaction peak highlighted in region 2 of Figure 7. This peak is unexpected as it is present only in the delithiated material that is tested at 0 % SOC and actually shows a stronger peak-heat-generation rate than the 100 % SOC electrodes. A potential source of this reaction can be inferred from the relative strength of the peak in the different composites. This region 2 reaction is very strong in both $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$, but is quite weak in $\text{Cu}_2\text{Sb-TiC}$. This leads to the conclusion that the presence of carbon black in the composite is likely the source of this reaction, which is somewhat supported by the observed exothermic peak for carbon black in Figure 6c. In addition, the electrolyte reaction peaks at $\sim 230 - 250\text{ }^{\circ}\text{C}$ are much more pronounced for $\text{Cu}_2\text{Sb-TiC}$, with its weak region 2 reaction, suggesting that the electrolyte is also involved in the exothermic

reaction observed in $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$. A high temperature region 3 is also identified in the $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ material due to its lack of a strong exothermic electrolyte peak at $\sim 250^\circ\text{C}$ as observed for milled Cu_2Sb and both of the other composites. The lack of a peak likely arises from a more completedelithiation of $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ that leads to consumption of most or all of the lithium from the electrode before the electrolyte reaction temperature is reached. A potentially advantageous observation can be made in Figure 7b at 100 % SOC where it appears that the inclusion of TiC contributes a small endothermic peak at $\sim 150^\circ\text{C}$. However, as the peak is rather weak and overlapped with other exothermic reactions, it is difficult to make a solid conclusion.

The calculated low-temperature heat generation values for these composite materials is also observable in Table 2 where it can be seen that all three composites show a reduced heat generation relative to the milled Cu_2Sb . This further supports the assertion of thermal stability improvements offered by the inclusion of reinforcing phases. In addition, all three materials have heat generation values only slightly above that of pure Cu_2Sb (0.48 J mAh^{-1}) from our previous study, suggesting that the incorporation of Cu_2Sb into a composite with the reinforcing phases tested here almost completely offsets the negative thermal stability impact of the milling process. Higher temperature heat generation analysis was also conducted on these samples near the region 2 reaction associated with carbon black inclusion. These values can also be seen in Table 2. In that region, the two samples without carbon black, Cu_2Sb and $\text{Cu}_2\text{Sb-TiC}$, have respective heat generation values of 2 and 45 J g^{-1} while the materials containing carbon black, $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$ and $\text{Cu}_2\text{Sb-TiC}@\text{C}$, have much higher heat generation values of, respectively, 129 and 114 J g^{-1} . The quantitative values here agree with the qualitative observations previously made that the peak is associated with carbon black content. This point is further confirmed in Figure S6

showing increased heat generation in the temperature range of 180 – 210 °C for Cu₂Sb-C composites with increasing carbon black content.

Because of its significant contribution to the heat generation of the composite electrodes in the 0 % SOC state, further investigation of the region 2 reaction is carried out by employing FTIR analysis on fully delithiated electrodes at temperatures just below (180 °C) and just above (230 °C) where the reaction occurs. Figure 8a shows the low-temperature FTIR spectra for Cu₂Sb-TiC@C. All of the composite materials showed nearly identical spectra at 180 °C, so this is treated as a representative spectra for all three materials. Observed in this spectra are primarily peaks associated with the EC:DEC electrolyte solvent (1800 cm⁻¹, 1768 cm⁻¹, 1472cm⁻¹, 1394 cm⁻¹, 971 cm⁻¹, 900 cm⁻¹, 773 cm⁻¹, and 727 cm⁻¹) and the PVDF binder material (1394 cm⁻¹, 1160 cm⁻¹, 1070 cm⁻¹, 971 cm⁻¹ and 880 cm⁻¹). Another key peak observed is the P-F bond from the LiPF₆ salt at 838 cm⁻¹. [11,38] Figure 8b shows the high-temperature spectra for Cu₂Sb-TiC@C where reaction 2 has occurred. This spectra was also nearly identical to that of Cu₂Sb-Al₂O₃@C, the other electrode material in which a strong region 2 reaction was observed, so is once again considered representative of both materials. In this spectra, a number of changes can be seen, the most notable of which is the disappearance of the P-F peak from the lithium salt at 838 cm⁻¹. In addition, the PVDF peak at 880 cm⁻¹ has disappeared and it appears that the broad PVDF peak at 1394 cm⁻¹ has also disappeared, with the narrow peaks from the electrolyte solvent still present in the same location. These two peaks are associated with the C-H₂ vibrations in the PVDF structure. [39,40] Also observed are sharpening and strengthening of peaks associated with EC:DEC at 1472 cm⁻¹, 1394 cm⁻¹, 971 cm⁻¹, 773 cm⁻¹, and 727 cm⁻¹ with additional peaks previously unobserved but still associated with the electrolyte becoming observable at 1740 cm⁻¹, 1550 cm⁻¹, and 1231 cm⁻¹.

While this analysis does not elucidate the full nature of what is occurring in region 2, it appears that the primary reaction is the low-temperature breakdown of the LiPF_6 salt facilitated by the addition of carbon black to the electrode in the delithiated condition. If a lithium ion is liberated from the LiPF_6 degradation, it could react with PVDF; however, the typical products of LiPF_6 decomposition are LiF and PF_5 gas. In addition, such reactions between lithium and PVDF don't usually occur until much higher temperatures and result in dehydrofluorination, which would cause a similar weakening or disappearance of the C-F peaks as well.[11,37,38] As such, the disappearance of the C-H₂ peaks from the PVDF spectra remains quite curious and a mechanism for it is not proposed here. The strengthening of the electrolyte peaks is believed to be a result of the removal of dissolved lithium salt from the solvent. Figure 8c shows the high temperature spectra for $\text{Cu}_2\text{Sb-TiC}$ in which the reaction in region 2 does not occur. As expected, there is no observable change from the low-temperature FTIR spectra because there is no reaction occurring in the range of 180 – 230 °C.

Conclusion

The thermal stabilities of $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, $\text{Cu}_2\text{Sb-TiC}$, and $\text{Cu}_2\text{Sb-TiC}@\text{C}$ composite anodes have been tested and compared to a baseline milled Cu_2Sb intermetallic material. The use of the milled Cu_2Sb baseline allows determination of the performance effects from both the additional phases present in the composites and the milling process used to synthesize them. In general, it is shown that milled nanocomposites of Cu_2Sb have a reduction in the stability of Li_3Sb lithiated phase relative to un-milled Cu_2Sb with significant delithiation occurring by 200 °C. However, comparison to pure milled Cu_2Sb reveals that this reduction in phase stability is associated entirely with the HEMM process and that the incorporation of reinforcing phases can actually lead to a slight improvement in the Li_3Sb stability. Heat generation profiles show that

the low-temperature SEI-layer reactions in all the tested samples are not significantly affected by either the milling process or the addition of reinforcing phases. This is a promising observation as the low-temperature range is the most critical for anode stability and it suggests that the steps needed to extend the cycle life of antimony and Cu_2Sb electrode materials will not lead to a worsening of their low-temperature safety performance. At higher temperatures in 100 % SOC electrodes, the primary differences arise from the milling process with an increase in heat generation arising from the lower lithiated phase stability, but once again minimal change is attributed to the reinforcing phases. However, an unusual exothermic peak is observed in 0 % SOC electrodes at relatively low temperatures of $\sim 200^\circ\text{C}$ that is determined to be caused by the addition of carbon black to the electrode and is associated with a reaction involving the breakdown of the electrolyte salt LiPF_6 at a lower temperature than usual. While this reaction is not fully understood, it suggests that efforts to improve the cycle life performance of alloy anodes should attempt to minimize the inclusion of carbon black as a composite phase in order to avoid this destabilization of the delithiated electrode material.

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References

- [1] D. Lisbona and T. Snee, *Process Saf. Environ. Prot.* 89 (2011) 434–442.
- [2] Y. Baba, *Solid State Ionics* 148 (2002) 311–316.
- [3] J. Yamaki, Y. Baba, N. Katayama, H. Takatsuji, M. Egashira, and S. Okada, *J. Power Sources* 119–121 (2003) 789–793.
- [4] J. Yamaki, H. Takatsuji, T. Kawamura, and M. Egashira, *Solid State Ionics* 148 (2002) 241–245.
- [5] U. von Sacken, E. Nodwell, A. Sundher, and J. R. Dahn, *J. Power Sources* 54 (1995) 240–245.
- [6] H. Yang, H. Bang, K. Amine, and J. Prakash, *J. Electrochem. Soc.* 152 (2005) A73.
- [7] O. Haik, S. Ganin, G. Gershinsky, E. Zinigrad, B. Markovsky, D. Aurbach, and I. Halalay, *J. Electrochem. Soc.* 158 (2011) A913.
- [8] T. Zheng, A. S. Gozdz, and G. G. Amatucci, *J. Electrochem. Soc.* 146 (1999) 4014.
- [9] A. M. Andersson and K. Edström, *J. Electrochem. Soc.* 148 (2001) A1100.
- [10] J. Jiang, H. Fortier, J. N. Reimers, and J. R. Dahn, *J. Electrochem. Soc.* 151 (2004) A609.
- [11] N.-S. Choi, I. A. Profatlova, S.-S. Kim, and E.-H. Song, *Thermochim. Acta* 480 (2008) 10–14.
- [12] H. Maleki, G. Deng, I. Kerzhner-Haller, A. Anani, and J. N. Howard, *J. Electrochem. Soc.* 147 (2000) 4470.
- [13] J. Jiang and J. R. Dahn, *Electrochim. Acta* 49 (2004) 4599–4604.
- [14] Z. Chen, Y. Qin, Y. Ren, W. Lu, C. Orendorff, E. P. Roth, and K. Amine, *Energy Environ. Sci.* 4 (2011) 4023.
- [15] H. F. Xiang, H. Wang, C. H. Chen, X. W. Ge, S. Guo, J. H. Sun, and W. Q. Hu, *J. Power Sources* 191 (2009) 575–581.
- [16] J. Cho, H. Jung, Y. Park, G. Kim, and H. S. Lim, *J. Electrochem. Soc.* 147 (2000) 15.
- [17] E. Allcorn and A. Manthiram, *J. Electrochem. Soc.* (submitted April 2015).
- [18] W.-J. Zhang, *J. Power Sources* 196 (2011) 13–24.

- [19] W.-J. Zhang, *J. Power Sources* 196 (2011) 877–885.
- [20] L. M. L. Fransson, J. T. Vaughey, R. Benedek, K. Edström, J. O. Thomas, and M. M. Thackeray, *Electrochem. commun.* 3 (2001) 317–323.
- [21] D. Applestone, S. Yoon, and A. Manthiram, *J. Mater. Chem.* 22 (2012) 3242.
- [22] E. Allcorn and A. Manthiram, *ACS Appl. Mater. Interfaces* 6 (2014) 10886–10891.
- [23] E. Allcorn and A. Manthiram, *J. Phys. Chem. C* 118 (2014) 811–822.
- [24] E. Allcorn and A. Manthiram, *J. Mater. Chem. A* 3 (2015) 3891–3900.
- [25] S. Yoon and A. Manthiram, *Chem. Mater.* 21 (2009) 3898–3904.
- [26] C.-M. Park and H.-J. Sohn, *J. Electrochem. Soc.* 157 (2010) A46.
- [27] C.-M. Park and H.-J. Sohn, *Electrochim. Acta* 55 (2010) 4987–4994.
- [28] M. Morcrette, D. Larcher, J. M. Tarascon, K. Edström, J. T. Vaughey, and M. M. Thackeray, *Electrochim. Acta* 52 (2007) 5339–5345.
- [29] J. Jiang and J. R. Dahn, *J. Electrochem. Soc.* 153 (2006) A310.
- [30] E. Gaffet, F. Bernard, J.-C. Niepce, F. Charlot, C. Gras, G. Le Caër, J.-L. Guichard, P. Delcroix, A. Mocellin, and O. Tillement, *J. Mater. Chem.* 9 (1999) 305–314.
- [31] D. L. Zhang, *Prog. Mater. Sci.* 49 (2004) 537–560.
- [32] J. Hassoun, G. Derrien, S. Panero, and B. Scrosati, *Electrochim. Acta* 54 (2009) 4441–4444.
- [33] S. Yoon and A. Manthiram, *J. Mater. Chem.* 20 (2010) 236.
- [34] Y. S. Park and S. M. Lee, *Bull. Korean Chem. Soc.* 32 (2011) 145–148.
- [35] M. N. Richard and J. R. Dahn, *J. Electrochem. Soc.* 146 (1999) 2078.
- [36] A. Du Pasquier, *J. Electrochem. Soc.* 145 (1998) 472.
- [37] J. S. Gnanaraj, E. Zinigrad, L. Asraf, H. E. Gottlieb, M. Sprecher, M. Schmidt, W. Geissler, and D. Aurbach, *J. Electrochem. Soc.* 150 (2003) A1533.
- [38] I. A. Profatilova, T. Langer, J. P. Badillo, A. Schmitz, H. Orthner, H. Wiggers, S. Passerini, and M. Winter, *J. Electrochem. Soc.* 159 (2012) A657.

- [39] N. Durand, B. Ameduri, K. Takashima, K. Ishida, S. Horie, and Y. Ueda, Polym. J. 43 (2010) 171–179.
- [40] T. Wentink, L. J. Willwerth, and J. P. Phaneuf, J. Polym. Sci. 55 (1961) 551–562.

Tables

Table 1. Description and measured properties of the anode electrode powders

Electrode Material	Component Ratio	Milling Time (h)	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	Tap Density (g cm^{-3})	Reversible Capacity (mAh g^{-1})	Cycle Time (h)
Cu_2Sb	100	6	5.21	3.67	255	2.4
$\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$	66 : 14 : 20	24	3.36	1.40	405	4.2
$\text{Cu}_2\text{Sb}-\text{TiC}$	70 : 30	40	1.02	3.25	291	2.9
$\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$	55 : 30 : 15	40	8.00	1.25	295	2.1

Table 2. Thermal generation values for tested anode materials.

	Heat Generation at < 150 °C, 100 % SOC		Heat Generation at 180 – 210 °C, 0 % SOC
	J g^{-1}	J mAh^{-1}	J g^{-1}
Cu_2Sb	184	0.72	2
$\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3@\text{C}$	220	0.54	129
$\text{Cu}_2\text{Sb}-\text{TiC}$	165	0.57	45
$\text{Cu}_2\text{Sb}-\text{TiC}@\text{C}$	148	0.50	114

Figure Captions

Figure 1. Comparison of the cycle life of pure antimony and the Cu_2Sb intermetallic composites under investigation.

Figure 2. XRD patterns of as-synthesized powders: (a) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (b) $\text{Cu}_2\text{Sb-TiC}$, and (c) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ as well as SEM images for the same materials: (d) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (e) $\text{Cu}_2\text{Sb-TiC}$, and (f) $\text{Cu}_2\text{Sb-TiC}@\text{C}$.

Figure 3. *Ex situ* XRD patterns for lithiated electrodes: (a) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (b) $\text{Cu}_2\text{Sb-TiC}$, and (c) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ with peak markers.

Figure 4. *Ex situ* XRD patterns of lithiated electrodes: (a) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (b) $\text{Cu}_2\text{Sb-TiC}$, and (c) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ after heating to 200 °C and 300 °C.

Figure 5. DSC curves of milled Cu_2Sb electrodes in OCV condition, at 0 % SOC after 2 conditioning cycles, and at 100 % SOC after 2 conditioning cycles.

Figure 6. Baseline DSC of OCV composite phases: (a) Al_2O_3 , (b) TiC , and (c) acetylene black carbon.

Figure 7. DSC curves of the composite electrodes: (a) $\text{Cu}_2\text{Sb-Al}_2\text{O}_3@\text{C}$, (b) $\text{Cu}_2\text{Sb-TiC}$, and (c) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ electrodes in OCV condition, at 0 % SOC after 2 conditioning cycles, and at 100 % SOC after 2 conditioning cycles.

Figure 8. FTIR absorbance spectra for (a) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ electrode after heating to 180 °C at 0 % SOC, (b) $\text{Cu}_2\text{Sb-TiC}@\text{C}$ after heating to 230 °C at 0 % SOC, and (c) $\text{Cu}_2\text{Sb-TiC}$ after heating to 230 °C at 0 % SOC. All electrodes were heated in the presence of 1 M LiPF_6 in EC/DEC electrolyte.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8