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Cu$_2$Sb Thin Film Electrodes Prepared by

Pulsed Laser Deposition for Lithium Batteries

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Abstract

Thin films of Cu_2Sb, prepared on stainless steel and copper substrates with a pulsed laser deposition technique at room temperature, have been evaluated as electrodes in lithium cells. The electrodes operate by a lithium insertion/copper extrusion reaction mechanism, the reversibility of which is superior when copper substrates are used, particularly when electrochemical cycling is restricted to the voltage range 0.65-1.4 V vs. Li/Li^+. The superior performance of Cu_2Sb films on copper is attributed to the more active participation of the extruded copper in the functioning of the electrode. The continual and extensive extrusion of copper on cycling the cells leads to the isolation of Li_3Sb particles and a consequent formation of Sb. Improved cycling stability of both types of electrodes was obtained when cells were cycled between 0.65 and 1.4 V. A low-capacity lithium-ion cell with Cu_2Sb and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ electrodes, laminated from powders, shows excellent cycling stability over the voltage range 3.15 - 2.2 V, the potential difference corresponding to approximately 0.65-1.4 V for the Cu_2Sb electrode vs. Li/Li^+. Chemical self-discharge of lithiated Cu_2Sb electrodes by reaction with the electrolyte was severe when cells were allowed to relax on open circuit after reaching a lower voltage limit of 0.1 V. The solid electrolyte interphase (SEI) layer formed on Cu_2Sb electrodes after cells had been cycled between 1.4 and 0.65 V vs. Li/Li^+ was characterized by Fourier-transform infrared spectroscopy; the SEI layer contributes to the large irreversible capacity loss on the initial cycle of these cells. The data contribute to a better understanding of the electrochemical behavior of intermetallic electrodes in rechargeable lithium batteries.

Introduction

Sb-containing intermetallic compounds such as InSb,[1-4] Cu_2Sb,[5] SnSb,[6-8] MnSb,[9] $CoSb_3$,[10] $CrSb_2$[11] and Zn_4Sb_3[12] have recently been suggested as alternative negative electrodes to graphite in rechargeable lithium batteries. Two advantages of intermetallic electrodes are 1) their ability to operate several hundred millivolts above metallic lithium, which may improve cell safety, and 2) their high volumetric capacity, which is significantly larger than that of graphite (820 mAh/cm^3). For example, the theoretical volumetric capacity of tetragonal Cu_2Sb (*P4/nmm*)[13,14] is 2749 mAh/cm^3 based on its high crystallographic density of 8.51 g/cm^3. Unlike other intermetallic electrodes, such as InSb and SnSb, in which both metal components are electrochemically active, only the Sb atoms in Cu_2Sb have an affinity for lithium. The reaction between pure Sb metal and lithium to form Li_3Sb[15,16] produces a large specific capacity and is accompanied by a significant volume change of 137% that can cause electrochemical-mechanical disintegration of particles during cycling.[4,5] Such large volumetric changes can be suppressed in binary intermetallic compounds on reaction with lithium; these systems tend to show improved reversibility during cycling when structural relationships between parent and lithiated compounds are maintained.[17] For example, it has been reported that lithium insertion into Cu_2Sb is accompanied by the extrusion of 50% of the Cu atoms, which induces a transformation to a cubic intermediate Li_2CuSb structure (*F-43m*)[18] with a [CuSb] zinc-blende framework.[5] This reaction is followed by the formation of cubic Li_3Sb (*Fm3m*),[19] *via* $Li_{2+x}Cu_{1-x}Sb$, on complete extrusion of Cu at *x*=1. During the lithium insertion/copper extrusion process, the Sb atoms maintain their face-centered-cubic spatial arrangement.

The extruded metallic Cu, which shows no significant reactivity with lithium, can be reincorporated into the Sb array during the reverse reaction. In particular, it has been shown that a powdered Cu_2Sb electrode with a copper foil current collector has shown stable cycling behavior (25 cycles) over the full voltage range 0.0-1.2 V [5]; it delivers 290 mAh/g, which is close to the theoretical capacity of Cu_2Sb (323 mAh/g). (These calculations, however, ignored a possible small contribution to the capacity from the powdered acetylene black current collector that had been added to the Cu_2Sb electrode.) Longer term cycling of Li/Cu_2Sb cells tends to lead to an irreversible capacity loss. However, by analogy to the $Li_xCu_6Sn_5$ system,[20] it is anticipated that the irreversible behavior of Cu_2Sb electrodes would be inhibited, or at least restricted, if the voltage window was limited to the topotactic $Cu_2Sb \rightarrow Li_2CuSb$ reaction. Less ambiguous information about the capacity of electronically-conducting electrode materials, such as intermetallic systems, can be obtained if they are in thin film form because conductive additives and binders, which are necessary for powder-based electrodes, are not required.[21-24] Furthermore, nanometer-scale electrode materials that can be homogeneously deposited are of particular interest because they can be more tolerant to structural-mechanical changes during electrochemical cycling.[24-26] Lastly, a smooth thin film electrode lends itself particularly well to interfacial studies of surface reactions.

In this work, nanometer-scale thin films of Cu_2Sb, prepared on stainless steel (SS) and copper substrates by pulsed laser deposition (PLD), have been used as a model system to study the electrochemical properties and reaction mechanisms of intermetallic electrodes in the absence of carbon and binder materials. Various voltage windows for cycling have

been used to determine reversible cycling regions. For comparison, the electrochemical behavior of powder Cu_2Sb electrodes in a $Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ lithium-ion configuration is reported.

Experimental

The Cu_2Sb films were prepared on 6 mm diameter (3 mm thick) SS disks and Cu foil (25 μm thick) substrates with PLD at room temperature with 10 minutes deposition in 10 mtorr of Ar. Deposition was accomplished using a XeCl eximer laser with an energy density of 3-4 mJ/cm^2 at 10 Hz impinging on a target pressed from ball-milled Cu_2Sb powder. The distance between the target and the substrates was approximately 5 cm. The SS substrates were mounted on a Si wafer, partially masking the Si during PLD. The film on the Si was used for film thickness evaluation, whereas the films on SS were reserved for electrochemical measurements. Cu_2Sb films were deposited on Cu substrates without using a Si wafer; in this case, the film thickness was estimated from deposition parameters. The as-prepared films appeared shiny and light blue in color.

The thickness of a Cu_2Sb film (SS substrate) was evaluated by tilting a partly broken piece of film-coated wafer in a field emission scanning electron microscope (JEOL 6340 FESEM) to see the cross-section. The crystal structure of the film was identified by X-ray diffraction using a Siemens D5000 diffractometer with Ni filtered Cu Kα radiation at 40 kV and 30 mA, and a scan rate of 1.5° / min from 20 to 60° 2θ with 0.05° steps.

An electrochemical cell containing a Cu_2Sb/SS electrode was assembled by embedding the 3 mm-thick disk into the end of a Kel-F rod that was inserted into a

polypropylene cell fitted with Li reference electrode (RE) and counter electrode (CE) foils and filled with about 5 ml of 1M $LiPF_6$/EC+DEC (1:1) electrolyte (EM Industries). Cell assembly and electrochemical characterization were carried out in a helium-filled glove box. The films on stainless steel and Cu substrates, henceforth denoted as Cu_2Sb/SS and Cu_2Sb/Cu, respectively, were cycled at a constant current of 35 $\mu A/cm^2$ between 0.0 or 0.1 V and 1.2 V vs. Li/Li$^+$, using an Arbin Battery Cycler (College Station, TX). Films were also cycled between 0.1-0.7 V and 0.65-1.4 V for voltage window experiments. Cyclic voltammetry (CV) was carried on Cu_2Sb/SS electrodes between 0.65 and 1.4 V to determine a diffusion coefficient for the electrochemical reaction; sweep rates from 0.1 to 50 mV/s were controlled by an EG&G 273 Potentiostat.

For comparison, the electrochemical behavior of Cu_2Sb powder electrode was monitored in a Cu_2Sb/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ lithium-ion cell. The anode consisted of 70% Cu_2Sb ball-milled powder,[5] 20% carbon (10% SFG-6 graphite and 10% acetylene black) and 10% PVDF binder on Cu foil. The particle size of the Cu_2Sb powder, as determined by scanning electron microscopy (SEM), was typically in the range 10-20 μm. The electrodes were cycled in Swagelok® cells with a Li RE, a Celgard 2300 separator and a 1M $LiPF_6$/EC+DEC (1:1) electrolyte (EM Industries). The cells were cycled between voltage limits of 4.0-2.4 V and 3.28-2.2 V, which corresponded to the voltage limits of approximately 0.1-1.2 V and 0.65-1.4 V, respectively, for the Cu_2Sb electrode vs. the Li RE. A current density of 50 $\mu A/cm^2$ was used to measure the initial cycling behavior of the cells; this procedure was followed by constant current cycling at various C-rates from C/20 to C/2.

The surface images of Cu_2Sb/SS films before and after electrochemistry were obtained using an atomic force microscope (AFM, Picoscan by Molecular Imaging) attached to N_2-filled glove box, operating in contact mode with Si_3N_4 cantilever (cantilever force constant = 0.05 N/m). A Cu_2Sb/SS film cycled between 0.1-1.2 V was removed from the cell, thoroughly washed with dimethyl carbonate (DMC, EM Science) and dried in the glove box at room temperature. The surface chemistry of a Cu_2Sb/SS electrode, cycled between 0.65-1.4 V, was examined by *ex-situ* FTIR spectroscopy, using a Nicolet Nexus 870 Spectrometer, equipped with a broadband Mercury-Cadmium-Telluride (MCT) detector. The FTIR spectrum was acquired in the Attenuated Total Reflection (ATR) mode using a hemispherical Ge optic with spectral resolution of 4 cm^{-1} with a total of 1024 scans co-added. The penetration depth of the (mid-)infrared light (2000 cm^{-1}) into a medium with n = 1.5 (an optical constant typical for organic compounds) is approximately 400 nm.

Results and Discussion

Film Characterization

The FESEM cross-section image of a Cu_2Sb/SS film, shown in Fig. 1(a), revealed a film thickness of 26 nm. The X-ray diffraction pattern of the Cu_2Sb film showed several of the major reflections of the tetragonal Cu_2Sb structure, some of which overlapped with peaks from the stainless steel substrate (Fig. 2). No detectable Sb metal was observed in this X-ray diffraction pattern. The thickness of the Cu_2Sb/Cu film, as estimated from deposition parameters, was approximately 300 nm thick. In a surface SEM image, shown

in Fig. 1(b), the Cu_2Sb/Cu film appeared to be more crystalline than the Cu_2Sb/SS film, the individual crystallites having an average size of approximately 0.25μm.   It was not possible to obtain an acceptable XRD pattern of the Cu_2Sb/Cu electrode because of difficulties in placing a sufficiently flat Cu_2Sb/Cu film in the X-ray diffractometer.

Cu₂Sb/SS Films

The initial galvanostatic charge-discharge voltage profiles of lithium half-cells with Cu_2Sb/SS thin film electrodes, cycled over a wide voltage range (0.1-1.2 V) and over a limited range (0.65-1.4 V), are shown in Figs. 3(a) and 3(b), respectively.   We define *charge* as the cathodic addition of Li to Cu_2Sb because Cu_2Sb is being considered as the negative electrode (anode) for full lithium-ion cells, such as the $Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cell described later in this paper.   The integrated *discharge* (anodic) capacities of the $Li/Cu_2Sb/SS$ cells are shown in Fig. 3(c).   These values represent minimum capacities because the weight of Cu_2Sb in the film was estimated from the film thickness and crystallographic density.   The data clearly show the superior cycling stability of the Cu_2Sb electrode over the limited voltage window (0.65-1.4 V).   The individual reaction processes in the potential profiles are more clearly distinguished from one another in differential capacity plots (Fig. 4(a) and (b)), which also demonstrates the complex nature of the electrochemical reactions.   In Fig. 4(a) (0.1-1.2 V), the initial cathodic curve shows a small peak at 1.85 V that has been attributed to the reduction of the surface impurities such as oxides.[5]   The peak at approximately 1.5 V coincides with the calculated reduction potential of the EC electrolyte component used in this study (1.46 V).[27]   The

doublet peak near 0.8 V is attributed, in part, to reduction of the DMC electrolyte component (the calculated reduction potential is 0.86V [27]), which forms a SEI layer on the lithiated Cu_2Sb particles and, in part, to lithium insertion into Cu_2Sb, which generates the intermediate lithiated zinc-blende-type phase, Li_2CuSb. This process is followed by a peak at ~0.6 V that is attributed to the simultaneous insertion of lithium into, and Cu extrusion from, Li_2CuSb to yield a solid solution, $Li_{2+x}Cu_{1-x}Sb$ with the end member Li_3Sb on complete reaction with lithium (x=1). During the reverse process, two major anodic peaks are observed, one close to 1.0 V and the second near 1.1 V. On subsequent anodic reactions, the peak at 1.0 V shifts to more anodic potentials, implying that that the composition of the Cu_2Sb electrode changes during each cycle, which is consistent with a decreasing amount of copper that is reincorporated into the Sb array on consecutive cycles; the peak at 1.1 V is attributed to the formation of metallic Sb directly from Li_3Sb particles that become disconnected from the extruded Cu particles during the electrochemical reaction. During subsequent cathodic reactions, two major reduction processes occur, one at 0.93 V and the second at 0.5 V (Fig. 3(a) and Fig. 4(a)). The reduction process at 0.93 V is attributed to a Sb $\rightarrow$ Li_3Sb transition, whereas the low voltage reaction at ~0.5 V to the formation of Li_3Sb from a Li-Cu-Sb phase resembling Li_2CuSb. Note that the reduction processes that occur at ~0.8 V on the initial electrochemical reaction of lithium with the Cu_2Sb electrode are no longer strongly visible in the differential capacity plot in Fig. 4(a). This behavior suggests that after the initial "break-in" cycle, the Cu_2Sb electrode is comprised essentially of two components: 1) Sb and 2) a Li-Cu-Sb phase that operates by a reversible lithium insertion/copper extrusion reaction mechanism. The composition

of the Li-Cu-Sb electrode varies according to the extent to which copper is reincorporated into the structure during cycling. There is considerable hysteresis associated with the electrochemical reaction (Fig. 3(a)), which is consistent with data reported previously for powder Cu_2Sb electrodes.[5] The possibility that the Sb phase generated electrochemically from Li_3Sb contains a small amount of some residual lithium (or copper) cannot be discounted.

When cycled over a limited potential range (1.4-0.65 V vs. Li/Li^+), the Cu_2Sb/SS electrode shows the same initial cathodic reaction at ~0.8 V (Fig. 4(b)) and the shift of anodic and cathodic peaks that were observed during electrochemical cycling over the wide voltage range (Fig. 4(a)). Fig. 3(c) shows that when cells are cycled over the limited voltage range, the Cu_2Sb/SS electrode operates with superior electrochemical stability, delivering a capacity between 300 and 200 mAh/g for 50 cycles. The steady loss in capacity on cycling is attributed to the continuing loss of contact of the extruded copper particles with the parent intermetallic structure. Note, however, that a capacity of 300 mAh/g exceeds the theoretical value for an ideal $Cu_2Sb \rightarrow Li_2CuSb$ reaction (215 mAh/g) that is expected to occur between 1.4 and 0.65 V. This observation is consistent with the formation of Sb, which is apparent from the onset of a cathodic process at 0.93 V in both the voltage profile (Fig. 3(b)) and the differential capacity plot (Fig. 4(b)), on the second cycle. The presence of Sb increases the expected capacity of the electrode because the Sb $\rightarrow Li_3Sb$ reaction delivers all its capacity above 0.65 V in a lithium half-cell.

By contrast, the Cu_2Sb/SS electrode capacity in cells that were cycled between 1.2 and 0.1 V fell below 100 mAh/g after ten cycles (Fig. 3(c)). One Cu_2Sb/SS electrode was

cycled over a low potential range (0.1-0.7 V) to monitor the effect of restricting the electrochemical reaction to the $Li_2CuSb \rightarrow Li_3Sb$ transition; in this case, the electrode delivered a relatively low initial capacity (275 mAh/g) that declined steadily to ~50 mAh/g after 50 cycles.   These "voltage-window" experiments highlight the increased irreversibility of the electrochemical reactions when large amounts of copper are extruded from the electrode structure.

Cu_2Sb/Cu Films

The voltage profiles of lithium cells with Cu_2Sb/Cu electrodes, cycled over two voltage ranges (0.0-1.2 V and 0.65-1.4 V) are shown in Fig. 5. Differential capacity plots of these profiles are shown in Fig. 6(a) and 6(b), whereas capacity vs. cycle number plots of the cells are provided in Fig. 7(a) and 7(b), respectively. The differential capacity plot of the films cycled over both voltage ranges show an initial cathodic process at 0.97 V (which was not observed during the initial reaction of cells with Cu_2Sb/SS electrodes) that corresponds to the very short plateau in the voltage profile (arrowed in Fig. 5(a)); it is attributed to the lithiation of a small amount of Sb that was deposited on the Cu substrate during the PLD process. The voltage of this reaction coincides with the first reduction process that occurs at ~0.93 V during the second cycle of $Li/Cu_2Sb/SS$ cells (Fig. 4), thereby providing support for the hypothesis that Sb is generated during the cycling of Cu_2Sb/SS electrodes, when Li_3Sb becomes isolated from extruded copper in extensively lithiated electrodes. Two weak peaks at approximately 0.86 and 0.80 V, corresponding to the reduction of DMC [27] and the formation of a Li_2CuSb-type structure are visible in Fig.

6(a); however, the prominent reduction process involving lithium insertion and copper extrusion from the Cu_2Sb/Cu electrode occurs at 0.64 V. Although the electrochemical reconstruction of the Li_2CuSb-, Cu_2Sb- and Sb-type phases are distinct during the initial anodic reaction, the resolution of these peaks diminished on cycling and disappeared by the 25th cycle. By contrast, greater structural resolution was maintained when Cu_2Sb/Cu electrodes were cycled between 1.4 and 0.65 V (Fig. 6(b)). Anodic peaks corresponding to the formation of Li_2CuSb-, Cu_2Sb- and Sb-type phases could still be detected after 25 cycles, indicating that greater structural order and reversibility was maintained when lithium insertion into, and copper extrusion from, the parent electrode was restricted to an end composition close to Li_2CuSb. Note that after prolonged cycling (90 cycles) of both Cu_2Sb/SS and Cu_2Sb/Cu electrodes between 1.4 and 0.65 V, the electrochemical reaction appears to be associated predominantly with a Sb $\rightarrow$ Li_3Sb-type transition as reflected by the major reduction peak at approximately 0.97 V in Figs 4(b) and 6(b), respectively.

A comparison of the capacity vs. cycle number plots for the Cu_2Sb/Cu electrodes (Fig. 7) with the Cu_2Sb/SS electrodes (Fig. 3(c)) strongly suggests that a copper substrate, aided by the extruded copper particles from the Cu_2Sb electrode provides superior current collection when the electrode operates over the wide voltage window (1.2-0 V). It appears that the enhanced reversibility of the Cu_2Sb $\rightarrow$ Li_2CuSb reaction when Cu_2Sb/Cu electrodes are cycled over the narrower 1.4-0.65 V range has the effect of restricting the amount of electrochemically-formed Sb. Consequently, the delivered capacity of Cu_2Sb/Cu electrodes is smaller over this voltage range in comparison to Cu_2Sb/SS electrodes.

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Although further work is required to optimize the electrochemical performance of thin-film Cu_2Sb electrodes, our data seem to suggest that a Cu substrate promotes the reversibility of the $Cu_2Sb \rightarrow Li_2CuSb \rightarrow Li_3Sb$ reaction more than a SS substrate does. However, in both cases, the reversibility of the reaction is compromised when extensive copper extrusion takes place. In this respect, rapid capacity fade can be expected as a result of the loss of both particle contact and matrix conductivity. The superior reversibility of Cu_2Sb/Cu film electrodes during the early cycles is tentatively attributed to a more homogenous dispersion of nano-sized Cu particles when they are extruded from the Cu_2Sb electrode and deposited onto the Cu substrate in close proximity to the Li_3Sb grains. It is proposed that in such an instance, the extruded Cu particles participate more actively in the functioning of the electrode and, in particular, provide superior electronic conductivity and connectivity to the electrode matrix. This active participation of extruded Cu has already been demonstrated for Cu_6Sn_5/Cu films.[28]

Film Morphology Change Before and After Cycling

The morphology of the Cu_2Sb/SS film and the changes in morphology on cycling between 0.1 and 1.2 V were studied with AFM. The surface image before cycling, as shown in Fig. 8(a), indicates that the film was typically a few hundred Angstroms thick, had a smooth surface (10.7 Å roughness), and covered the relatively rough surface of the stainless steel substrate (76 Å roughness). Statistical analysis of the film surface revealed a peak-to valley distance of a few hundred Angstroms, from which a root mean square (rms) roughness of the films has been determined. However, the surface morphology of the film

changed dramatically with cycling, with the rms roughness increasing by a factor of about 8 (85 Å). Aggregation of individual grains was apparent after cycling (Fig. 8(b)), consistent with a report that the electrochemical reaction of lithium with nano-sized intermetallic particles leads to aggregation rather than pulverization.[25] It is believed that this aggregation occurs as a consequence of Cu extrusion from the Cu_2Sb and lithiated compounds such as Li_2CuSb, leading to electrochemical sintering of the Cu particles and the isolation of Li_3Sb particles. Such processes are believed to contribute to the observed degradation of the structural integrity of the thin-film and the capacity fade of the electrode during cell cycling.

Side Reactions

Most metal alloys that have been proposed as alternative anodes for Li-ion cells show an unacceptably high irreversible capacity loss on the first cycle of the cells. This capacity loss is predominantly due to the reduction of electrolyte solvents on the surface of the electrode that forms the so-called solid electrolyte interface (SEI) layer. The ability of this layer to passivate the surface of the electrode from further solvent reduction and to conduct Li ions is critical to the operation of any low potential, carbon-based or intermetallic electrode. The formation of an SEI layer on a Cu_2Sb/SS electrode was monitored by charging a Li-Cu_2Sb/SS cell to 0.1 V at a constant current density of 35 $\mu A/cm^2$ and, thereafter, allowing the cell to relax on open circuit for 18 hours (Fig. 9). The rise in electrochemical potential of the cell is, in part, a function of the chemical self discharge with the electrolyte that creates the SEI layer.

The FTIR spectrum of the SEI layer formed on a Cu_2Sb/SS electrode that had been cycled between 0.65-1.4 V is displayed in Fig. 10. The residual electrolyte components were removed from the film by washing thoroughly in DMC prior to collecting the FTIR spectrum. The absence of peaks at 1804 and 1769 cm^{-1}, characteristic of the carbonyl group from ethylene carbonate (EC) confirmed the removal of this electrolyte solvent from the sample. Although it is extremely difficult to make an unequivocal interpretation of the infra-red data, it was possible to make some tentative assignments to the vibrational modes in Fig. 10.

1. Four peaks at 2955, 2926, 2854 and 2874 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of methyl (CH_3) and methylene (CH_2) groups, respectively, indicating the presence of a $-CH_2CH_3$ group.[29,30] The presence of additional peaks near 1465 and 1460 cm^{-1}, and peaks at 1388 and 1375 cm^{-1}, due to the asymmetric and symmetric deformation modes of methylene and methyl groups, respectively, confirmed this assignment.

2. The most prominent peak at 1728 cm^{-1} was attributed to the $\nu(C=O)_s$ mode of an -COO- ester group.[29,30] The appearance of three equal intensity bands at 1728 cm^{-1} ($\nu(C=O)_s$), 1194 cm^{-1} ($\nu(COO)_{as}$) and 1148 cm^{-1} ($\nu(OCC)_{as}$ involving ester oxygen and carbon in an alkyl chain) indicates the presence of a saturated ester -COOR group (R denotes alkyl chain). We were unable to determine unequivocally whether the ester group was associated with a pure ester or an ester-containing species. However, because pure esters are generally soluble in DMC, we conclude

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that the signature of the ester group is more likely to be a result of an ester-containing species.

3. The relatively broad feature at 1600-1650 cm^{-1} is characteristic of the carboxylate group, $-CO_2^-$. Lithium oxalate ($Li_2(O_2C)_2$) and lithium succinate ($Li_2(O_2CCH_2)_2$), which have been found to be components of the SEI layer on graphite anode,[31] show this $–CO_2^-$ band at 1675 and 1555cm^{-1}, respectively, together with other fingerprints in the lower frequency region.[29-31] Because the characteristic peaks of lithium oxalate and lithium succinate were absent in the FTIR spectrum of our cycled film, we attribute the vibrational modes at 1600-1650 cm^{-1} to a carboxylate-metal salt on the surface of the film. Peaks in the 1000-1270 cm^{-1} region of the FTIR spectrum, which could be attributed to the stretching modes of C-O, C-C-O and C-O-O functional groups of esters and carboxylates, support our assignments of these species to the SEI layer.

4. Vibrational modes at 860 and at 1062 cm^{-1}, characteristic of a C-O ether group[31] were assigned to $LiOCH_3$.

5. A common component of the SEI layer on lithiated graphite electrodes is Li_2CO_3; it has three characteristic peaks at 1510, 1430 and 870 cm^{-1} corresponding to the asymmetric and symmetric stretching modes of C=O and the bending mode of CO_3^{2-}, respectively.[29-31] These features are observed in Fig. 10. However, the peaks are of low intensity and, therefore, reflect a low concentration of Li_2CO_3 in the SEI layer.

6. The relatively small and broad peak at 840-900cm^{-1} is attributed to a combination of several overlapping peaks from v(P-F), δ(CO$_3^{2-}$) from Li$_2$CO$_3$, and O-C-C groups.[29-31]

7. In summary, the spectrum in Fig. 10 suggests that the surface SEI layer on a Cu$_2$Sb/SS electrode is composed of predominant amounts of CH$_3$(CH$_2$)$_n$CO$_2$M-type compounds (M=Cu/Sb/Li), -COOR ester-containing species and PF-containing salts, and minor amounts of LiOCH$_3$ and Li$_2$CO$_3$. This preliminary FTIR study, therefore, provides evidence that the composition of the SEI layer on lithiated intermetallic electrodes may be considerably different to those that form on lithiated graphite electrodes.[31]

Cyclic Voltammetry of Cu$_2$Sb/SS Films

Cyclic voltammetry was used to examine the kinetics of the electrochemical processes in Cu$_2$Sb/SS electrodes. Cyclic voltammograms were recorded over the potential range 0.65-1.4 V vs. Li/Li$^+$ with sweep rates (v) that varied from 0.1 to 50 mV/s. These data are provided collectively in Fig. 11a in which the vertical axis is represented by pseudo capacitance (i/v) rather than current (i), for clarity.

At the lowest scan rate (0.1 mV/s), it was assumed that the initial charge (cathodic) reaction between 1.4 and 0.65 V was associated with the formation of a Li$_2$CuSb-type product at the surface of the electrode and that on the subsequent discharge (anodic) reaction, 2 Li were removed from this product to yield a two-phase electrode consisting of Cu$_2$Sb and Sb. The observation of two peaks during the anodic scan at the low rate is

consistent with this assumption (Fig. 11(a)). These peaks become more diffuse or merge into a single peak at higher sweep rates, when the reaction is dictated more by surface processes rather than a combination of surface and bulk processes.[21,22,24,32-36]

Fig. 11(b) and 11(c) show the variation of the primary anodic peak current with sweep rate. The height (I_p) of the anodic peaks shows a linear dependence on sweep rate at $v < 5mV$ (Fig. 11(b)). This is attributed to a finite-length, diffusion-controlled process and is typical of the equilibrium behavior of an intercalation electrode. This changes to a square-root dependence at higher sweep rate (Fig. 11(c)), characteristic of a semi-infinite diffusion process. We calculated a chemical diffusion coefficient from the slope of peak height (I_p) vs $v^{1/2}$,[24,35,36] assuming that the anodic peak current corresponds to the removal of two Li^+ ions from Li_2CuSb, as described earlier. For this calculation, the theoretical density of Li_2CuSb (5.16 g/cm^3)[5,18] was used to obtain the molar volume. The calculated diffusivity of 7.1×10^{-13} cm^2/s is little higher than that determined for Mg_2Si thin film electrodes, 10^{-14} cm^2/s,[24] and is approximately the same order of magnitude as the diffusivity for a LiBi thin layer electrode obtained from ac impedance measurements.[37] Since the diffusivity of the electrolyte solution is about 10^{-6} cm^2/s, we propose that solid-state diffusion is the dominant rate-limiting parameter in thin-film Cu_2Sb electrodes.

$Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Li-ion Cell

In an attempt to gain more insight into the practicality of using Cu_2Sb as the anode in a lithium-ion cell configuration, a Cu_2Sb (powder) laminated electrode was evaluated against a $1cm^2$ $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode and a Li RE. In the

$Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ full-cell, the source of Li is provided entirely by the cathode. Matching the capacities of the two electrodes is critical to the final performance of the cell,[38] particularly when there is a large, first cycle inefficiency, which is common to many intermetallic electrode systems. Assuming an irreversible capacity loss of 34% on the first cycle, the reversible anode and cathode capacities were chosen to be 1 mAh/cm^2 and 0.84 mAh/cm^2, respectively, which corresponded to a capacity ratio of 1.2:1.

Two identical cells were assembled and cycled over different voltage windows at various rates from C/20 (0.05 mA/cm^2) to C/2 (0.5 mA/cm^2). The first cell was cycled between 4.0 and 2.4 V (Fig. 12(a)), which corresponded to the range 0.1-1.2 V for the Cu_2Sb electrode vs. Li/Li^+. The full cell showed the expected large irreversible capacity loss on the first cycle; the cell continued to lose capacity steadily on further cycling, even at the lower current rates (Fig. 12(b)). The shape of the voltage profile is dominated, as expected, by the Cu_2Sb electrode because the voltage profile for lithium intercalation-deintercalation in the single phase $Li_{1-z}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ electrode (against a metallic lithium reference electrode) is gently sloping with no strong features.[39] For example, the first slow discharge of the full cell at a C/20 rate shows two distinct voltage steps between 2.9 and 2.7 V that correspond to the two processes between 0.9 and 1.1 V for the reference Li/Cu_2Sb cell (Fig. 12(a)).

A second cell was cycled 100 times in the voltage window 3.45-2.2 V (Fig. 13(a) and 13(b)); this range corresponds to 0.65-1.4 V for the Li/Cu_2Sb reference cell. In this case, significantly superior cycling stability was obtained after the initial charge/discharge reaction. At a low current rate (C/25), the cell provided a capacity of 0.65 mAh/cm^2,

whereas at a C/3 rate, a reversible capacity of 0.3 mAh/cm^2 was achieved (Fig. 13(b)).

These cell capacities correspond to anode capacities of 128 and 59 mAh/g, respectively.

The data demonstrate that, despite the ability of these low-capacity lithium-ion cells to

show relatively stable electrochemical behavior when the end potential of the Cu$_2$Sb

electrode is restricted to approximately 0.65 V vs. Li/Li$^+$, the major challenge that still

remains is to overcome the first cycle, irreversible capacity loss associated with

intermetallic electrodes.

Conclusions

Intermetallic Cu$_2$Sb electrodes, made either in thin film form by pulsed laser deposition, or

as laminates from powder samples, show enhanced stability when cycled over a limited

voltage window (0.65-1.4 V vs. Li/Li$^+$). When cycled over a wider voltage range (0-1.2

V), the performance of the thin-film electrodes deteriorates more rapidly when stainless

steel substrates rather than copper substrates are used. On continued cycling, the capacity

of the Cu$_2$Sb electrode becomes dominated by a direct Sb $\rightarrow$ Li$_3$Sb reaction rather than by

a lithium insertion/copper extrusion reaction. The superior performance of the Cu$_2$Sb/Cu

electrodes over Cu$_2$Sb/SS electrodes was attributed to 1) the more active participation of

the extruded copper in the electrochemical reaction, 2) the higher electronic conductivity

of Cu, and 3) greater compatibility between the extruded Cu and the substrate, leading to

greater electronic connectivity between the extruded Cu and the remaining Li-Cu-Sb or Li-

Sb components of the electrode matrix. The SEI layer on Cu$_2$Sb electrodes was

determined to be considerably different to the composition of the SEI layer on lithiated

graphite electrodes; the formation of this layer accounts for the large irreversible capacity loss that is typically observed in cells with intermetallic electrodes on the first charge/discharge cycle, consistent with the findings of others.

Acknowledgments

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Figure captions

Figure 1. SEM images for (a) a cross-section of a Cu_2Sb/SS film and (b) the surface morphology of a Cu_2Sb/Cu film.

Figure 2. X-ray diffraction pattern of a Cu_2Sb/SS film prepared by PLD at room temperature; S notes the peaks from the stainless steel substrate.

Figure 3. Voltage profiles of lithium cells with Cu_2Sb/SS electrodes at (a) 0.1-1.2 V, (b) 0.65-1.4 V at constant current ($35\mu A/cm^2$), and (c) the calculated discharge (anodic) capacities obtained by cycling at 0.1-1.2 V (-●-), 0.65-1.4 V (-○-) and 0.1-0.7 V (-Δ-).

Figure 4. Differential capacity plots of lithium cells with Cu_2Sb/SS electrodes in the voltage range (a) 0.1-1.2 V and (b) 0.65-1.4 V, recorded at various cycle numbers.

Figure 5. Voltage profiles of lithium cells with Cu_2Sb/Cu electrodes at (a) 0.0-1.2 V, (b) 0.65-1.4 V at constant current ($35 \mu A/cm^2$).

Figure 6. Differential capacity plots of lithium cells with Cu_2Sb/Cu electrodes in the voltage range (a) 0.0-1.2 V and (b) 0.65-1.4 V, recorded at various cycle numbers.

Figure 7. Comparative plots of specific discharge (anodic) capacities obtained by cycling lithium cells with Cu_2Sb/Cu film electrodes at (a) 0.0-1.2 V and (b) 0.65-1.4 V.

Figure 8. Surface morphology of a Cu_2Sb/SS film electrode observed by AFM (a) before cycling and (b) after cycling between 0.1-1.2 V vs. Li/Li^+.

Figure 9. Open circuit response of a lithium cell with a Cu_2Sb/SS film electrode after charging the electrode to 0.1 V at $35 \mu A/cm^2$.

Figure 10. FTIR spectrum of a Cu_2Sb/SS film electrode, after cycling in a lithium cell between 0.65 and 1.4 V.

Figure 11. (a) Cyclic voltammograms of a Cu_2Sb/SS film at sweep rates of 0.1-50 mV/s between 0.65-1.4 V, (b) a plot of I_p vs. v, and (c) a plot of I_p vs. $v^{1/2}$.

Figure 12. (a) Charge/discharge profiles of a $Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ lithium ion cell together with the corresponding profiles of the $Li(RE)/Cu_2Sb$ cell between 2.4-4.0V, and (b) a plot of specific capacity vs. cycle number at different C-rates.

Figure 13. (a) Charge/discharge profiles of a $Cu_2Sb/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ lithium ion cell together with the corresponding profiles of the $Li(RE)/Cu_2Sb$ cell between 2.2-3.28V, and (b) a plot of specific capacity vs. cycle number at different C-rates.