



Anomalous, High-Voltage Irreversible Capacity in Tin Electrodes for Lithium Batteries

S. D. Beattie,* T. Hatchard,* A. Bonakdarpour, K. C. Hewitt, and J. R. Dahn**z

Department of Physics, Dalhousie University, Halifax, Nova Scotia, B3H 3J5, Canada

Anomalous, high-voltage irreversible capacity is observed in electrodeposited and sputtered Sn films when used as working electrodes in electrochemical lithium cells. Sn electrodes can function as expected in Li/Sn cells provided the upper cutoff potential, while removing lithium from the Sn electrode, is kept below about 1.4 V. However, when the upper cutoff potential is increased to about 1.5 V and above, an anomalous irreversible high-voltage plateau in the voltage-capacity curve is often observed during subsequent lithiation. We discuss the relationship between the recharge cutoff voltage and the presence of anomalous high-voltage irreversible capacity. The dependence of the amount of anomalous, high-voltage irreversible capacity vs. discharge rate of the cell is investigated. A model is proposed to explain the anomalous high-voltage irreversible capacity, including strategies to avoid it. One of the strategies is to alloy Sn with Cu.

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Sn has been studied as a negative electrode in lithium cells for many years¹⁻⁴ and its voltage-capacity curve is well understood.⁵ During our investigation of electrodeposited and sputtered Sn electrodes we discovered something that had not been reported in the literature, anomalous high-voltage irreversible capacity in Li/Sn cells. A Li/Li_xSn cell should show little to no capacity above 0.9 V;⁵ however, when electrodeposited and sputtered Sn electrodes were cycled to above 1.5 V, anomalous, high-voltage irreversible capacity can be observed. Figure 1 shows data from two different Li/Sn cells. Two electrodes were cut from the same electrodeposited Sn film and cycled vs. Li. The first cell was cycled to an upper cutoff of 0.8 V, represented by the dashed line in Fig. 1. The dashed line in Fig. 1 is a typical voltage profile for Sn cycled in a Li cell. All the plateaus in the voltage curve are observed as expected.⁵ The second cell was cycled to an upper cutoff voltage of 1.6 V, and its voltage-capacity curve is the solid line in Fig. 1. Cycling conditions for both cells were identical except for the upper cutoff voltage. Anomalous, high-voltage irreversible capacity is obtained in the cell cycled to 1.6 V. This paper discusses the occurrence of anomalous, high-voltage irreversible capacity in both sputtered and electrodeposited Sn electrodes. We discuss its effect on cycling performance, ways to avoid its detrimental effects, and suggest a mechanism for its formation.

Experimental

Sn can be electroplated from a wide variety of plating baths. We used four different aqueous baths described in Table I (first four) to deposit Sn. All baths were operated at room temperature with no agitation. A PVC vessel was used for all electrodepositions. It has a volume of 270 mL with the following dimensions: 4.6 cm wide × 6.9 cm long × 9.1 cm high. Titanium was used as the anode; however, sacrificial, high-purity Sn was also used. Films were typically deposited on Cu foil, although Ni foil was also used. To ensure minimal contamination of the bath and a clean deposition surface, the Cu foil was pretreated. The foil was wiped with acetone, soaked in a 15% H₂SO₄ solution for 5 min, then removed and rinsed with distilled water. 3M Plater's tape was used to secure the foil to the PVC backing around the immersed edges to prevent deposition on the back of the foil. Ni foil was prepared in the same way, with the exception of the acid dip. The PVC vessel and anode were also wiped down with acetone and rinsed with distilled water prior to deposition.

All Cu₆Sn₅ samples were deposited from a Lucent SnTech + 0.0164 M CuSO₄·5H₂O bath. Table II describes the pulse plating parameters used in the preparation of Cu₆Sn₅ samples. Using

pulsed deposition, the ratio of Cu to Sn in the deposit could be varied from almost 0 → almost ∞. The pulse length, current density, and number of cycles were all varied to achieve different stoichiometric ratios. Typically Cu₆Sn₅ was deposited surrounded by a pure Sn phase. Galvanostatic deposition was performed using an EG&G Princeton Applied Research model 273 potentiostat/galvanostat. Pulsed deposition was performed using a Keithley 236 Source Measure unit. Both units were controlled remotely. Packaged software was used to control the M273 (Creative Electrochemistry software) while a Visual Basic program was written to apply pulsed waveforms using the Keithley. All deposits were performed galvanostatically.

Sputtered films were prepared by dc magnetron sputtering (Corona Vacuum Coaters V-3T system with 2 in. diam targets). Using a 500 L/s turbo pump and a Polycold system, the ultimate base pressure of the system is 6 × 10⁻⁸ Torr. Sn films were deposited on 100 μm thick copper foil. Sputtering was done using an argon pressure of 2 mT and a power of 50 W. The target-substrate distance in the sputtering system is 55 mm.

Scanning electron microscopy (SEM) studies were performed with an energy-dispersive X-ray spectrometer (EDAX) using a Si(Li) EDAX/KeveX analyzer coupled to a JEOL JSM-35Cf electron

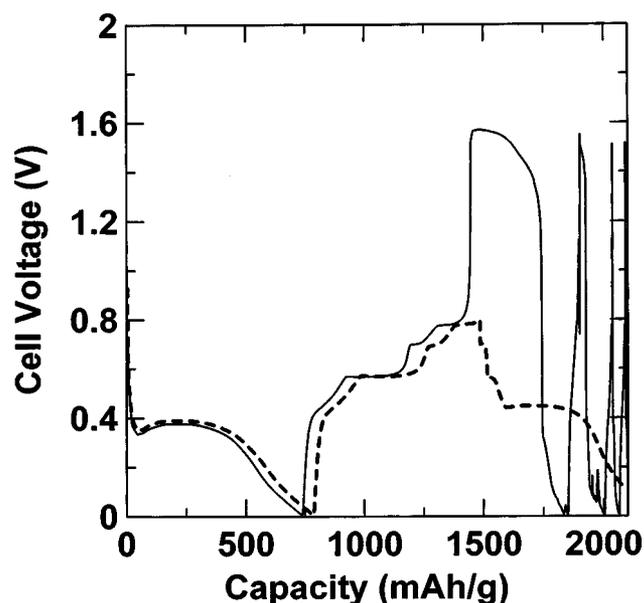


Figure 1. Voltage vs. capacity for two Li/Sn cells with electrodes cut from the same electrodeposited film.

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

z E-mail: jeff.dahn@dal.ca

Table I. Plating bath recipes.

Bath name	Constituents
Sulfate	60 g/L SnSO ₄ 40 g/L H ₂ SO ₄ 40 g/L phenylsulfonic acid 2 g/L gelatin 1 g/L β-naphthol
E-Brite	20 mL/L 180 M 7.5 mL/L 180-B 24 g/L SnSO ₄ 100 mL/L H ₂ SO ₄
SnTech	150 mL/L SnTech acid concentrate 67 mL/L SnTech tin make-up 40 mL/L SnTech additive A 20 mL/L SnTech additive B
Pyrophosphate	36 g/L Sn ₂ P ₂ O ₇ 137 g/L K ₄ P ₂ O ₇ 0.3 g/L gelatin
Bronze	150 mL/L SnTech acid concentrate 67 mL/L SnTech tin make-up 40 mL/L SnTech additive A 20 mL/L SnTech additive B 4 g/L CuSO ₄ ·5H ₂ O

microscope. Images of the electroplated deposits were taken with the same microscope.

X-ray diffraction (XRD) experiments were conducted at room temperature with a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and diffracted-beam monochromator.

All electrochemical cells were tested in 2325 coin cell hardware. The cells use a polypropylene microporous separator, 1 M LiPF₆ dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) (33:67 vol., Mitsubishi Chemical) electrolyte and lithium metal as the negative electrode. All cells were assembled in an argon-filled glove box and tested using constant charge and discharge currents.

Results

In this paper, sustained capacity above 1.0 V is considered anomalous, high-voltage irreversible capacity. In Fig. 1 it was shown that when a Li/Sn cell is charged to 1.6 V there is an anomalous, irreversible high-voltage plateau near 1.5 V. After this plateau, the cell exhibits dramatically reduced capacity and cycles very poorly (Fig. 1, solid line). The behavior shown in Fig. 1 has been reproduced dozens of times, and it is not specific to electrodeposited films.

Figure 2 is very similar to Fig. 1, showing data taken from two Li/Sn cells. The Sn electrodes were prepared by magnetron sputter deposition. Two electrodes were cut from the same sputtered Sn film and cycled in two different coin cells. Cycling conditions for the two cells were identical except for the charging cutoff voltage. The charging cutoff voltage in the cell represented by Fig. 2a was 0.8 V, like the dashed line in Fig. 1. The cell represented by Fig. 2b had a charging cutoff voltage of 1.6 V, like the solid line in Fig. 1. Electrodeposited and sputtered Sn electrodes have the same behavior:

Table II. Pulsed deposition parameters.

Film used in figure	Calculated thickness per pulse (nm)	Sn pulse (mA/cm ²)	Cu pulse (mA/cm ²)	Number of cycles	Total thickness (μm)
6	100	3.20	0.08	20	4
7a, b	10	3.57	0.07	150	3
7c, d	100	3.57	0.70	20	4

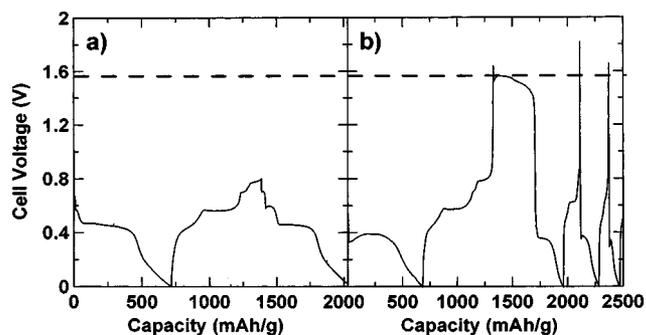


Figure 2. Voltage vs. capacity for two Li/Sn cells with electrodes cut from the same sputtered film.

When cycled below 0.8 V, no anomalous behavior is observed; however, when cycled above 1.5 V anomalous, high-voltage irreversible capacity is observed in both cases.

Figure 3 shows three voltage-capacity profiles for three different electrodeposited Sn films. In Fig. 3a anomalous high-voltage irreversible capacity is observed during the first and second lithiations. In Fig. 3b anomalous high-voltage irreversible capacity does not occur until the second lithiation. What has changed between the first and second lithiation to cause the anomalous high-voltage irreversible capacity? In Fig. 3c anomalous high-voltage irreversible capacity is not initiated until the third lithiation. What could have happened after two full lithiation/delithiation cycles to initiate the anomalous, high-voltage irreversible capacity?

Figures 1-3 show that anomalous, high-voltage irreversible capacity is initiated when the cell is charged (removing Li from the Sn) above about 1.5 V. Figure 3c shows that anomalous, high-voltage irreversible capacity is initiated only after the cell has breached a sufficiently high potential, ~1.5 V. In Fig. 3c the cell potential does not go above 1.5 V during the first and second lithiation/delithiation cycles, however, when the cell potential does go above 1.5 V, anomalous high-voltage irreversible capacity is initiated. The cell described by Fig. 3b shows the same trend. Apparently, the anomalous high-voltage irreversible capacity is initiated during delithiation to potentials above about 1.5 V. The rest of this paper documents our attempt to explain the anomalous high-voltage irreversible capacity.

SEM and XRD analysis were performed on many electroplated Sn films that showed anomalous high-voltage irreversible capacity to look for abnormalities. Figure 4 shows an XRD pattern and an SEM image of a typical electrodeposited film. The diffraction pattern shows only the expected peaks from crystalline Sn and the copper substrate. The SEM image shows micrometer-scale crystallites that are uniform across the plated film. Neither the diffraction pattern nor the SEM image suggests why electroplated Sn would exhibit anomalous high-voltage irreversible capacity.

Although we do not show the data here, the same anomalous irreversible capacity has been observed for pure Sn electrodes delithiated above 1.6 V, then lithiated again, in cells with LiClO₄/PC and LiPF₆/PC electrolytes. The same type of behavior has been observed for electroplated Sn electrodes prepared from each of the first four baths described in Table I, as well as for sputtered Sn and powdered Sn electrodes. This strongly indicates that pure Sn itself is the cause of the anomalous high-voltage irreversible capacity.

We hypothesized that the amount of anomalous, high-voltage capacity could be related to the discharge rate of the cell. To test our theory, cells with nominally identical electrodes cut from the same piece of electroplated Sn film (SnTech solution) were discharged with different specific currents and the anomalous high-voltage irreversible capacity was measured during the first lithiation. The anomalous high-voltage irreversible capacity was taken as all the capacity measured above 1.0 V. Figure 5 shows that the anomalous

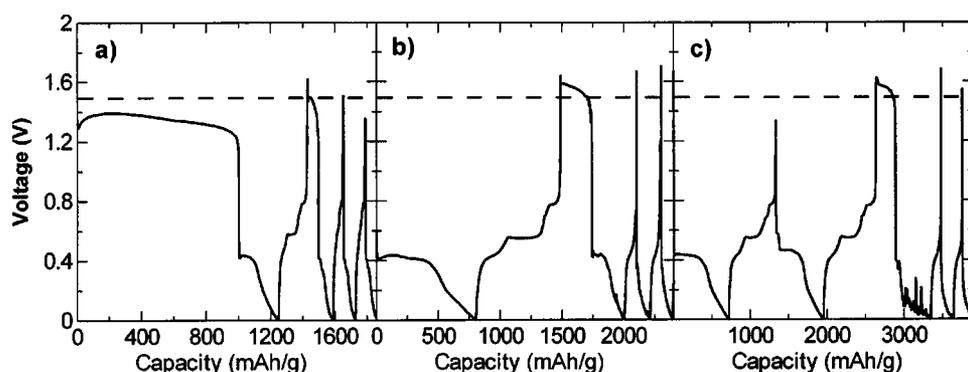


Figure 3. Voltage vs. capacity for three Li/Sn cells with electrodes cut from electroplated Sn films.

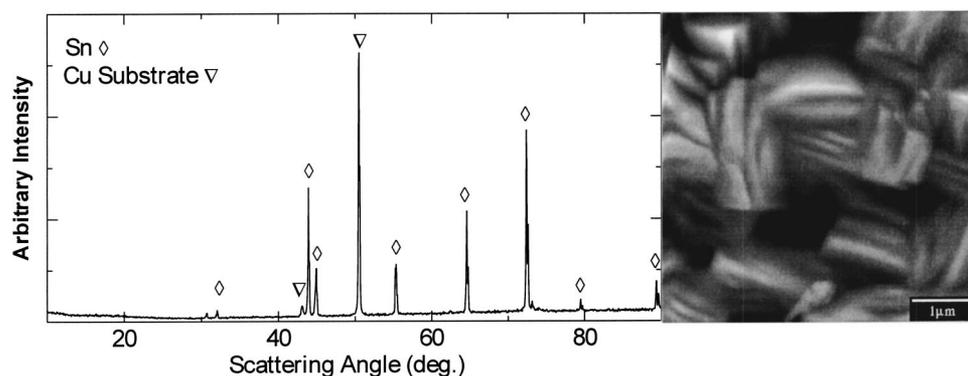


Figure 4. XRD and SEM analysis of electroplated Sn from a sulfate bath deposited at 20 mA/cm².

high-voltage capacity decreases rapidly as the specific current increases.

The work discussed strongly points to Sn as the cause of anomalous, high-voltage irreversible capacity. Another way to test the culpability of Sn is to deposit a Sn alloy instead of pure Sn. This is easily done by electrodeposition. We used the same SnTech bath with the addition of 0.0164 M CuSO₄·5H₂O as described in Table II. Figure 6 shows the voltage vs. capacity of a Li/(Cu-Sn alloy) cell. Recall that Sn electrodes cut from films deposited in a pure SnTech solution exhibit anomalous high-voltage irreversible capacity. When Cu is added to the bath and alloyed with Sn, no anomalous high-voltage capacity is present.

Pulsed deposition techniques allow films of different Cu-Sn stoichiometries to be deposited from the same bath. Two films of different Cu:Sn ratios were deposited from the same Lucent SnTech + 0.0164 M CuSO₄·5H₂O bath as described by Table II. The first film consists of Cu₆Sn₅ with trace amounts of Sn. The second film is predominantly Sn, with trace amounts of Cu₆Sn₅. Figure 7a shows the voltage profile of the mostly Cu₆Sn₅ deposit cycled above 1.8 V. No anomalous high-voltage irreversible capacity is observed. Figure 7b shows an XRD pattern of the film used in the cell described by Fig. 7a. The data in Fig. 7b confirms that the film is mostly Cu₆Sn₅. Figure 7c shows the voltage profile of the predominantly Sn film and anomalous high-voltage irreversible capacity is observed, as expected from a predominantly Sn film. The XRD pattern in Fig. 7d shows that the film used in the cell described by Fig. 7c is mostly Sn. The only difference between the two films was the plating current density, which controls the Cu:Sn ratio.

Discussion

The contrasting behavior shown in Fig. 1, 2, and 3 is not easy to explain. The behavior is not an experimental artifact, we have observed it dozens of times and so have others.^{6,7}

We presented preliminary data at the joint ECS and ISE conference in San Francisco in the fall of 2001.⁸ Subsequent to the meet-

ing, Tamura *et al.* published results⁶ recognizing the existence of anomalous high-voltage irreversible capacity in Sn-based electrodes. The data presented in Fig. 1 and 2 show that the behavior is observed in both electroplated and sputtered Sn. Figure 3 shows that the appearance of anomalous irreversible capacity depends strongly on the upper-cutoff potential used during delithiation. Figure 5 shows that the anomalous irreversible capacity is reduced at high rates of discharge.

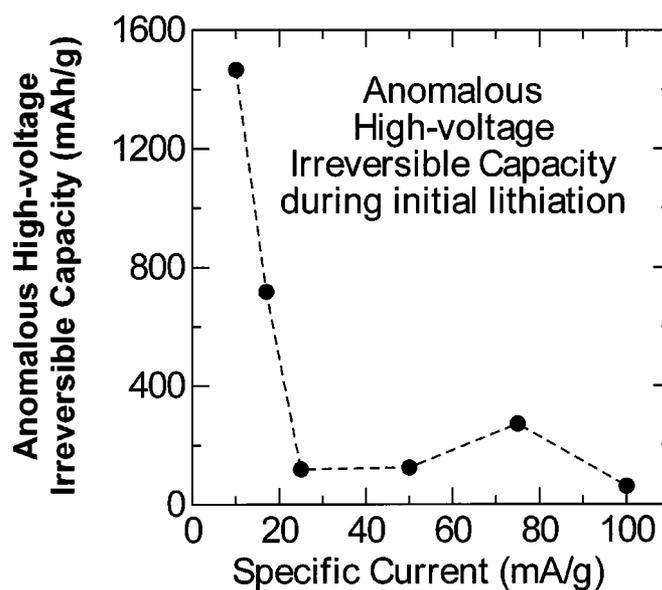


Figure 5. Anomalous high-voltage irreversible capacity vs. specific current for Li/Sn cells with electrodes prepared from a SnTech solution. The anomalous capacity (all capacity above 1.0 V) during the first lithiation is shown.

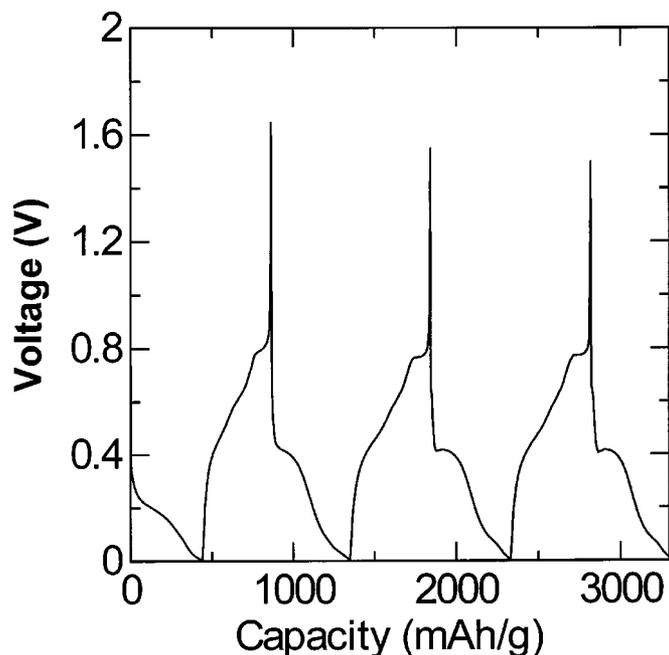


Figure 6. Voltage vs. capacity for a Li/Cu₆Sn₅ cell.

We propose the following mechanism to describe the anomalous high-voltage irreversible capacity: We believe that pure Sn must have a crystal face (or faces) that acts as a catalyst for the decomposition of electrolyte. Severe decomposition of electrolyte, leading to the anomalous high-voltage irreversible capacity, apparently only occurs at high potentials, ~ 1.5 V, vs. Li, where the Sn electrode would contain negligible amounts of lithium. The electrolyte decomposes until a thick layer is built up, thus blocking the catalytic surface and preventing subsequent decomposition. The layer of decomposed electrolyte also serves to inhibit the diffusion of Li, decreasing the overall capacity in subsequent cycles. Figures 1, 2b, 3a-c, and 7c clearly show reduced capacity following anomalous

high-voltage irreversible capacity. Sometimes the irreversible capacity is observed during the first discharge. We believe this occurs in cases where a very clean Sn surface exists. If the Sn surface is "dirty" then it can be "cleaned" during a lithiation/delithiation cycle. For example, during such a complete cycle, thin layers of Sn oxides are converted to Sn and Li₂O. If the cell voltage is subsequently raised above about 1.5 V, all the lithium is removed from the Sn and the clean catalytic surface is exposed. If the cell voltage is only raised to about 0.8 V (as in Fig. 1 and 2a), then Li-Sn alloys are still present and the catalytic surface is not, so anomalous high-voltage irreversible capacity is not observed.

Presumably, the catalytic decomposition can support some maximum rate, supported by Fig. 5. If lithium is supplied to a pure Sn electrode at a rate greater than this maximum decomposition rate, then Li/Sn alloys form, and the catalytic action presumably stops according to our model. Therefore, we believe that rapid first lithiations to potentials near 0.8 V will strongly reduce or eliminate anomalous high-voltage irreversible capacity during the first lithiation. Provided then that the cells are not charged above about 0.8 V (see Fig. 1), anomalous high-voltage irreversible capacity would never be observed. We recently showed that this was true in an *in situ* atomic force microscope (AFM) study of the Sn surface during electrochemical reaction with lithium.⁷

Note that the anomalous high-voltage irreversible capacity cannot be described by cracking and pulverization. It is well known that there are large volume changes that occur as lithium reacts with Sn electrochemically.¹ It is well known that these volume changes cause electrode particles to fragment and crack, exposing fresh surfaces.¹ It is well known that solid electrolyte interface layers must form on these fresh surfaces and that this irreversibly consumes some lithium atoms.¹ However, the behavior in Fig. 1 and 2 cannot be explained by stating that volume changes have occurred, fresh surfaces have formed, and hence, irreversible behavior is expected. Notice that the electrodes in Fig. 1 have cycled through almost the same capacity in their first lithiation and delithiation and the electrodes have therefore undergone almost the same volume expansion and contraction. Nevertheless, the cell represented by the solid line in Fig. 1 shows an anomalous, high-voltage plateau during its second lithiation, while the cell represented by the dashed line in Fig. 1 does not.

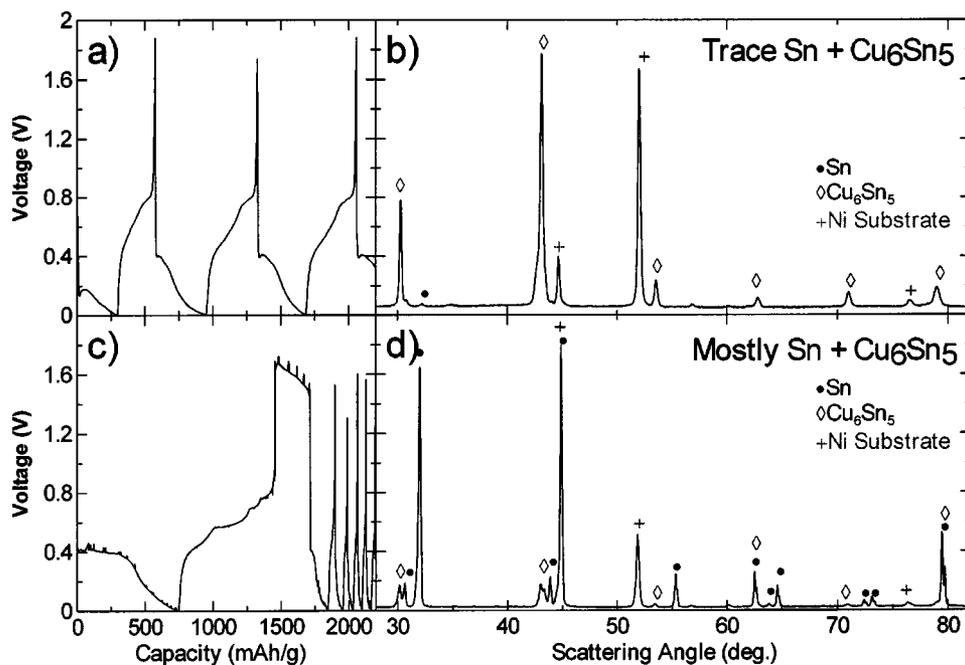


Figure 7. Cu₆Sn₅ and pure Sn can be deposited from the same bath: (a) voltage vs. capacity for a Li/Cu-Sn cell, (b) XRD analysis shows mostly Cu₆Sn₅ for the cell in (a), (c) voltage vs. capacity for a second Li/Cu-Sn cell, and (d) XRD analysis of film used to make cell in (c) shows mostly Sn.

The only difference between the treatments of the two cells in Fig. 1 is the choice of upper cutoff potential. We speculate that the surface of fresh Sn, not Li_xSn alloys, is a catalytically active surface for the decomposition of electrolyte. The electrode in the cell in Fig. 1, charged to potentials near 0.8 V, presumably still had enough incorporated lithium to avoid catalytic action. When delithiation is carried out up to 1.6 V (as in the solid line in Fig. 1), Sn electrodes are essentially lithium-free and catalytic electrolyte decomposition occurs.

Despite the large amount of research previously done on Sn electrodes for Li-ion batteries, this anomalous high-voltage irreversible capacity has only recently been reported. Further work is needed to understand the nature of the catalytic Sn surface(s).

Conclusions

This is the first time anomalous high-voltage irreversible capacity in Sn electrodes for Li-ion batteries has been carefully discussed. We have shown that the behavior occurs in both electrodeposited and sputtered Sn electrodes. Other groups⁶ have also observed this behavior. The behavior is initiated only at sufficiently high voltages, ~ 1.5 V. The performance of the cell dramatically declines after anomalous high-voltage irreversible capacity has occurred. We have shown that the amount of anomalous high-voltage irreversible capacity depends on the discharge rate. A model involving catalytic decomposition of electrolyte by pure Sn crystallites was proposed to explain the high-voltage irreversible capacity. Two ways of avoiding

the anomalous high-voltage irreversible capacity are to rapidly discharge the cell to 0.8 V, then limit the recharge voltage to below ~ 1.5 V,⁷ or alloy some other metal with Sn so that pure Sn crystallites are not present.

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