Short communication

Pyrolysis of an alkyltin/polymer mixture to form a tin/carbon composite for use as an anode in lithium-ion batteries

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Abstract

In the search for a nanocomposite which can cycle reversibly as a lithium-ion secondary battery anode while utilizing the electrochemical activity of the matrix material, carbon was chosen as the low weight, low volume expansion phase in a nanocomposite with tin. The nanocomposites were synthesized by pyrolysis of a polymer in the presence of a tin precursor. The samples with the most fine-grained, well distributed tin particles exhibited reversible capacities on the order of 400–500 mAh/g. The nanocomposites were analyzed by X-ray diffraction, BET, TEM, and electrochemical cycling.
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1. Introduction

Tin forms a $Li_{22}Sn_5$ compound with lithium, which has been shown to form electrochemically [1]. The use of pure tin as an anode in a lithium-ion battery system results in a theoretical gravimetric capacity of almost 1000 mAh/g. Since the theoretical capacity of tin is more than double the theoretical capacity of commercial graphite (372 mAh/g), tin systems are viable candidates to replace carbon-based systems as reliable, high-capacity battery anode materials [2]. Although tin is a very ductile metal, its macroscopic mechanical properties are not great enough to withstand the stresses that occur during lithium alloying. Proper cycling requires the formation of nanocrystalline tin, which is quite difficult [3,4]. Synthesis of nanocrystalline tin in a composite structure would increase the strength of the active particles in the nanocomposite [5–11].

In order to form a material which has a significantly greater gravimetric capacity than commercial graphite, a light-weight matrix phase would be needed. The requirement of low formula weight led to the selection of pure carbon. Since it is known that carbon can handle the rigors of lithium cycling in the form of graphite, it is safe to say that it may be strong enough to deal with high-capacity cycling. Many have tried to form graphite doped with tin in some way [12], but our goal here is different. Rather than contribute small amounts of tin to an active material in order to "boost" the capacity of graphite, the tin should be the main active phase due to its high theoretical capacity and the carbon should provide structural support. The formation of carbon that can withstand the stress of Li/Sn alloying is vital to the task of forming an anode that can cycle reversibly. Since tin and carbon do not alloy with one another, a more difficult task to ensure cyclability would be the formation of an intimate mixture of fine-grained tin and carbon. Such a microstructure would be desirable for allowing a homogeneous expansion of the composite during lithium alloying. In order to create a homogenous dispersion of Sn particles in a carbon matrix, a synthesis method was developed.

Although tin and carbon are not known to form any compound or solid solution, it may be possible to form a one-to-one composite of the two, without segregation. During thermal treatments necessary to form tin from a tin precursor, the carbon would, most likely, segregate itself. Therefore, the simultaneous formation of tin and carbon would be necessary in order to form a composite of close proximity. If heat treatments do not last long enough such that the pure phases can diffuse and grow, then there is a distinct possibility that the particle size of the composite constituents could be kept near the size of the initial nuclei nuclei.

Pyrolysis of a polymer was chosen as a method to form carbon, based on the fact that a porous polymer could absorb

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a liquid or dissolved tin precursor. In addition, another function of the newly formed carbon would be to create barriers between tin particles, keeping the tin particles from migrating to one another, and thusly inhibiting grain growth.

The criteria for the polymer starts with its ability to decompose into pure carbon. During this decomposition, though, it is important that the gaseous components do not oxidize the tin. In order to minimize the risk of tin oxidation, a polymer containing no oxygen was chosen as the carbon source. Other attributes of the polymer indicate how the carbon will form in spatial relation to the tin. Because the desired structure of the composite is nano-sized particles of tin surrounded by carbon, it is important that the polymer can entrap appreciable quantities of the tin precursor. If such were the case, then it would be possible for the carbon to reduce contact of tin nuclei, and therefore diffusion between particles.

In order to achieve such a composite structure, a highly porous, cross-linked polymer was sought. If the polymer's pores could contain the tin precursor molecules during heat treatment and the carbon atoms densify upon decomposition of the polymer, then the composite might exhibit the desired characteristics, designed to contain molecules and having favorable thermal characteristics. An engineered polymer that is "particularly suitable for the efficient sorption of high molecular weight organic molecules" [13] is the Macronet MN-200, which is made by the Purolite company and exhibits the desired characteristics.

A solid organotin was sought in order to utilize a solid-state processing technique for infiltration of the organometallic molecule into the polymer. Tetraphenyltin is a solid at room temperature and forms an ordered crystal. This means that it should be able to withstand the heat of high energy mechanical milling [14]. HEMM also provides

a solvent-free mixing technique for preparing the precursor prior to heat treatment. We have already shown the potential of this approach where a liquid organotin precursor was used to infiltrate the polystyrene resin followed by pyrolysis in inert atmosphere. The resultant composite exhibited a stable capacity of ∼500 mAh/g after 30 cycles when cycled at a current of 100 μA/cm^2 [15].

The combination of these two starting components should yield the composite structure desired when the processing conditions are optimized. If these processing goals are met, then the result should be a nanocomposite of tin and carbon that was made in a simple two-step process of mixing and heat treating. The resultant material should also, in turn, be able to retain the high-capacity capability of tin and cycle reversibly as a lithium-ion secondary battery anode.

2. Experimental

The crosslinked polystyrene polymer was obtained from the Purolite company in Philadelphia. The resin, called Macronet MN-200, was tested for thermal behavior (Fig. 1) in order to determine the carbon yield, and thus, the concentration needed to match one carbon for one tin in the precursor. A corresponding amount was weighed in air and added to steel milling balls in a hardened steel Spex milling vial. The tetraphenyltin, obtained from Alfa Aesar (F.W. = 427.11 g/mole), was weighed assuming no evaporation of tin-containing molecules, as shown by the TGA plot of pure tetraphenyltin (Fig. 2). The mass percent of a mole of tin atoms in a mole of tetraphenyltin molecules is approximately 27%, similar to the stabilized mass percent of the plot in Fig. 2. This shows that the organometallic solid could decompose fully into pure tin, in an absence
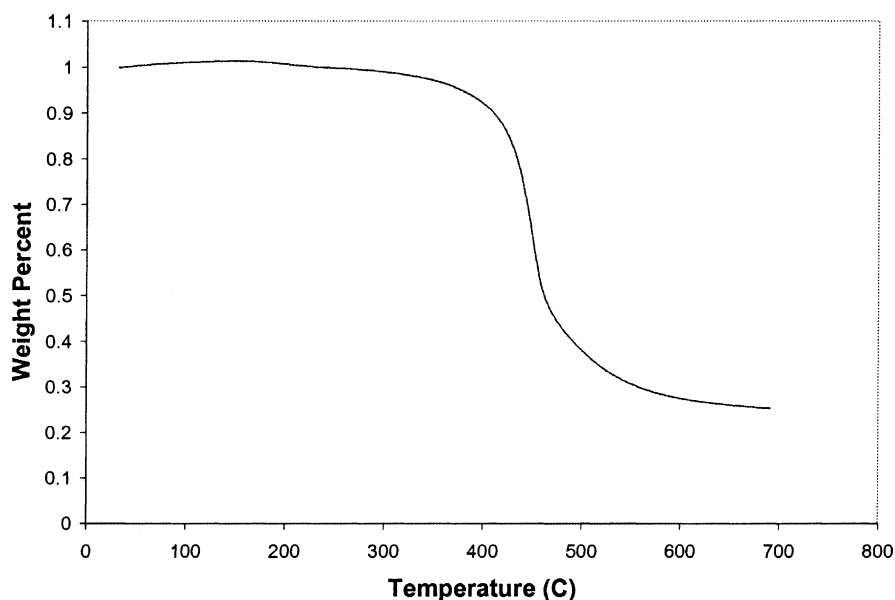

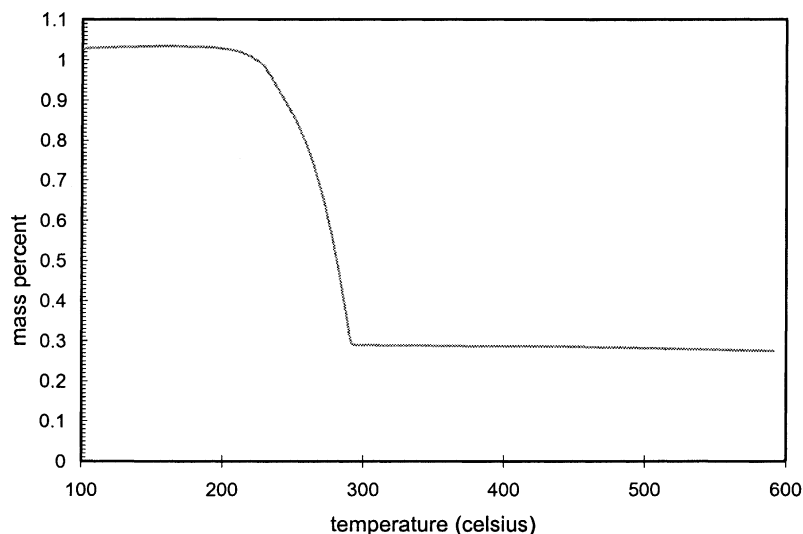Fig. 1. TGA plot of Macronet MN-200 in an alumina crucible, under argon, flowing at 84.7 mL/min.

Fig. 2. TGA plot of tetraphenyltin in an alumina crucible, under argon, flowing at 84.7 mL/min.

of oxygen and heating at 10 °C/min. Analysis of the TGA plot shows decomposition occurs below 300 °C, and since tetraphenyltin does not begin to boil until temperatures above 420 °C, it can be assumed that very little vapor loss will occur. Although, the crystalline molecule melts between 224 °C and 227 °C, making the infiltration into the polymer network vital for synthesis of a homogeneous nanocomposite of tin and carbon.

The 3.22 g charge, consisting of the polystyrene resin (0.22 g) and tetraphenyltin (3 g), was loaded into the hardened steel milling vial in air, but only after the polymer beads were dried in a 100 °C vacuum drying oven for at least 8 h. The mass of the milling media was slightly more

than 30 g, giving an approximate ball to charge ratio of 10:1. After milling for 30 min in a Spex 8000M mixer/mill, the precursor was collected from the vial in air and tested using a Quantachrome NOVA 2000 analyzer which utilizes the Brunauer Emmett Teller (BET) method to determine the change in surface area due to milling. Then, the mixture was placed in a quartz crucible with a lid and taken to a tube furnace. Under argon, flowing at 95.7 mL/min, the mixture was heat treated inside a mullite tube to decompose the polymer and form crystalline tin. After fully cooled, the sample was removed and crushed with a mortar and pestle to form a uniform powder. The powder was analyzed by XRD in a Philips X'Pert diffractometer using Cu Kα radiation, and by
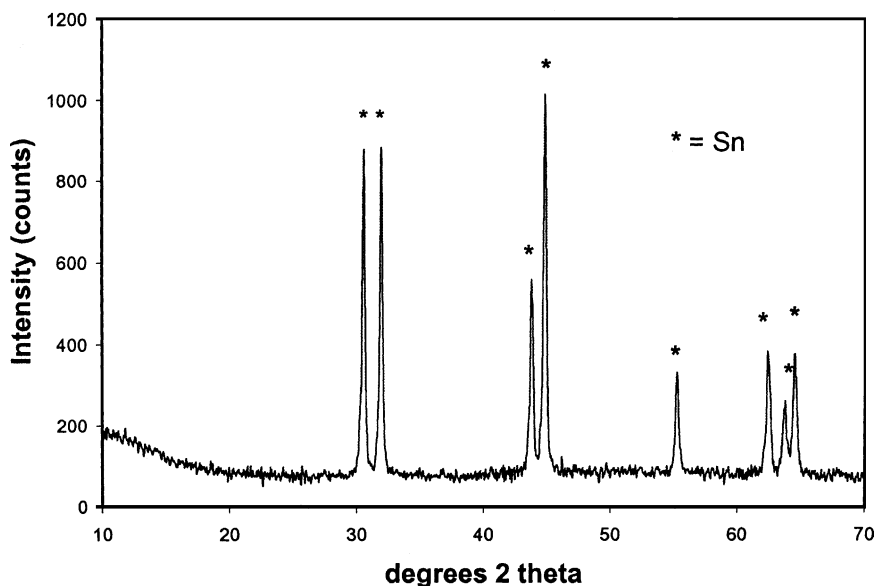

Fig. 3. X-ray diffraction pattern of Macronet MN-200 and tetraphenyltin, post-milling (for 30 min with a ball to charge ratio of 10:1) and post-heat treatment (under argon flowing at 95.7 mL/min, heated to 600 °C at 10 °C/min, dwell for 1 h), showing metallic tin peaks of considerable breadth, and no peaks for carbon, which is amorphous.

a TA Instruments SDT 2960 TGA-DTA under argon flowing at approximately 84.7 mL/min before being cast into electrodes for electrochemical testing.

The electrode was made by roll casting a slurry comprised of the composite, Ensaco 350 G carbon black (from Erachem Europe) with an approximate surface area of $770 \, m^2/g$, and polyvinylidenefluoride binder (Aldrich) in N-methylpyrrolidinone (Fisher). The solution of 5.6 wt.% polyvinylidenefluoride (PVDF), dissolved in the N-methylpyrrolidinone (NMP), is added to the two solid components (87.1 wt.% active material, and 7.3 wt.% car-

bon), and mixed for a minimum of 2 h, to ensure full mixing. Once the slurry is well-mixed, the slurry is cast onto copper foil (Insulectro) using a roller, to make a thin, even coating. The electrode is transferred into a drying oven at 70 °C, and dried for a minimum of 6 h in air. This dried product is then punched into circles (to be used as electrodes), and then vacuum dried at 100 °C to remove any remaining moisture.

After fully dried, the electrodes are moved into an argon filled glove box for assembly of the test cells. The prototype battery is constructed of a polyethylene outer casing with
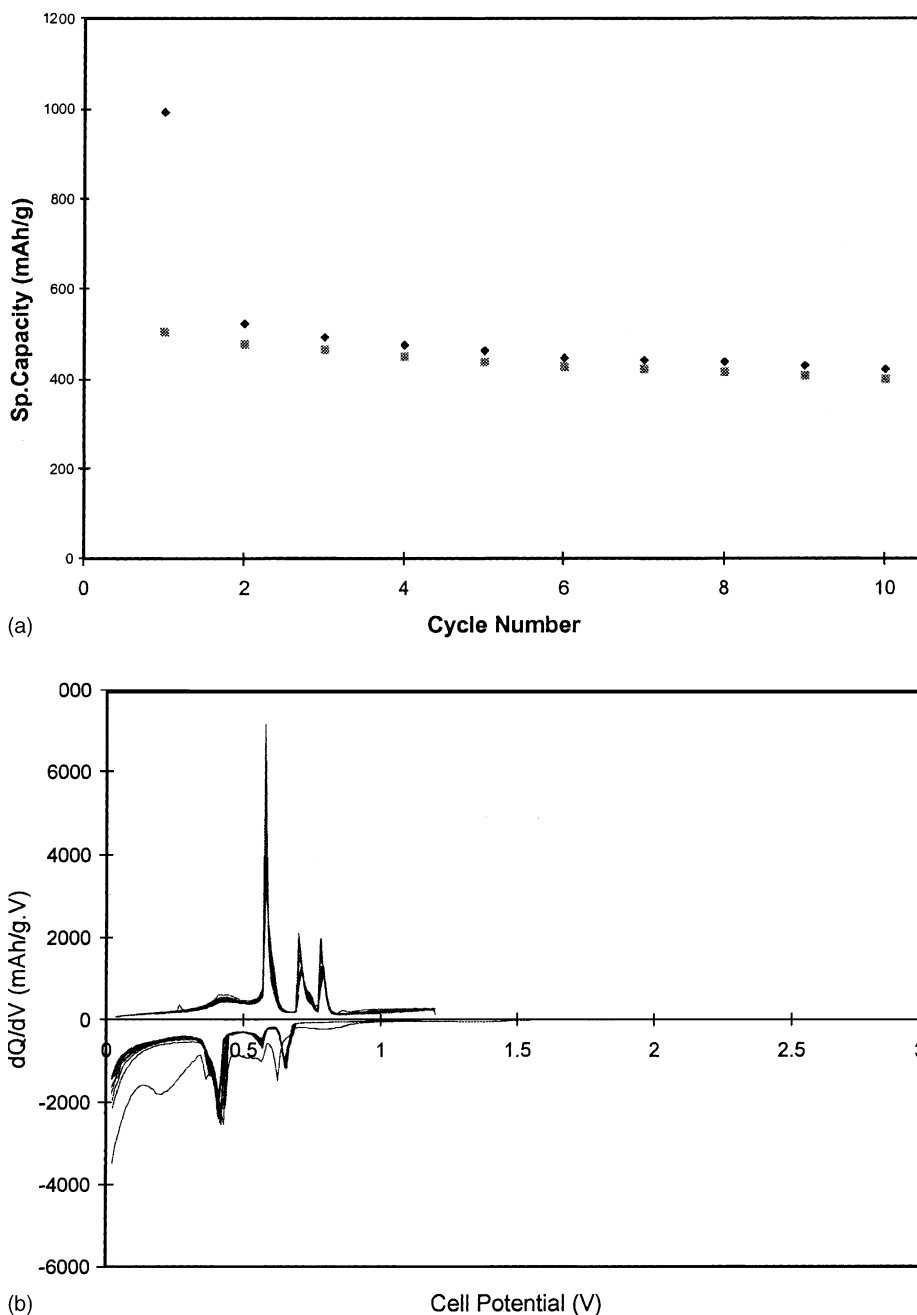

Fig. 4. Cyclic electrochemical response, at 100 μA over the range of 0.02–1.2 V, of tin/carbon derived from tetraphenyltin and macronet, pyrolized at 600 °C for 1 h under argon flowing at 95.7 mL/min with a heating rate of 10 °C/min: (a) capacity vs. cycle number; (b) differential capacity.

electrical components, including a spring for maintaining contact, made of steel and copper, which do not react with lithium over the testing range. The battery components contained within the polyethylene shell are submerged within the electrolyte, LiPF$_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (EC : DMC = 2 : 1). Once the cell is assembled, it is sealed in a plastic jar, with three electronic connections in the lid. These are connected to the Arbin Electrochemical Analyzer for galvanostatic testing. The tests were conducted at 100 μA/cm^2 over the voltage range, 0.02–1.2 V. The results of these battery tests can be seen in Section 3.

Heat treated powders were also examined using a fully calibrated Jeol 2000 EX transmission electron microscope (TEM) operating at 200 kV. The powder samples were submerged in small amounts into a vial of methanol, shaken up, then a holey carbon grid was passed through the suspension. The grids were placed in a vacuum oven at 70 °C for 12 h prior to observation in the TEM.

3. Results and discussion

Tetraphenyltin is a solid organotin at room temperature. Based on the XRD analysis, pyrolization of tetraphenyltin results in pure tin after heat treatment. Infiltration of this organotin into a polymer should result in formation of tin within a carbon matrix. In addition, the polymer should trap the organometallic during heat treatment. Fig. 1 shows that the polymer matrix decomposes throughout the temperature range where tin will be formed. The fact that this polymer collapses during pyrolosis should assist in trapping tin within the network of carbon. It is anticipated that the carbonized polymer aids in preventing tin loss during heat treatment by completely encapsulating the tin particles. From Fig. 2, it is apparent that the decomposition of tetraphenyltin into metallic tin is complete by approximately 300 °C. The mixture is heat treated to 600 °C in order to allow for dense carbon formation around the tin particles and removal of hydrogen from the decomposed polymer, enhancing the electrochemical properties of the composite.

In order to attain the combination of a highly networked, porous polymer that would trap tin atoms while segregating them, to decrease grain growth, that also forms carbon without oxidizing the tin, an engineered polymer would be necessary. Macronet, an engineered polystyrene resin made by the Purolite company, is highly porous, hygroscopic, and contains no oxygen. Macronet is polystyrene-based, and therefore contains no oxygen. The mixed resin is at least 80% polystyrene, with the rest consisting of the cross-linking agent. This high level of cross-linking gives the polymer a stable three-dimensional structure, within which the organotin can penetrate. The polymer comes in the form of beads, which range from 0.3 to 1.2 mm. Although they are porous, this macro-sized shape requires some high-energy processing in order to fully infiltrate

the tin source into the three-dimensional network of the polymer. In addition, it can be high energy mechanically milled to form a higher surface area powder out of the bead form in which it is obtained from the manufacturer. Milling for half-an-hour increases the surface area from 759 to 950 m^2/g. The advantage of increased surface area is the exposure of a greater number of pores to the surface, allowing for the organometallic molecules to be trapped within the polymer network. Also, mechanical milling mixes the components so that a homogeneous mixture of tin and carbon results after heat treatment.

This high level of mixing means milling can be used as a solvent-free method to create a mixture of the polymer and tetraphenyltin. The two components were milled together
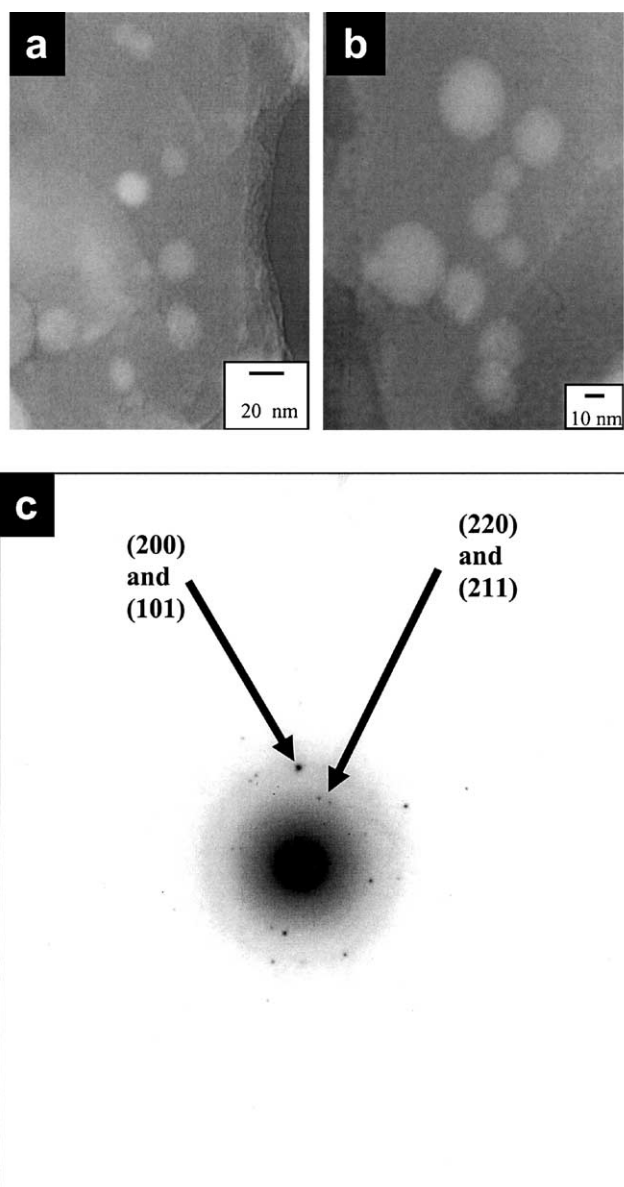

Fig. 5. TEM images at 400 000× (a), 500 000× (b), and (c) selected area electron diffraction pattern (60 cm camera length) of tetraphenyltin and purolite, pyrolized at 600 °C for 1 h under argon flowing at 95.7 mL/min with a heating rate of 10 °C/min.

for half-an-hour before being heat treated. The XRD pattern of the resultant composite is shown in Fig. 3. Although the capacity increases as more tetraphenyltin is added, there is a definite point of saturation. Since tetraphenyltin is a relatively bulky molecule, the homogeneous dispersion of the tin precursor by HEMM is not likely in higher concentrations.

The electrochemical response of the composite resulting from pyrolysis in argon for 1 h at 600 °C shows promising electrochemical cycling behavior (Fig. 4a). The large irreversible loss in the first cycle is due to the amorphous regions of carbon allowing lithium ions to be inserted into the structure, but not removed. Still, the reversible capacity of the material is greater than 400 mAh/g. This large re-

versible capacity shows that not only are the tin particles of small enough size, but also that the tin and carbon phases are mixed among one another. From the dQ/dV plot shown in Fig. 4b, it is apparent that the main electrochemical activity was due to the metallic tin, as the peaks are very sharp, indicating the crystalline nature of the active material.

Transmission electron microscopy images, shown in Fig. 5a and b at 400 000× and 500 000×, respectively, show light tin particles surrounded by dark gray, amorphous carbon. As shown, the particle size was approximately 10–20 nm. Heat treatment for longer time may not to increase the particle size of the tin, since the carbon prevents tin particle growth.
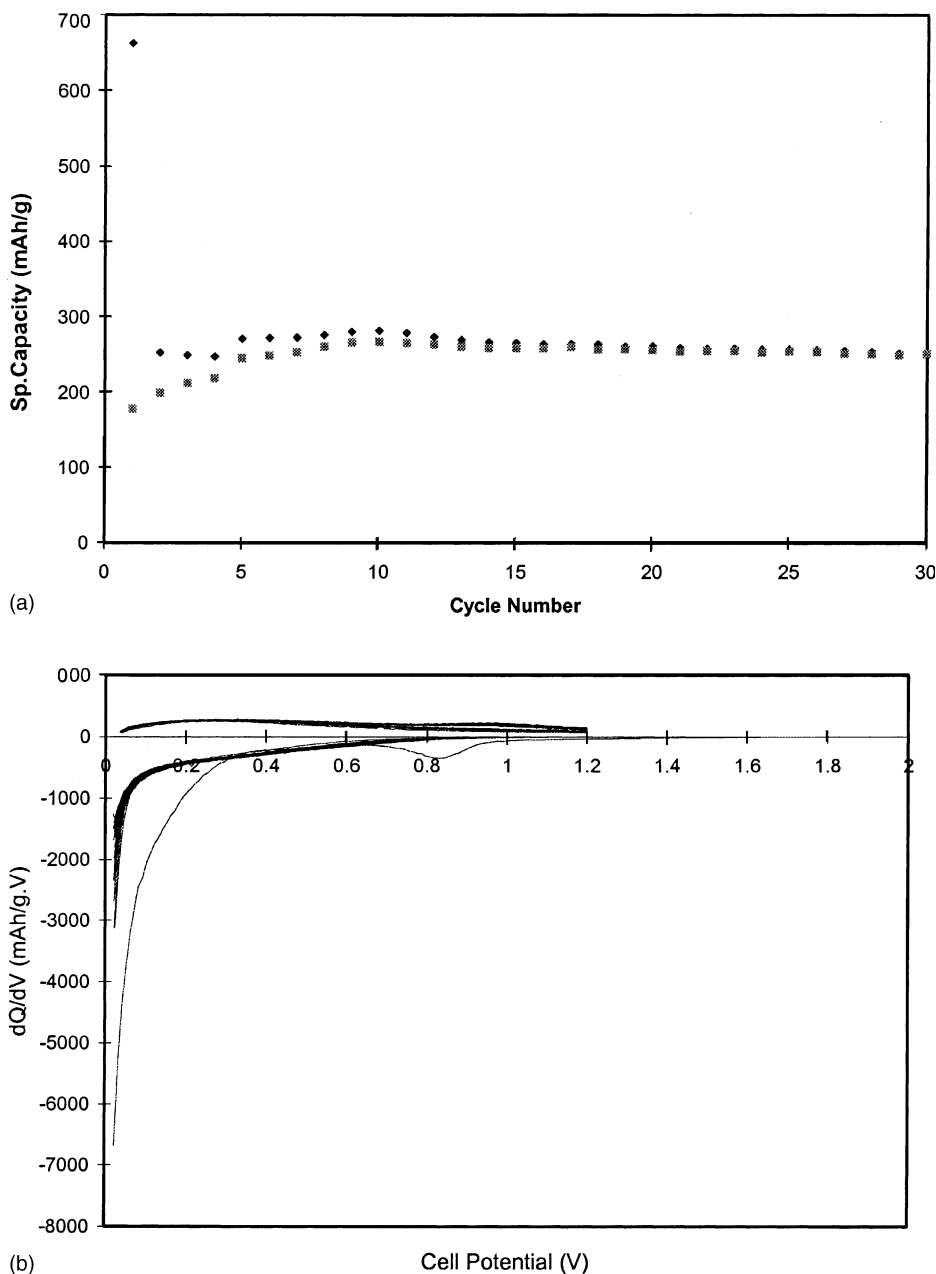

Fig. 6. Cyclic electrochemical response, at 100 μA over the range of 0.02–1.2 V, of macronet, pyrolized at 600 °C for 1 h under argon flowing at 95.7 mL/min with a heating rate of 10 °C/min: (a) capacity vs. cycle number; (b) differential capacity.

The selected area electron diffraction pattern (Fig. 5c) showed spots typical of nanocrystalline materials, corresponding to the (2 0 0) and (1 0 1) planes as well as the (2 2 0) and (2 1 1) planes of tetragonal (metallic) tin. The presence of rings along with spots indicates the crystal size of tin to be in the nano range.

In order to determine what amounts of carbon and tin remained in the composite after pyrolosis, a sample was analyzed using TGA in air. The product from the air TGA experiment was analyzed using XRD and found to be all SnO_2. Since the final mass was 55% of the original mass, the amount of tin present in the original sample can be cal-

culated. The result of this calculation was that the molar ratio between C:Sn is approximately 12:1. A composite of this concentration has a theoretical capacity of 448 mAh/g. This is lower than the first few discharges of the composite due to the contribution of the carbon matrix. The irreversible loss is due to reaction of lithium ions with amorphous carbon. This is a hard carbon, which is also active, though no intercalation reaction occurs. From Fig. 6a and b, one can see that plain purolite, heat treated to 600 °C, has some capacity itself. So this nanocomposite is not actually an active/inactive anode, but rather a high capacity/low capacity nanocomposite.
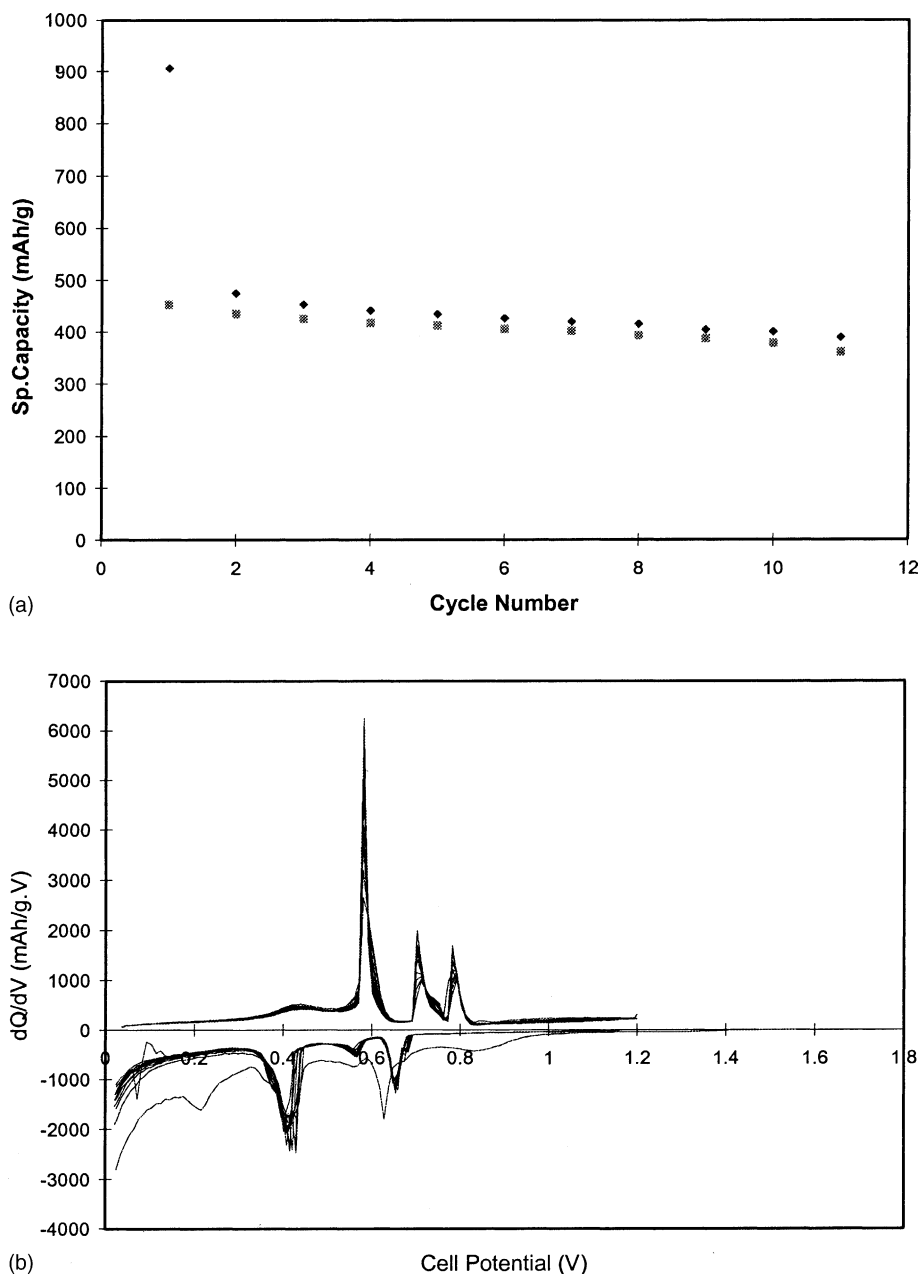

Fig. 7. Cyclic electrochemical response, at 100 μA over the range of 0.02–1.2 V, of tin/carbon derived from tetraphenyltin and macronet, pyrolized at 600 °C for 5 h under argon flowing at 95.7 mL/min with a heating rate of 10 °C/min: (a) capacity vs. cycle number; (b) differential capacity.

Although the microstructures of the samples obtained after 1 and 5 h of heat treatment are very similar, the electrochemical responses are quite different (Fig. 7a and b). Upon comparison with the 1 h sample, it is apparent that the first cycle discharge of the 5 h sample is lower, but it also cycles at a lower capacity. It appears that there is just a lower concentration of tin in the longer heat treated sample. This could be due to evaporation of the active phase during the longer duration at high temperature.

In order to lower the irreversible loss, it appears that a heat treatment for longer time is not necessary. Rather, higher temperatures could be the method needed to reduce the irreversible loss although tin loss will be a problem. Nevertheless, the performances of the Sn/C nanocomposites show that the carbon formed from pyrolosis of a polymer can withstand the stresses involved with lithium alloying and de-alloying with tin, and give promise to future optimization of the material.

4. Conclusions

The composites of tin and carbon tested in this study showed capacities greater than commercially-used graphite anodes. The stable cycling was a promising sign for the viability of the materials as next-generation anode materials, however, further refinement of processing variables could help decrease the irreversible loss of capacity in the first cycle. It was shown that the shorter heat treatment time retained more active mass than extended heat treatment. In addition, the use of high-energy mechanical milling proved to be an effective mixing method to produce a homogeneous composite. Once the first cycle loss is decreased to a reasonable level, these composites would be ready for a simple, two-step milling pyrolysis industrial production process for manufacture of lithium-ion battery anodes.

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