Scalable Solvo-plasma Production of Porous Tin Oxide Nanowires

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ABSTRACT

This paper reports a fast, scalable method for synthesizing tin oxide nanowire powder using cheap starting material of commercial tin oxide particles and an atmospheric microwave plasma reactor. Specifically, the synthesis concept involves plasma oxidation of tin oxide powder combined with potassium hydroxide for few seconds to a minute which is orders of magnitude lower than that using hydrothermal or vapor-liquid-solid (VLS) techniques. Even at lab scale, large-scale production of tin oxide nanowire powder as high as 10 grams per hour has been produced. Systematic studies reveal nucleation and growth of K_2SnO_3 nanowires from molten alloy involving KOH and tin oxide. A simple annealing step is used to convert K_2SnO_3 intermediate nanowires into pure tin oxide nanowires. The extremely short reaction time of 20 seconds is three orders of magnitude faster than that of traditional hydrothermal method. It was shown that our tin oxide nanowire powder shows a high reversible capacity of 848 mAh g⁻¹ after

55 cycles at a current density of 100 mA g⁻¹. The scalable production technique presented here and the applicability of resulting tin oxide nanowire powders makes it as suitable for practical implementation into lithium-ion battery applications.

Introduction

Tin oxide nanowires is one of the most promising 1D nanostructures for advanced applications in lithium-ion batteries¹, solar cells², sensors³, optical devices⁴, and electronic devices⁵. However, the wide-spread use of nanowire based materials in to energy device applications has been limited due to the fact that there are no scalable manufacturing methods, yet. For example, the lithium-ion battery electrodes will require production on the order of kilograms even for simple pouch cell prototyping. Thus, the development of reliable, reproducible and simple techniques for production of tin oxide nanowires and their testing into energy devices is of great interest. Up to date, several approaches have been proposed to prepare tin oxide nanowires including chemical vapor deposition⁶, laser ablation⁷, template method⁸ and most predominantly hydrothermal technique⁹.

Hydrothermal synthesis has been traditionally used to prepare nanostructured materials including nanoparticles and nanowires. However, this approach requires long time scale, high pressure, multiple steps and expensive precursors¹⁰. Further, in most cases, hydrothermal techniques require the use of surfactant to control the nanowire growth. Also, no clear mechanism for tin oxide nanowires have been proposed. Importantly, the hydrothermal techniques are limited to lab scale (few milligrams to hundred milligrams a batch)^{11, 12}. Two recent hydrothermal based approaches are microwave assisted hydrothermal and continuous flow hydrothermal method, which can increase the production rate to about 5g/day and 10g/hour, respectively^{13, 14}. However, these hydrothermal methods have been shown to work only for nanoparticles (NPs) and not to make nanowires. Another popular method for making nanowire growth is that using vapor-liquid-solid (VLS) process for many semiconductors including tin oxide⁶. However, VLS processes require the use of low pressure, high temperatures, high fabrication cost and Au as catalyst.

In this work, we report a facile, fast "solvo-plasma" production of tin oxide nanowires using tin oxide particles as a low-cost source. This study demonstrates, for the first time, the

direct conversion of tin oxide particles to tin oxide nanowires with reaction time scales on the order of a minute or lower. More importantly, various experimental studies are used to understand the underlying principle of nucleation and growth of tin oxide nanowires in the presence of alkali hydroxides. Thin films made using the resulting tin oxide nanowire powders are also investigated for their performance as high capacity anodes in lithium ion batteries.

Experimental

Tin oxide nanowires are synthesized in an upstream microwave plasma reactor whose details have been described in detail elsewhere¹⁵. Briefly, tin oxide particles (1÷5 μm size, Atlantic Equipment Engineer, Inc) are mixed with KOH powder in a 3:1 ratio by weight and water is added to make the precursor paste. The precursor paste is then sprinkled on the top of a 1 x 1 inch quartz substrate (Figure 1a), which is then carefully exposed to the plasma flame at power of 1.0-1.4 kW, 8 lpm of Air flow for 10 seconds to 5 min. The as-synthesized materials are dispersed in 0.1 M HCl solution for 1 h to facilitate ion exchange, washed with deionized water, and annealed by exposure to plasma flame for 1 to 5 min. The samples are characterized using a scanning electron microscope (SEM) (FEI Nova 600), X-ray diffraction (Bruker D8 Discovery with Cu $K\alpha$ radiation), and a transmission electron microscope (TEM) (Tecnai F20 FEI TEM operating at 200 kV).

Figure 1. Photograph of an actual experiment: plasma exposure of tin oxide precursor and KOH paste on quartz substrate a), a bottle of tin oxide nanowire powder of 10 grams produced in one hour reaction time

The electrochemical measurements are performed using a battery tester (16 Channel Arbin Instruments, USA). The electrode materials were prepared using 70 wt% active materials with 20 wt% AB (acetylene black) and 10 % PVDF binder in NMP. The well-mixed slurry was casted onto a copper foil using a doctor blade. The electrode is dried at 180°C for 4 h under vacuum. The typical loading of active materials is 0.2 to 0.5 mg/cm². The CR-2032 coin-type assembling is performed in a dry argon-filled glove box. The electrodes are separated by two pieces of glass fiber filter. The electrolyte solution was 1M LiPF₆-EC:DMC (1:2 by volume).

Results and Discussion

All experiments are performed using inexpensive, commercial tin oxide particles without any further purification by mixing them with KOH and exposing to atmospheric plasma flame for 15 seconds to 1 minute. Using a 1-inch square substrate, we were able to demonstrate production of tin oxide nanowires at a scale of 10 grams in one hour (Figure 1b). The exposure time used here is less than a minute which is about 3.5 orders of magnitude faster than that using a hydrothermal method. Figure 2a shows SEM images of the resulting tin oxide nanowires that are 2 microns in length and about 50 to 100 nm in diameter. The TEM images of tin oxide nanowires show highly porous structures of tin oxides, which is due to HCl ion exchange and plasma annealing step (Figure 2b, c). The BET surface area of the porous tin oxide nanowires turned out to be 37 m²/g. The BET surface area could be increased further by controlling the ion exchange and annealing parameters. The phase transformation of intermediate nanowires to tin oxide nanowires created the porous structures where potassium and water vapor are removed. The porous structures consisted of interconnected tin oxide nanoparticles. The underlying mechanism for porous structure formation seems to be similar to that suggested in many other reports using hydrothermal synthesis with additional annealing step⁹. However, the actual mechanism is not completely clear in terms of how phase transformation leads to porous nature within the nanowires. Figure 2c also revealed the twining effect where the boundary in the top left corner clearly showed merging of two nanowires. The merging maybe due to the high surface diffusion of tin atoms on nanowire surface under plasma exposure¹⁶. The HR-TEM

image in Figure 2d showed the match of interplanar lattice spacing of 3.35 Å and 2.64 Å for the plane (110) and (101), respectively.

Figure 2. Scanning electron microscopy of tin oxide nanowire powder after annealing a), TEM images b) and c) showing the porous structure and twinning effect, (inset) SAED of tin oxide nanowires, HR-TEM image showing the matching interplanar lattice spacing of (110) and (101) plane of tin oxide nanowires d).

Figure 3. Powder XRD pattern of samples after annealing in plasma showing the pure phase of rutile tin oxide while the as-synthesized samples showing additional intermediate compounds.

Figure 4. HR-TEM images of as-synthesized samples showing well-matched interplanar lattice spacing of rutile tin oxide in (a) and (b), $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ in (c) and (d)

The powder XRD pattern of tin oxide nanowires after annealing in plasma is shown in Figure 3. The diffraction peaks revealed that tin oxide nanowires have tetragonal crystal structure with lattice parameters $a = b = 4.74 \text{ \AA}$ and $c = 3.18 \text{ \AA}$, corresponding bulk rutile tin oxide (PDF-00-005-0467). The selected area diffraction pattern also confirms the pure phase tin oxide as in Figure 2b. No other impurity peaks are detected in the tin oxide nanowire samples after annealing in plasma. The Raman spectroscopy of the tin oxide nanowires after annealing shows fundamental peaks at 474 , 633 , and 775 cm^{-1} that is well matched with rutile tin oxide¹⁷ (Figure S1). In addition to the peaks of tin oxide phase, the XRD pattern of as-synthesized samples (Figure 3) showed peaks of $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ (PDF-00-019-0993). The HR-TEM images showed well-matched interplanar lattice spacing of SnO_2 (Figure 4a, b) and layered structure $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ (Figure 4c, d). The lattice spacing of $6.54 \text{ \AA}$, $3.16 \text{ \AA}$ and $2.78 \text{ \AA}$ correspond to the peaks of 13.5° , 28.2° , and 32.2° of $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$. EDS analysis shows that the as-synthesized nanowires contain about 13 at.% of potassium. This confirms that the intermediate compound or as-synthesized compound is K_2SnO_3 . The hkl index of $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ is not available to our knowledge. However, the lattice spacing of tin oxide in Figure 2d shows that tin oxide nanowires grown along $[001]$ direction that is in agreement with previous reports^{10, 18}. $[001]$ direction has highest surface energy that favored the 1D growth^{11, 19}.

Figure 5. SEM images of (a) tin oxide precursor and as-synthesized K_2SnO_3 nanowires at weight ratios of SnO_2 to KOH of (b) 3:1, (c) 1:1, (d) 1:3. Experiments were conducting using plasma flame with power of 1.2 kW at a duration of 60 seconds

Even though, the above results clearly demonstrate the formation of one-dimensional structures with plasma exposure of tin oxide powder mixed with KOH, there are several questions remain unanswered about the observed 1-D growth. So, experiments were conducted for different weight ratios of SnO_2 to KOH to understand initial stages of growth. Figure 5 showed the SEM images of as-synthesized samples at different weight ratios of SnO_2 to KOH in comparison with the tin oxide particle precursor. Thin, short nanowires of about 70 nm in diameter and 2 to 4 microns in length are observed at weight ratio of 3 to 1. When the weight ratio for precursors decreased to 1 to 1, there is more change in the nanowire diameter and length. As shown in Figure 5c, the resulting nanowires are of 100 to 300 nm in diameter and 20 to 30 microns in length. The image also shows that nanowires bunch up and seem to be fusing together for samples grown using precursors at a weight ratio of 1 to 1. Such sintering of nanowires could be the reason for twining effect seen in Figure 2c. The nanowire diameter increased further when using precursor ratio to 1:3. However, there is the presence of excess KOH on top of nanowires that make it difficult to quantify diameters. The increase in diameter for resulting nanowires can probably be explained with decreasing supersaturation with decreasing SnO_2 to KOH ratio from 3:1 to 1:3.

Figure 6. SEM image of as-synthesized sample using a) SnO_2+KCl , b) $\text{Sn}+\text{KOH}$, c) $\text{Sn}+\text{KCl}$, d) $\text{SnO}+\text{KOH}$, e) K_2SnO_3 , f) SnO_2+KOH . Sample a) to e) prepared using plasma heating for 60 seconds, sample f) prepared using thermal heating at 900°C for 2 hrs.

Experiments were also performed using different tin precursors such as tin oxide, tin and tin monoxide to determine their impact on reaction time scales and nanowire growth rates. As shown in Figure 6, K_2SnO_3 nanowires are obtained using a mixture of tin metal powder or tin mono-oxide particles with KOH . Nanowires obtained using tin metal powder have random diameters and lengths. Nanowires obtained using tin mono-oxide have diameters of about 50 to 100 nm and lengths up to 50 microns (Figure 6d). In fact, tin oxide nanoparticles are always found together with K_2SnO_3 nanowires when tin metal powder used as starting material (Figure 6b, c). No nanowires formed with either mixture of H_2O or KCl with tin oxide particles (Figure 6a). In another experiment, the same mixture of tin oxide particles and KOH at mass ratio of 3 to 1 is put onto a quartz substrate and was thermally heated to 900°C for 2 hours in a box furnace. The similar tin oxide nanowire morphology but longer in length is observed (Figure 6f).

Figure 7. Schematic showing the proposed growth mechanism for growth of tin oxide nanowires. a) Mixture of tin oxide particle and KOH in plasma flame, b) KOH got melted into free moving K^+ and OH^- ions, c) diffusion of oxygen radicals, K^+ and OH^- ions into tin oxide particle to form K_2SnO_3 , d) K_2SnO_3 nucleus forming under supersaturation of K_2SnO_3 , e) layered structure K_2SnO_3 grown due to active edge.

Based on all the experimental observations, we propose a mechanism to explain tin oxide nanowire growth in a three step sequence as shown in Figure 7: (1) continuous dissolution of tin oxide particles with KOH results in supersaturation of tin oxide in molten phase containing K-Sn-O , (2) phase segregation and bulk nucleation of K_2SnO_3 on the surface of tin oxide particles due to non-stable molten phase containing K-Sn-O , (3) K_2SnO_3 formation started from surface of tin oxide particles by diffusion-driven self-arrangement and basal attachment²⁰. The resulting $\text{K}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ phase has layered structure with active sites at the end making it grow faster at ends leading to the one-dimensional growth of layer structured K_2SnO_3 nanowires. Extra exposure of K_2SnO_3 nanowires also result in tin oxide nanowires. So, the final product can contain pure tin oxide nanowires. But, based on our experimental data, the formation of K_2SnO_3 1-D structures occurs first and then transforms to pure phase tin oxide nanowires. Previous studies using hydrothermal method suggested that the formation of tin oxide nanowires was due to decomposition of intermediate phase of $\text{Na}_2\text{Sn}(\text{OH})_6$ to tin oxide nuclei followed by condensation to form tin oxide nanowires^{10, 21}.

In principle, KOH can easily be melted into free moving K^+ and OH^- ions under plasma exposure or thermal heating up to 406°C or higher. Indeed, an in-situ measurement of surface

temperature using a Pyrometer which showed the temperature to be lower than its minimum detection limit of 475°C after 17.4 seconds of exposure time. KOH probably melted sooner than 10 seconds of exposure time as shown in Figure S2. Free moving K^+ and OH^- ions and oxygen radicals^{22, 23} produced by atmospheric plasma flame quickly diffuse into tin oxide structure to form a thin layer of molten melted of K_2SnO_3 on the surface of tin oxide particles.

Fast diffusion of K^+ , OH^- ions and oxygen radicals into tin oxide particles make tin oxide quickly dissolved to form a molten phase containing K, Sn and O in which the K_2SnO_3 phase forms and nucleates out. K_2SnO_3 is a layered structure itself in which the growth predominantly happens at its ends (at edge sites). The growth direction along the wide d-spacing of 6.54 Å was confirmed in all of the TEM analysis of the as-synthesized samples. Availability of K^+ and OH^- ions make the edge, where nucleus is in contact with molten K_2SnO_3 , is the only active edge that nucleus can propagate to form nanowire.

Under thermal heating, the reaction (1) can be revised as shown in reaction (2). Under thermal heating up to 900°C, KOH also became molten into free moving K^+ and OH^- ions. The same growth mechanism can be applied in case of thermal heating. Gibbs free energy of K_2SnO_3 is not available yet. However, by assuming that the Gibbs free energy of K_2SnO_3 is a specific value of X_{KSO} , then we could calculate Gibbs free energy change of above reactions at 900°C. $G_{1,900}$ and $G_{2,900}$ are of $X_{KSO}+256.45$ and $X_{KSO}+432.84$ kJ. The difference of 176.39 kJ in Gibbs free energy indicates that presence of plasma makes the reaction (1) more spontaneous than reaction (2). Indeed, fast nanowire growth rate of 1 m/min is observed with plasma heating while thermal heating resulted in slow nanowire growth rate of 0.04 m/min. As a main specie of atmospheric plasma, highly active oxygen radicals²³ with K^+ , OH^- ions diffuse quickly into tin oxide structure to form K_2SnO_3 . Fast diffusion of oxygen radicals, K^+ , and OH^- ions results in fast growth rate of nanowires in plasma heating.

In another experiment, tin mono-oxide is used as starting material. The reaction occurs as reaction (3). The Gibbs free energy ($G_{3, 900}$) is calculated to be $X_{\text{KSO}} + 87.75$ kJ which is 168.70 kJ lower than that of reaction (1) where tin oxide is used. As expected, the use of tin mono-oxide has increased the nanowire growth rate up to 40 m/min that is 40 times faster than the use of tin oxide with plasma heating and 1000 time faster than the use of tin oxide with thermal heating.

The use of tin metal as starting material made a big difference. Tin metal can react directly with KOH to form K_2SnO_3 nanowires as reaction (4). Tin metal can also get oxidized to tin mono oxides, tin oxides and then these oxides react with KOH to form K_2SnO_3 nanowires. Therefore, random nanowire lengths are observed as tin mono-oxides tend to form long nanowire while tin oxides produce short nanowires. Several resulting tin mono-oxide or tin oxide particles, did not get in contact with KOH and are observed as particles in any experiments using tin metal as starting material.

Figure 8. XRD pattern of a) K_2SnO_3 particle precursor, b) as-synthesized nanowires using K_2SnO_3 particles, c) as-synthesized nanowires using tin mono oxide particles, d) tin mono oxide particle precursor, e) as-synthesized nanowires using tin oxide particles for 10 seconds exposure

time, f) as-synthesized nanowires using tin oxide particles for 60 seconds exposure time, g) SnO_2 particle precursor

The structure of as-synthesized nanowires using different starting materials for tin is investigated to understand the transformation of tin-based particle precursor to K_2SnO_3 nanowires. Figure 8 shows the XRD pattern of as-synthesized nanowire samples using tin oxide, tin mono-oxide and K_2SnO_3 particles. Clearly, the nanowires prepared using K_2SnO_3 particles exhibit the same peaks of K_2SnO_3 phase as shown in Figure 8a and 8b. Peaks of K_2SnO_3 appear in the samples prepared using tin oxide particles after 10 seconds of exposure time (see Figure 8e). As the exposure time increased to 60 seconds, the intensity of these peaks increase significantly as shown in Figure 8f. In other experiment with K_2SnO_3 particles as precursor, K_2SnO_3 remains the same phase but the morphology changes from particle form to nanowire form (Figure 8a, b and Figure 6e). The formation K_2SnO_3 nanowires using K_2SnO_3 particles will be investigated for more detail in another study. The use of tin mono oxide as precursor does not show the formation of K_2SnO_3 . As shown in Figure 6d, the long nanowires prepared using tin mono oxide probably experience high temperature gradient and transform directly to tin oxide phase under plasma exposure. This is advantageous as it can further increase the production capacity of tin oxide nanowires using a roll-to-roll setup and expected to introduce a new commercial production of tin oxide nanowire powder for practical applications such as lithium ion batteries, solar cells. As shown in Figure 9, the production capacity can be controlled by the thickness of precursor film, width of belt, speed of belt and plasma power. In our setup, the belt width of 2 inches, the plasma power of 0.8 to 2.5 kW, belt speed of 1 to 2 inches per minutes for exposure time of 30 seconds to 1 minute, the precursor film thickness 100 μm to 1 mm. A simple calculation for plasma power of 1.5 kW, belt speed of 1 inch per minute, results in a production rate of 31 to 310 grams/hour for precursor thickness of 100 μm to 1 mm using estimated density of dried precursor film of 4 g/cm^3 .

Figure 9. a) Roll-to-roll setup for commercial production of tin oxide nanowire powder; b) A photo of lab-scale conveyor belt

Availability of porous tin oxide nanowires in large quantities should be very interesting for prototyping applications in batteries, gas sensors and catalysts²⁴. For lithium ion battery application, tin and its oxides are one of the most important anode materials due to their highest volumetric capacity and decent gravimetric capacity of 7.25 Ah cm^{-3} and 994 mAh g^{-1} for tin, 5.47 Ah cm^{-3} and 781 mAh g^{-1} for tin oxide, respectively^{25, 26}. Moreover, nanowire structures are also known to provide fast charge transport and stress accommodation for lithium ion batteries. In spite of these advantages, tin oxide has been shown to suffer from two major challenges. In addition to mechanical degradation due to volume change (about 250%)²⁷, tin oxide also suffers from chemical degradation, i.e., pulverization of tin oxide into tin and non-conducting Li_2O phase. Typically, tin and tin oxide based materials suffer from large irreversible capacity loss in

first few cycles and continue to fade in capacity with cycling. Recently, Meduri et al. reported that tin nanocluster on tin oxide nanowires could accommodate the volume expansion and increase the conductivity which is resulted in high reversible capacity of 814 mAh g^{-1} after 100 cycles¹. Based on this concept, the resulting nanowire powders from our synthesis have been treated and tested in lithium ion battery anodes.

Figure 10. Galvanostatic curves a) and discharge capacity vs. cycle number b) of tin nanoclusters covered tin oxide nanowires at current density of 100 mA/g

The resulting tin oxide nanowire powders from our plasma oxidation technique are partially reduced in a hydrogen microwave plasma reactor to form tin nanocluster on the surface

of tin oxide nanowires. The tin nanocluster covered tin oxide nanowires are used as active materials for battery testing. To confirm the durability of the tin oxide nanowire electrodes, all of the electrodes are charged and discharged in the voltage range of 0.005-2.2 V at a current density of 100 mA/g (Figure 10). The high initial capacity of 1700 mAh g⁻¹ is due to the decomposition of electrolyte to form solid electrolyte layer, the reduction of tin oxide to tin, and the insertion of Li ion into tin oxide and tin to form Li_{4.4}Sn alloy. The capacity decreases in first few cycles and remained stable at 614 mAh g⁻¹ after 55 cycles. Another set of experiments with lower loading of 0.2 mg/cm² shows exceptional high initial capacity of 3059 mAh g⁻¹. The capacity drops quickly in the second cycle to 1623 mAh g⁻¹ and remains stable at 848 mAh g⁻¹ after 55 cycles at the same current density of 100 mA/g. This is one of the highest capacity retentions obtained for tin oxide. We believe that this high capacity is derived from (1) porous structure of tin oxide which provide high electrode-electrolyte contact area to accommodate the volume change during cycling and to provide pathways for fast transportation of lithium ions and easy accessibility of electrolytes²⁸; (2) lower loading leading to minimum delamination which has been reported as a major issue with tin oxide nanowires²⁹.

Conclusions

In summary, a simple concept for fast, scalable method is presented and studied for converting tin oxide particles to tin oxide nanowires by mixing it with potassium hydroxide and exposing to an atmospheric microwave plasma reactor. The reaction time scales have been found to be on the order of few tens of seconds to a minute which makes this technique highly scalable. A production capacity of 300 grams per hour can be obtained by a simple lab-scale roll-to-roll setup. A systematic set of experiments revealed the presence of intermediate phase (K₂SnO₃.H₂O) formation which could be held responsible for the observed one-dimensional growth. Further acid wash and annealing of K₂SnO₃.H₂O allowed for formation of porous tin oxide nanowires. The resulting porous tin oxide nanowires showed a high reversible capacity of 848 mAh g⁻¹ after 55 cycles at a current density of 100 mA/g.

ASSOCIATED CONTENT

Supporting Information: Raman spectrum of porous tin oxide nanowires, In-situ measurement of sample surface temperature, Thermodynamic data and growth rate calculations.

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