Nanostructured Composite Electrodes for Lithium Batteries

(Final Report for Grant No. DE-FG02-01ER15220)

PI: Meilin Liu, MSE; Co-PI: James Gole, Physics
Georgia Institute of Technology
Atlanta, GA 30332-0245

A. Brief Summary of Technical Progress

Multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs)-based electrodes:^[1-2]

Both MWNTs (prepared through catalytic decomposition of a ferrocene-xylene mixture) and SWNTs (prepared by electric arc discharge) are studied as anodes for rechargeable lithium batteries. While the SWNTs contain some amorphous carbon, the MWNTs were extremely pure and free of amorphous carbon. Various electrochemical techniques have been used to study the electrochemical insertion (extraction) of lithium into (from) both MWNTs and SWNTs. Results indicate that lithium insertion and extraction is highly reversible. In addition, the rate capability and cyclability of the MWNT is quite good. The excellent reversibility and small hysteretic loss of the MWNTs is attributed to their extremely pure structural character. Apart from an irreversible capacity fade during the first 5 cycles, there is little capacity fade during the subsequent 80 cycles. The regular MWNTs were further doped with nitrogen and chopped using an acid treatment in order to explore the effect of these modifications on their electrochemical behavior. For further details please see References [1] and [2].

Three-dimensional nano-structured foam electrodes prepared by an electrochemical deposition process:^[3-5]

Nanoporous metallic electrodes (of Cu and Sn) have been successfully prepared using an electrodeposition process. This represents a novel way of creating porous structures that allow not only fast transport of gas and liquid but also rapid electrochemical reactions due to high surface area. The sizes of the pores and the branches in the foam wall were tunable depending on the composition of the deposition bath. The porous structures are ideally suited for electrodes in electrochemical devices such as fuel cells, batteries, and chemical sensors. From the electrochemical co-deposition of Cu and Sn, three-dimensional (3-D) porous Cu_6Sn_5 alloy was fabricated as a negative electrode for rechargeable lithium batteries. The walls of the foam structure are highly-porous and consist of numerous small particles. The Cu_6Sn_5 samples delivered a reversible capacity of about 400 mAhg^{-1} up to 30 cycles. In particular, at an extremely high current drain of 10 mAcm^{-2} (20C rate), the obtainable capacity was more than 50% of the capacity at 0.5 mAcm^{-2} (1C rate). The extraordinary rate capability is attributed to the unique porous structure and the large surface area of the 3-D porous Cu_6Sn_5 for fast mass transport and rapid surface reactions. [3-5]

Meso- to macro-porous tin oxide electrodes prepared by an anodization process:^[6,7] Highly open, nano-porous structures of tin oxide have been fabricated for the first time using an anodic oxidation process. The resulting tin oxides are characterized by irregular channels with diameter of several tens nanometers nearly perpendicular to the tin substrate. Further, numerous disk-shaped nano- (micro-) pores are also observed inside the tin oxide. The as-prepared amorphous tin oxides can be transformed to a crystalline stannic structure after annealing with little micro-structural changes. The powder specimens were prepared by scratching the anodic tin oxides from substrates and then crashing the tin oxides ultrasonically to make fine powders. Both as-prepared and annealed tin oxide powder specimens were tested as anode materials for lithium batteries. The reversible capacity of both samples is about $700\text{--}800 \text{ mAhg}^{-1}$ after the first lithium insertion process. ^[6,7]

Nanostructured electrodes prepared by a glycine-nitrate process:^[8] Porous nano-structured spinel LiMn_2O_4 has been successfully synthesized using a glycine-nitrate combustion process. The average primary particle size of the as-synthesized powders was about 10 nm, but increased to about 100 nm with improved crystallinity after calcination at 800°C for 2hrs. Yet, the calcined powders were still highly porous and displayed reversible capacity of about 112 mAh/g at a discharge rate of $49.0 \text{ }\mu\text{A/cm}^2$ (C/5 rate). At a high discharge rate of 2.44 mA/cm^2 (10 C rate), the obtainable reversible capacity was 57 mAhg^{-1} . [8]

Porous silicon (PS)-based nanostructured alloy electrodes:^[9,10,16] Silicon wafers (100) were chemically and electrochemically etched to produce porous silicon (PS) with honeycomb-type channels and nanoporous walls. The diameters of the channels are about 1 to $1.5 \text{ }\mu\text{m}$ and the depth of the channels can be up to $100 \text{ }\mu\text{m}$. The etching

conditions have been studied systematically to obtain optimum microstructures. The electrochemical behavior of the PS samples has been studied; lithium can be readily deposited on the walls of PS and the alloying/dealloying of lithium is quite reversible. The channeled structure of the PS electrodes remained essentially the same after 30 CV cycles in spite of the severe deformation of the channel wall during the repetitive lithium alloying/dealloying process. The specific capacity of the PS was critically dependent on the degree of activation of the PS before the galvanostatic charge/discharge experiment. For example, the specific capacity of the PS, pre-activated by 20 CV cycles, reaches $43 \mu\text{Ahcm}^{-2}$ (at 20th galvanostatic cycle), while the capacity increased by 40 % ($60 \mu\text{Ahcm}^{-2}$) after subsequent 10 CV cycles. The CV cycling number needed to fully activate the PS channel decreases with the morphology of larger pores. And the degradation process is also deferred. The redox reaction shows good reversibility up to 60 CV cycles before the degradation begins. The discharge capacity is about $70 \mu\text{Ahcm}^{-2}$ after 40 CV cycles. Besides, we have successfully used the PS as a matrix for Si-Li-based alloy electrodes. Other component(s) of the electrode can be incorporated into the PS either by electrochemical plating, electroless metallization, or by kinetically controlled vapor deposition (KCVD). For further details please see Reference [9,10].

Construction of a combustion chemical vapor deposition (CCVD) system:^[11] A state-of-the-art system for combustion CVD has been designed and constructed in our laboratory capable of producing nanoparticles and nanostructured electrodes or interfaces of various materials. Combustion CVD is an open-air, flame-assisted CVD method. It is a non-line-of-sight process capable of producing powders and a wide range of coating morphologies from smooth-and-dense to porous. In liquid fuel combustion CVD, chemical precursors of the material are dissolved in a flammable organic solvent. The resulting solution is aerosolized and burned in air. Powders or coatings are usually deposited onto a substrate placed near the end of the flame. Specific compositions are easily obtained by adjusting the ratios of the various chemical precursors in the solution. The ability to deposit CVD coatings using inexpensive precursors (e.g., nitrates) without the use of a furnace or vacuum chamber is economically attractive.

Nanostructured powder electrodes prepared by combustion CVD:^[11,12] Nanostructured powders, including LiCoO_2 , LiMn_2O_4 , and SnO_2 , have been successfully produced using our CCVD system. TEM and XRD analyses show that the synthesized powders have desired structures with particle sizes of 10 to 30 nanometers. The initial capacity of nano-sized LiCoO_2 powders is about 120 mAh/g and 70% percent of the capacity was retained at a very high discharge rate (2C rate). However, the rate of degradation in performance was relatively high and the cause of degradation is still under investigation. Further, doped- LiMn_2O_4 such as $\text{LiCo}_{1/8}\text{Mn}_{15/8}\text{O}_4$ has also been successfully synthesized by CCVD, as confirmed by EDX analysis. Currently, we are further optimizing the deposition conditions so that nanostructured composite electrodes can be directly deposited on current collectors (including Al or Cu) for lithium cells.^[11,12]

Vertically oriented square-shaped SnO_2 nanotube arrays created by combustion CVD:^[13,14] Tin dioxide box beams, or tubes with square or rectangular cross sections, were synthesized on quartz substrates using a combustion chemical vapor deposition (CVD) method in an open atmosphere at 850°C to 1150°C . The cross-sectional width of the as-synthesized SnO_2 tubules was tunable from 50 nm to sub-micrometer depending on synthesis temperature. Each tubule was found to be a single crystal of Rutile structure with four {110} peripheral surfaces and <001> growth direction. Although several growth patterns were observed for different samples, the basic growth mechanism is believed to be a self-catalyzed, direct vapor-solid (VS) process, where most new material was incorporated into the bottom parts of the existing SnO_2 tubules through surface diffusion. The tubes are readily aligned in the direction perpendicular to the substrate surface to form tube arrays. These well-aligned SnO_2 tubule arrays with tunable tube size could be the building blocks or templates for fabrication of functional nano-devices, especially those relevant to energy storage and conversion such as nano-batteries, nano-fuel cells, and nano-sensors.

Nanostructured porous columnar thin film deposited by a combustion chemical vapor deposition (CCVD)^{[11, 15]:} Thin porous film of electrodes (such as SnO_2 and LiCoO_2) with columnar structure were deposited on $\text{Si/SiO}_2/\text{Pt}$ or $\text{Si/SiO}_2/\text{Au}$ substrates by a combustion CVD process. The thickness were readily controlled by the deposition time, varying typically from 1 to 5 μm . The average size of secondary particles is about 300 nm, and the average size of primary particles is about 8 nm. The electrochemical behaviors of the thin film electrodes have been studied. In the case of negative electrode for rechargeable lithium batteries, tin oxide thin film exhibits high specific discharge capacity and good cycleability. There is a slight increase in capacity with increasing cycle number. The initial specific capacity is close to $2\text{mA}/\text{cm}^2$, and is gradually increased to a maximum value $\sim 3.3 \text{ mA}/\text{cm}^2$. It displayed a reversible capacity of about $3\text{mA}/\text{cm}^2$ up to 80 cycles at a charge/discharge rate of $0.3 \text{ mA}/\text{cm}^2$. When discharged at $0.9 \text{ mA}/\text{cm}^2$, the capacity obtained was about $2.1 \text{ mA}/\text{cm}^2$, 64% of the capacity of that at 0.3

mA/cm². [15] In the case of positive electrode, annealed LiCoO₂ thin film exhibits better electrochemical behavior than as prepared LiCoO₂ thin film. It could deliver a reversible capacity of ~0.07 mA/cm² in the initial discharge. About 75% of initial discharging capacity were obtained after 20 cycles.

B. List of Publications/Presentations Resulting from the Grant (DE-FG02-01ER15220)

1. Electrochemical Insertion of lithium into multi-walled carbon nanotubes prepared by catalytic decomposition, H. C. Shin, M. Liu, B. Sadanadan, and A. Rao, *J. Power Sources*, **112** (2002) 216-221.
2. Lithium Intercalation into Chemically-Etched Multi-Walled Carbon Nanotubes, H. C. Shin, M. Liu, B. Sadanadan, and A. Rao, *J. Solid State Electrochemistry*, **8**(11) 908-913, 2004.
3. Nanoporous Structures Prepared by an Electrochemical Deposition Process, H. C. Shin, J. Dong, and M. Liu, *Advanced Materials*, **15** (19) (2003) 1610-1614.
4. Three-Dimensional Porous Copper-Tin Alloy Electrodes for Rechargeable Lithium Batteries, H. C. Shin and M. Liu, *Advanced Functional Materials*, **15**(4), 582-586, 2005.
5. Copper Foam Structures with Highly-Porous Nanostructured Walls, H. C. Shin and M. Liu, *Chemistry of Materials*, **16**(25), 5460-5464, 2004.
6. Porous Tin Oxides Prepared by an Anodic Oxidation Process, H. C. Shin, J. Dong, and M. Liu, *Advanced Materials*, **16** (3) (2004) 237-240.
7. Porous Tin Oxide with Henycomb-like Channels for Lithium Batteries, H. C. Shin and M. Liu, Electrochemical Society, Pennington, NJ, PV 2003.
8. Nanostructured LiMn₂O₄ prepared by a glycine-nitrate process for lithium-ion batteries, Yuelan Zhang, H.-C. Shin, Dong Jian and Meilin Liu, *Solid State Ionics* **171** (1-2): 25-31 2004.
9. Porous Silicon-Based Electrodes for Lithium Batteries, H. C. Shin, Z. Shi, J. Gole, and M. Liu, *Solid State Ionic Devices III*, Edited by E. Wachman, K. Swider-Lyons, M. F. Carolan, F.H. Garzon, M. Liu, and J. R. Stetter, The Electrochemical Society, Pennington, NJ, PV 2002-26, pp. 518-525 (2003).
10. Porous Silicon Negative Electrodes for Rechargeable Lithium Batteries, H. C. Shin, J. Corno, J. Gole, and M. Liu, *J. Power Sources*, **139**(1-2) 314-320, 2005.
11. Nanostructured Electrodes Fabricated by Combustion CVD, Y. Liu, B. Rauch, and M. Liu, *Solid State Ionic Devices III*, Edited by E. Wachman, K. Swider-Lyons, M. F. Carolan, F.H. Garzon, M. Liu, and J. R. Stetter, The Electrochemical Society, Pennington, NJ, PV 2002-26, pp. 205-214 (2003).
12. Structural and Electrochemical Properties of Nanostructured Transition Metal Oxides by a Combustion Chemical Vapor Deposition (CCVD) Method, J. Dong, Y. Liu, H.-C. Shin, M. Liu, *J. Power Sources*, submitted.
13. Well Aligned "Nano-Box-Beams" of SnO₂, Y. Liu, J. Dong, and M. Liu, *Advanced Materials*, **16** (4) (2004) 353-356.
14. Growth of Vertically Oriented Square-shaped SnO₂ Tube Arrays, Y. Liu and M. Liu, *Advanced Functional Materials*, **15**(1), 57-62, 2005.
15. Nanostructured Columnar Tin Oxide Thin Film Electrode for Lithium Ion Batteries, Zhang, Y.; Liu, Y.; Liu, M., *Chemistry of Materials*, **18**, (19), 4643-4646, 2006.
16. Effects of the Morphology on the Electrochemical Behavior of the Porous Silica Anode for Lithium Ion Batteries Y. Zhang, J. Corno, J. Gole, M. Liu, in preparation.

Conference Presentations/Abstracts

1. Nanostructured Materials for Lithium Ion Batteries, H.-C. Shin, Z. Shi, A. Rao, J. Gole and M. Liu, presented in *Conference on Nanoscience and Nanotechnology*, Atlanta, Georgia, U.S.A., March 4-6, 2002.
2. Porous Silicon-Based Electrodes for Lithium Batteries, H.-C. Shin, W. Rauch, Z. Shi, L.T. Seals, J.L. Gole, and M. Liu, presented in 202nd Meeting of The Electrochemical Society, Salt Lake, UT, U.S.A., October 20-24, 2002.
3. Nanostructured Electrodes Fabricated by Combustion CVD, Y. Liu, B. Rauch, and M. Liu, presented in *202nd Meeting of The Electrochemical Society*, Salt Lake, UT, U.S.A., October 20-24, 2002.
4. Chopped Multi-Walled Carbon Nanotubes for Rechargeable Lithium Batteries, H.-C. Shin, M. Liu, B. Sadanadan, A.M. Rao, presented in *Conference on Nanoscience and Nanotechnology*, Atlanta, Georgia, U.S.A., October 30-November 1, 2002

5. Lithium Intercalation into Chemically-Etched Multiwalled Carbon Nanotubes, H.-C. Shin, M. Liu, B. Sadanadan, S. Chopra, and A. M. Rao, presented in Annual American Physical Society Meeting, Austin, Texas, U.S.A., March 3-7, 2003.
6. Nano-structured Electrodes for Lithium Batteries, H.-C. Shin, J. Dong, Y. Liu, M. Liu, presented in 105th Annual Meeting & Exposition of the American Ceramic Society, Nashville, Tennessee, U.S.A., April 27-30, 2003.
7. Nanosized Cathode Materials for Lithium Ion Batteries, J. Dong, Y. Liu, H. C. Shin, and M. Liu, presented in 77th American Chemical Society Colloid and Surface Science Symposium, Atlanta, GA, June 15-18, 2003.
8. Preparation of Nano-particle and Nanostructured Electrodes Fabricated by Combustion CVD, Y. Liu and M. Liu, presented in 77th American Chemical Society Colloid and Surface Science Symposium, Atlanta, GA, June 15-18, 2003.
9. Nano-structured Electrodes for Lithium Batteries Prepared by Templating Methods, H.-C. Shin and M. Liu, presented in 77th American Chemical Society Colloid and Surface Science Symposium, Atlanta, GA, June 15-18, 2003.
10. Fabrication of Nanostructured Electrode Materials by Chemical Synthesis, Y. Zhang, C. Xia, W. Rauch, and M. Liu, presented in 77th American Chemical Society Colloid and Surface Science Symposium, Atlanta, GA, June 15-18, 2003.
11. Nano-Porous Tin Oxides with Honeycomb-like Channels for Lithium Batteries, H. C. Shin and M. Liu, presented in 204th Meeting of The Electrochemical Society, Orlando, Florida, October 12-16, 2003.
12. Nanostructured Electrodes Prepared by Combustion CVD for Lithium Batteries, J. Dong and M. Liu, presented in 204th Meeting of The Electrochemical Society, Orlando, Florida, October 12-16, 2003.
13. Nano-Structured LiMn_2O_4 Positive Electrodes by a Glycine-Nitrate Process for Lithium Batteries, Y. Zhang, H.-C. Shin, J. Dong and M. Liu, presented in 205th Meeting of The Electrochemical Society, San Diego, Texas, May 9-14, 2004.
14. Development of Nano-Structure Materials for High Capacity Li-ion Batteries, Y. Zhang, H.-C. Shin, J. Dong, Y. Liu and M. Liu, presented to 1st Motorola Li-ion Conference, Lawrenceville, GA, Sept. 22-23, 2004.
15. Nanostructured Negative Electrodes for High Capacity Lithium Batteries, Yuelan Zhang, Heon-Cheol, Ying Liu, James Corno, James Gole and Meilin Liu, Strategic Energy Initiative Energy Research Exposition, Feb. 28 2006, Atlanta, GA.

C. Detailed Description of Significant Technical Progress

C. 1. Nano-Porous Structures Prepared by an Electrochemical Deposition Process

Ramification of electro-deposited metals such as copper and tin has been a very intriguing topic for several decades from both scientific and technological point of view.^[1,2] In particular, three-dimensional (3-D) nano-ramified metal deposits are ideally suited for electrodes in electrochemical devices such as fuel cells, batteries, and sensors. The open porous structure allows rapid transport of gas and liquid while the extremely high surface area is desirable for electrochemical reactions. To date, however, most studies have been focused just on avoiding the ramification of these metal deposits, as needed for the intended applications in electronic devices.^[2-4] The potential applications of these unique structures in electrochemical devices are yet to be explored.

While an electro-deposition process can easily create 3-D dendritic structure of metals, it is very difficult to control the microstructure with desired features. The trunks and branches in the porous dendritic structure are often unable to support the weight of numerous sub-branches, leading to collapses on itself in the electrolyte solution even with minimal convective forces. Furthermore, dendritic structures are easily overgrown to become a thick film with very low porosity, making it difficult for gas/liquid to transport through as required in electrochemical applications.

In this communication, we report a unique method to overcome the above problems in order to make self-supported nano-ramified (dendritic) deposits. This simple but very effective technique involves electrochemical deposition accompanying hydrogen evolution, which has been deliberately suppressed in typical electro-deposition processes to produce dense metallic components. In this process, hydrogen bubbles play a crucial role in the formation of the

porous structure; they function as a dynamic negative-template. The resulting structures are 3-D free-standing foams of metals (such as copper and tin) with highly porous ramified (dendritic) walls. A recent study by Zach and Penner^[5] has been also based upon a hydrogen co-evolution process. However, they have obtained just 2-D nano-crystalline nickel and the role of hydrogen evolution on electrochemical deposition (*i.e.* the size selective deposition of nanoparticles) is quite different from the role of hydrogen evolution in this work.

Shown in Fig. 1 are some typical SEM (Hitachi S-800 FEG Scanning Electron Microscope) micrographs of porous copper deposits created by electro-deposition for different periods of time. Clearly, the pore size of the 3-D micro-foam structure increased with the time of deposition (or the distance from the substrate). More importantly, the *walls* of the micro-foam are also highly porous due to vigorous hydrogen evolution originated not only at the substrate but also at the deposited copper dendrites.

Schematically shown in Fig. 2 is a simplified description of the formation process of the metal foams. The hydrogen bubbles, originating from the cathodic reaction on copper substrate, create a continuous path from the substrate to the electrolyte/air interface during the deposition process. Where there is a bubble, there will be no deposition of metals simply because there are no metal ions available. Thus, the numerous hydrogen bubbles evolved at different locations on the substrate generate the pores in the deposits. When the deposition rate is sufficiently high, the vicinity of the metal deposits quickly becomes depleted of metal ions and concomitantly incessant gas evolution disrupts the diffusion of reactive ions from bulk electrolyte to ion-depleted region. As moving bubbles open up a path, the growth of metal takes its way between gas bubbles. Consequently, a series of gas bubbles acts as a dynamic negative template during the course of metal growth, leaving metal deposits between gas bubbles (foam structure). Here, the pore size of the foam increases with the distance away from the substrate because of the coalescence of hydrogen bubbles (see Fig. 2), creating structures ideally suited for electrodes in fuel cells, batteries, and sensors.

Depending on the choice of the substrate and the porous metallic electrodes to be deposited, the actual deposition process could be more complicated. In the case of copper deposition, for example, hydrogen bubbles evolved from the substrate create the large pores while the hydrogen bubbles liberated from the freshly formed porous deposits create nano-pores as deposits form. In contrast, in the case of tin deposition, hydrogen bubbles are generated mostly from the copper substrate due to a higher hydrogen overvoltage on tin.^[6]

Fig. 3 depicts the 3-D foam structures of copper and tin deposits at different magnifications. The overall macroscopic features of the copper deposits are similar to those of the tin deposits. The foam walls are composed of numerous small-ramified coppers (Fig. 3a) or dendritic tins (Fig. 3b). It is noted that overgrowing (too dense) or preferential growing (*e.g.*, perpendicular to the substrate) was not observed. The feature size of the branches in copper and tin deposits are on the order of hundreds nanometers (Fig. 3e and 3f). It is also found that the porous deposits are cross-linked (networked) ramified (dendritic) products in all directions throughout the walls (Fig. 3c and 3d), leading to a mechanically well-supported structure. In fact, the porous deposits of both copper and tin always maintained the structural integrity during handling in the electrolyte and subsequent procedures for drying and characterization.

As we further examine the detailed microscopic features of the copper and tin deposits, two subtle differences are observed. One difference in morphology between copper and tin deposits is the shape of the branches. The branches of the tin deposits are longer and straighter than those of the copper deposits, as can be seen from Figure 3 (e) and (f). This result is consistent with the previous reports, where the typical copper and tin dendritic structures have been explained on the basis of diffusion-limited aggregation (DLA)^[7] and surface relief phenomenon^[8], respectively.

Another difference in detailed microstructure of the two deposits is that the branches of the copper foams contain nano-sized grains (and pores) whereas the branches of the tin deposits are relatively dense. Shown in Fig. 4(a) is the TEM (Hitachi HF-2000 Transmission Electron Microscope) image of the branch, revealing that the copper branches consist of copper particles of several tens nanometers. It is conceivable that hydrogen bubbles are liberated from the copper deposits as they form, creating nano-particles of copper (or nano-pores in the copper deposits). In contrast, no small grains (and pores) are observed in the dendritic tin branch because no hydrogen was generated on tin deposit due to the high hydrogen overvoltage on tin, as shown in Fig. 4(b).

The corresponding electron diffraction pattern of the copper deposits, inset in Fig. 4(a), shows discontinuous rings, indicating the different orientations of the individual particles. Although the diffraction of Cu₂O is also identified

along with that of copper, dark field image with the selected dots of Cu_2O in diffraction pattern shows that Cu_2O diffraction is only due to the oxide on copper surface, which is quite different from a recent report on electrodeposited copper filament,^[9] where copper nano-crystallites are separated by copper oxides. Considering the studies on reaction mechanism of electrodeposited copper,^[10,11] the absence of copper oxides inside the branches in this work can be attributed to the sufficiently high acidity in the deposition solution. That is, because of the abundant protons in the electrolyte, the growing copper tips always experience the highly acidic atmosphere around them, which suppresses the oxide formation and enhances the reduction of copper to metallic copper.

On the other hand, the polycrystalline copper branch is a characteristic feature of DLA-like copper deposits and its formation mechanism has been proposed on the basis of the oscillatory character in the nucleation kinetics.^[12] Additionally, owing to the rigorous gas evolution on growing copper tips in this work, a local turbulence of electrolyte might be created around the copper tips, disrupting continuous growth of the copper tips and promoting the formation of new nuclei with random orientation on the tips. This could be partly responsible for the polycrystalline character of the copper branches. In contrast, TEM image of a tin branch (Fig. 4(b)) and the corresponding electron diffraction pattern (inset in Fig. 4(b)) suggest that the tin branch is a single crystal, which is consistent with a previous report on tin whisker.^[8]

Shown in Fig. 5 are the X-ray diffraction patterns (Philips PW-1800 X-Ray Diffractometer) of copper and tin deposits (scratched off from the substrates), indicating that the copper deposits have a face-centered cubic structure while the tin deposits have a tetragonal structure with high crystallinity.

Shown in Fig. 6 are the thicknesses of the deposits, average diameters of the pores on the surface, and the amounts of deposits (in mol./cm^2) as a function of deposition time. The deposition rates (in thickness per unit time) of the copper (open circle) and the surface pore size (open square) are much smaller than those of the tin deposit (solid circle and square) under similar conditions. For example, to achieve similar thickness, the time needed for deposition of copper is about 4 times of that for deposition of tin. However, the apparent density of the deposited porous copper (open triangle) is much higher than that of the porous tin (solid triangle). Analysis of a Cu-deposit prepared by deposition for 40s indicated that the apparent density (mass / [substrate area $\times$ thickness]) of copper is about 0.6 gcm^{-3} ; on the other hand, the analysis of a tin deposit prepared by deposition for 10s indicated that the apparent density is about 0.2 gcm^{-3} . It is noted that the ratio of the apparent densities ($0.6 \text{ gcm}^{-3} / 0.2 \text{ gcm}^{-3}$) is far greater than the ratio of the intrinsic densities of the two metals ($8.92 \text{ gcm}^{-3} / 7.31 \text{ gcm}^{-3}$). The higher density of copper deposits is due to its lower aspect ratio (length/width). Another interesting point is that the diameters of the surface pores are comparable to (for copper) or larger than (for tin) the thicknesses of the deposits. This implies that the pore is not spherical, but ellipsoidal.

Among the deposition parameters studied, the concentration of the metal ions (especially Sn^{2+}) greatly influences the morphologies of the foam deposits, whereas the acidity and the applied current density had little effect on the foam structure if they are sufficiently high (*i.e.* $> 1.0 \text{ M H}_2\text{SO}_4$ and $> 0.5 \text{ Acm}^{-2}$). The higher content of tin(II) ions than the optimum amount (0.15 M) resulted in thicker and denser foam walls. Eventually, the pores disappeared completely when the content of tin ions was greater than $\sim 0.5 \text{ M}$. On the other hand, if the tin ion content is too low (less than $\sim 0.10 \text{ M}$), the walls of tin foam become too thin to form a 3-D foam structure. In contrast, the well-defined foam structure with walls of small ramified copper can be created in a relatively wide concentration range of copper ion (from 0.1 to 0.4 M Cu ion).

Nanoporous metallic electrodes have been successfully prepared using an electrodeposition process. This represents a novel way of creating porous structures that allow not only fast transport of gas and liquid but also rapid electrochemical reactions due to high surface area. The porous structures are ideally suited for electrodes in electrochemical devices such as fuel cells, batteries, and chemical sensors. In particular, the porous tin deposits are being directly used as 3-D nano-porous anode for lithium batteries and the nanoporous copper deposits are being used for construction of nanocomposite anodes (consisting of Cu and CeO_2) for solid oxide fuel cells. Further, the nanoporous copper deposits can be used as 3-D templates for preparation of porous structures of other functional materials, including electrodes for solid oxide fuel cells and solid state gas sensors.

Experimental

High-purity copper (Alfa Aesar, 99.8%), cleaned with acetone and dilute hydrochloric acid, was used as the substrate (cathode) for copper and tin deposition. Copper and tin (Alfa Aesar, 98.8%) plates with a superficial surface area of 5 cm² are used as the counter electrodes (anodes) for copper and tin deposition, respectively. The distance between anode and cathode is 2 cm. A constant current (as high as 3 Acm⁻²) was applied to the substrate using a Solartron 1285 potentiostat in an electrolyte of 1.5 M sulfuric acid (Aldrich) containing 0.20 M copper sulfate (Alfa Aesar) or 0.15 M tin sulfate (Alfa Aesar) at room temperature. Deposition was performed in a stationary electrolyte solution without stirring or N₂ bubbling.

References

- [1] E. Ben-Jacob, P. Garik, *Nature* **1990**, 343, 523.
- [2] R. Schetty, *Circuit World* **2001**, 27, 17.
- [3] I. Petersson, E. Ahlberg, *J. Electroanal. Chem.* **2000**, 485, 166.
- [4] B. Kim, T. Ritzdorf, *J. Electrochem. Soc.* **2003**, 150, C53.
- [5] M.P. Zach, R.M. Penner, *Adv. Mater.* **2000**, 12, 878.
- [6] M. Pourbaix, in *Atlas of Electrochemical Equilibrium in Aqueous Solution*, Oxford, New York, Pergamon Press, **1966**, p. 475.
- [7] T.A. Witten, L.M. Sander, *Phys. Rev. Lett.* **1981**, 47, 1400.
- [8] George T.T. Sheng, C.F. Hu, W.J. Choi, K.N. Tu, Y.Y. Bong, L. Nguyen, *J. Appl. Phys.* **2002**, 92, 64.
- [9] M. Wang, S. Zhong, X.-B. Yin, J.-M. Zhu, R.-W. Peng, Y. Wang, K.-Q. Zhang, N.-B. Ming, *Phys. Rev. Lett.* **2001**, 86, 3827.
- [10] F. Texier, L. Servant, J.L. Bruneel, F. Argoul, *J. Electroanal. Chem.* **1998**, 446, 189.
- [11] M.-Q. Lopez-Salvans, F. Sagues, J. Claret, J. Bassas, *Phys. Rev. E* **1997**, 56, 6869.
- [12] V. Fleury, *Nature* **1997**, 390, 145.

Figures

Fig. 1. SEM images of copper deposits showing the dependence of foam structure on deposition time. The electro-deposition has been performed for (a) 5 s; (b) 10 s; (c) 20 s. The pore size increases with the distance from the substrate due to coalescence of the hydrogen bubbles.

Fig. 2. Simplified mechanism for metal foam structure by electro-deposition. At the moment of metal growing, hydrogen bubbles originating from the substrate play a role in dynamic negative-template for foam structure: copper and tin grow only towards the space where the bubbles don't exist (*i.e.* the reacting Cu and Sn(II) ions are present). After the formation of metal foams, liberated bubbles move through the space they made before.

Fig. 3. SEM images of (a) copper (electro-deposited for 20 s) and (b) tin (electro-deposited for 5 s) deposits in different magnifications, showing porous foam walls composed of nano-ramified (dendritic) branches. (a-2) and its inset (cross-sectional view) exhibit the presence of lots of micro-pores throughout the whole walls due to gas evolution on the copper deposits.

Fig. 4. X-Ray diffractograms of copper (upper) and tin (lower) powders scratched from the substrates, showing high crystallinities of the deposits. Only main peaks have been indexed. Small Cu_2O peaks (*) have been also identified from the XRD pattern of copper (For the origin, see Fig. 5 and the corresponding explanation in the text).

Fig. 5. TEM images of (a) copper and (b) tin and the corresponding electron diffraction patterns (insets). The numbers on the diffraction pattern in (a) represent 1- Cu_2O (110); 2- Cu_2O (111); 3-Cu (111); 4-Cu (200); 5- Cu_2O (220); 6-Cu (220).

Fig. 6. Dependences of thickness of the deposits (circle), average diameters of the top pores projected to the substrate (square), and amount of the deposits (triangle) on the deposition time.

C.2. Nano-Porous Tin Oxides Prepared by an Anodic Oxidation Process

The formation of self-ordered nano-porous oxide by an anodization process has been a very interesting topic for several decades. To date, only a few metals such as Al^[1] and Ti^[2] have been successfully oxidized to form highly regular oxide structure such as honeycomb-like or nano-tubular structures. In particular, the nano-porous anodic alumite has been widely used as a template for preparation of nano-porous structures of many functional materials for optical, electronic, magnetic, and electrochemical applications.^[3-5] The nano-porous anodic titanates is anticipated to be used for catalytic and gas-sensing applications.^[6]

Tin oxide is a semiconductor and has been widely used for various applications, such as solid-state gas sensors, optical devices, and lithium secondary batteries.^[6-8] A variety of preparation methods have been explored to fabricate nano-structured tin oxides to dramatically improve the desired functionality. In particular, recently crystalline one-dimensional (1-D) tin-oxides such as nano-ribbons, nano-tubes, and nano-rods, have been successfully synthesized by a high temperature thermal oxidation process^[9,10] and low temperature solution-based synthesis^[11] for ultrasensitive gas-sensors in many applications. However, 1-D monolithic nano-porous tin oxides are yet to be created.

In this communication, we report for the first time the self-ordered monolithic nano-porous tin oxides, created by an anodic oxidation of pure tin metal in the trans-passive region. The detailed micro-structures of anodic tin oxides will be presented and the possible formation mechanism of the one-dimensional channel structure will be discussed.

The microstructure and morphology of anodic tin oxide films prepared by an anodization process were examined using an SEM (Hitachi S-800 FEG Scanning Electron Microscope). Shown in Fig. 1 are the surface views of an anodic tin oxide sample. The nano-sized pores, ranging from 30 to 60 nm, are uniformly distributed throughout the surface. It is noted that the anodic tin oxide has nano-channels nearly perpendicular to the substrate, as can be seen in Fig. 2(a). However, the channels are discontinuous since the porous tin oxide composed of stacked layers of several hundreds nanometers. As can be seen from the image of a lower magnification (Fig. 2(b)), numerous nano-gaps or disk-shaped nano-pores are present between the layers.

The discontinuous nano-channel structure is due probably to the disturbance of the formation of tin oxides by vigorous oxygen evolution reaction under severe anodizing conditions. The rapid liberation of oxygen could create turbulence in the electrolyte around the oxide/metal interface and/or induce a local mechanical stress as porous tin oxide is formed, destroying the long-range order of the nano-channeled structure. These additional nano- (micro-) pores inside the nano-channels would facilitate the gas and ionic transport through the porous film, whereas they could be harmful for fast electronic conduction.

In order to explore the detailed structures of the anodized samples, the top and side views of the porous tin oxide films were examined using a TEM (Hitachi HF-2000 Transmission Electron Microscope). It is noted that the shape of the pores in porous tin oxide is irregular (Fig. 3(a)) and the channels are not straight (Fig. 3(b)). In particular, the channel wall thickness ranges from 5 to 10 nm. Unlike the nano-porous alumite which is characterized by a centrally situated *circular* pore at an ordered *hexagonal* unit cell, the pore of the anodic tin oxide has the same shape as its irregular cell. Assuming the ideal honey-comb channel structure with *hexagonal* pores of cell size of 30 - 60 nm and wall thickness of 5 - 10 nm, the porosity of the present anodic tin oxide is estimated to be 75 - 92 %, which is much larger than that of porous alumite (24 %).^[13] Actually, the theoretical porosity was underestimated since the numerous nano-gaps in the real anodic tin oxide structure have been disregarded in the calculation. The scratched powder of anodic tin oxide film typically has a surface area of 99.1 m²/g, as measured by the Brunauer, Emmett, and Teller (BET) technique (ASAP 2000, Micromeritics).^[14]

Shown in Fig. 4 is a top view of the anodic tin oxide sample annealed at 500 °C for 3hrs. The microstructure of the annealed sample is essentially the same as those of the as-prepared samples: The channel diameter and the wall thickness remained the same (30-60 and 5-10 nm, respectively). Both the electron diffraction patterns (the insets in Figs. 3(a) and 4) and the X-ray diffraction patterns (Philips PW-1800 X-Ray Diffractometry) as shown in Fig. 5, indicate that the as-prepared amorphous tin oxide can be transformed to a crystalline stannic structure (cassiterite SnO₂) after annealing.

As shown in Fig. 6, the thicknesses of the porous tin oxide films seem to increase linearly with anodizing voltage and time. Well-defined nano-porous channels were produced with little structural difference when the anodizing voltages were greater than 5 V, which correspond to the trans-passive region. Although similar nano-porous structures are produced at voltages above 12 V, the resulting films had poor adhesion to the substrate and often delaminated from the substrate during anodizing or subsequent drying/handling process. This poor adhesion is due probably to more vigorous O₂ evolution near the oxide/tin substrate interface.

From the linear relationship between film thickness and anodizing time, the growth rate of nano-porous film is estimated to be ~ 78 nm·s⁻¹, which is much faster than the formation rate reported on the anodic porous alumite (< 5 nm·s⁻¹).^[15-17] In the case of anodic alumite, the formation mechanism of porous channels has been proposed on the basis of field-enhanced effect.^[1,18,19] For a typical three-layer Al | Al oxide | anodizing solution, both the transport of oxygen containing anions (O²⁻/OH⁻) from the solution/oxide interface to oxide/Al interface and the migration of Al³⁺ from Al/oxide interface to oxide/solution interface would be enhanced by the electric field during the anodization process. The transport of O²⁻/OH⁻ contributes to the oxide formation at the interface between Al and Al oxide while the migration of Al³⁺ leads to the dissolution of Al into solution. Since the electric field strength at the channel bottom is much greater than that at the channel wall, Al dissolution rate at the bottom is far greater than the rate at the wall, resulting in perpendicular growth of the channel with high aspect ratio.

Similarly, one of the possible explanations about the extremely fast growth of tin oxides is much shorter time needed for the transport of ions (O²⁻/OH⁻ and Sn ions) through tin oxide film formed on tin substrate, as compared to the time needed for ionic transport through anodic alumite film covering aluminum substrate. Considering that the barrier layer thickness is about half of the channel wall thickness,^[20] the wall thickness of 5 - 10 nm of anodic thin

oxide implies the barrier layer thickness of several nm order, which is much lower than that of anodic alumite (~ 50 nm),^[21] shortening the length of ionic transport in the solid state. In addition, severe anodizing conditions, including vigorous oxygen evolution, are likely to introduce lots of structural disorder as the oxide films are formed, resulting in a highly open amorphous structure. This facilitates fast ionic transport through the oxides. Nevertheless, the exact mechanism of fast channel formation is yet to be determined.

Porous tin oxide electrodes with quasi-parallel nano-channel have been successfully prepared using an anodic oxidation process. This represents a novel way of creating porous structures that allow fast transport of gas/liquid and rapid electrochemical reactions due to high surface area as well. The present monolithic tin oxide with additional nano-pores inside are ideally suited for electrodes in electrochemical devices such as batteries and chemical sensors. In particular, nano-channel structures of the as-prepared and annealed tin oxides are being directly used as nano-porous anode for lithium secondary batteries and the annealed tin oxide with stannic form is being tested for solid state gas sensors.

Experimental

High-purity tin (Alfa Aesar, 99.998%) was used as the working electrode (anode). Before anodizing, the tin surface was polished to a mirror finish with 1.0 and 0.3 μm alumina powder (in order to remove a native oxide film) and then rinsed in distilled water. Platinum wire was used as the counter electrode (cathode) for anodization. The distance between anode and cathode was 1 cm. A constant voltage (5 to 14 V) was applied to the substrate using a Solartron 1285 potentiostat in an electrolyte of 0.5 M oxalic acid (Aldrich) at room temperature. Anodization was performed in a stationary electrolyte solution without stirring or N_2 bubbling. After anodization, some samples have been annealed for 500 $^{\circ}\text{C}$ for 3hrs. Elemental analysis of as-prepared and annealed samples by energy dispersive x-ray spectrometer (EDS) shows that the only constituents of the samples are tin and oxygen. The as-prepared samples appear to be dark brown, indicating the presence of stannous oxide (SnO) in the sample.^[12] On the other hand, the annealed samples appear to be white, implying that it is close to stoichiometric stannic oxide (SnO_2).

References

- [1] J.P. O'Sullivan, G.C. Wood, *Proc. R. Soc. London, Ser. A* **1970**, 317, 511.
- [2] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E.C. Dickey, *J. Mater. Res.* **2001**, 16, 3331.
- [3] T.M. Whitney, J.S. Jiang, P.C. Searson, C.L. Chien, *Science* **1993**, 261, 1316.
- [4] P. Hoyer, N. Baba, H. Masuda, *Appl. Phys. Lett.* **1995**, 66, 2700.
- [5] H. Masuda, H. Asoh, M. Watanabe, K. Nishio, M. Nakao, T. Tamamura, *Adv. Mater.* **2001**, 13, 189.
- [6] A.M. Azad, S.A. Akbar, S.G. Mhaisalkar, L.D. Birkefeld, K.S. Goto, *J. Electrochem. Soc.* **1992**, 139, 3690.
- [7] P. Olivi, E.C. Pereira, E. Longo, J.A. Varela, L.O. de S. Bulhoes, *J. Electrochem. Soc.* **1993**, 140, L81.
- [8] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* **1997**, 276, 1395.
- [9] M. Law, H. Kind, B. Messer, F. Kim, P.D. Yang, *Angew. Chem. Int. Ed.* **2002**, 41, 2405.
- [10] Z.R. Dai, J.L. Gole, J.D. Stout, Z.L. Wang, *J. Phys. Chem. B* **2002**, 106, 1274.
- [11] F.-F. Zhang, L.-D. Sun, J.-L. Yin, C.-H. Yan, *Adv. Mater.* **2002**, 15, 1022.
- [12] L. Young, in *Anodic Oxide Films*, London, New York, Academic Press, **1961**, p.326.
- [13] Irrespective of the electrolyte chosen, the pore spacing and pore diameter of anodic alumite are proportional to the anodizing voltage with proportionality constants of 2.5 nm/V and 1.29 nm/V, respectively [K. Ebihara, H. Takahashi, M. Nagatama, *J. Met. Finish. Soc. Jpn.* **1983**, 34, 548; D. Crouse, Yu -H. Lo, A.E. Miller, M. Crouse, *Appl. Phys. Lett.* **2000**, 76, 49]. Accordingly, porosity of the anodic alumite is invariant with anodizing voltage and electrolyte chosen.
- [14] The SEM micrograms of the scratched powder indicated the anodic oxide was peeled off in the form of disk-shaped particles with a thickness of hundreds nanometers and a length of tens to hundreds micrometers. This means that the increase in surface area due to scratching and thereby crashing of the oxide layer, is too trivial to invalidate the reliability of BET result.
- [15] H. Masuda, F. Hesegwa, S. Ono, *J. Electrochem. Soc.* **1997**, 144, L127.
- [16] O. Jessensky, F. Muller, U. Gosele, *Appl. Phys. Lett.* **1998**, 72, 1173.
- [17] M.T. Wu, I.C. Lue, M.H. Hon, *J. Vac. Sci. Technol. B* **2002**, 20, 776.
- [18] J. Siejka, C. Ortega, *J. Electrochem. Soc.* **1997**, 124, 883.
- [19] V.P. Parkhutik, V.I. Shershulsky, *J. Phys. D: Appl. Phys.* **1992**, 25, 1258.

[20] The proportionality constant of 1.05 nm/V [G.E. Thompson, G.C. Wood, in *Corrosion Aqueous Process and Passive Films*, Academic Press, London **1982**] or 0.75 nm/V ^[21] has been proposed for barrier layer thickness of anodic alumite. This value is comparable to the half of the proportionality constant of the channel wall thickness.^[13]

[21] N. Stein, M. Rommelfangen, V. Hody, L. Johann, J.M. Lecuire, *Electrochim. Acta* **2002**, 47, 1811.

Figures

Fig. 1. Typical SEM micrographs of nano-porous tin oxide at different magnifications, created by anodic oxidation process.

Fig. 2. Cross-sectional views of anodic nano-porous tin oxide showing (a) nano-channeled structure and (b) numerous disk-shaped nano-gaps between the layers.

Fig. 3. TEM images of anodic nano-porous tin oxides with the electron diffraction pattern (inset in (a)). (a) Top view; (b) side view.

Fig. 4. TEM image (top view) of anodic nano-porous tin oxide after annealing at 500 °C for 3 hrs and the electron diffraction pattern (inset). The numbers on the diffraction pattern represent 1- cassiterite SnO_2 (200); 2- SnO_2 (211); 3- SnO_2 (002); 4- SnO_2 (222); 5- SnO_2 (402).

Fig. 5. X-Ray diffractograms of as-synthesized (upper) and annealed (lower) powders scratched from the substrates. The as-prepared amorphous tin oxide can be transformed to a crystalline stannic structure (cassiterite SnO_2) after annealing.

Fig. 6. Dependence of thicknesses of the anodic nano-porous tin oxide films on anodizing voltage and time.