NANO-SCALE ANODES FOR USE IN Li-ION BATTTERIES

J. Wolfenstine*, D. Foster, J. Read and W. K. Behl
Army Research Laboratory
AMSRL-SE-DC
2800 Powder Mill Road
Adelphi, MD 20783-1197

ABSTRACT

The energy demands of the Objective Force and Future Combat Systems require the development of Li-ion batteries with higher energy density and longer cycle life than what is presently available. In order to increase the energy density of Li-ion batteries active (metal that reacts with Li to form an alloy)/inactive (material that does not alloy with Li) composites are under consideration as anodes. However, active/inactive composites containing micron-sized particles suffer from a restricted cycle life that limits their use in both commercial and military applications. In order to increase the cycle life the use nano-scale (<100 nm) composites was investigated. Two different active/inactive composites; one containing an inactive metal (Cu) matrix and the other an inactive ceramic (Li_2O) matrix were investigated. The nano-scale Sn-Cu composite was prepared by a chemical route whereas the nano-scale $Sn-Li_2O$ composite was prepared by an in-situ method. Electrochemical testing revealed an improvement in cycle life for both nano-scale composites compared to similar composites with micron-scale particles. Reducing the micro structural features (i.e., particle/grain/phase size) features from the micron-scale to the nano-scale in composite anodes can lead to an increase in the cycle lifetime of a Li-ion battery.

1. INTRODUCTION

The Objective Force and Future Combat Systems require the development of new batteries that have more energy per unit weight/volume, discharged at higher rates, non-toxic, increased safety and cost less than the Li/SO_2 primary battery currently used by the Army (Hamlen at al. 2001). One new battery technology that meets the needs of the Objective Force and Future Combat Systems is a rechargeable battery based on Li-ion. At present, most commercial Li-ion batteries use a carbon-based material, such as graphite or coke, as the anode with lithiated cobalt oxide as the cathode and a lithium salt dissolved in a mixed organic solvent as the electrolyte (Goodenough 1994;Scrosati 2000). Carbon anodes have a limited reversible capacity which leads to a low energy density battery (i.e., heavier and/or more space) and safety problems when discharged/charged at high rates.

In order to improve Li-ion battery performance, alloys are now being considered as alternative anodes to carbon. Even though the alloy anodes have significant advantages over carbon for Li-ion batteries, there is one major problem that must be solved before they can be used in military applications. The major problem associated with the alloys is a large change in volume upon Li addition which leads to fracture. One potential solution to solve the fracture problem is to use a composite anode. The composite anode consists of a lithium active metal dispersed within an inactive matrix. The purpose of the inactive matrix is to reduce the mechanical stresses associated with Li insertion/removal during charging/discharging. However, active/inactive composites containing micron-sized particles still suffer from a restricted cycle life that limits their use in commercial and military applications. Hence, there is a need to develop ways to improve the cycle life of active/inactive composites so they can be used in practical applications.

One suggested approach to increase the cycle life of active/inactive composites is to reduce the microstructure (i.e., particle/grain/phase size) of the active/inactive composites to the nano-scale (<100 nm). It is the purpose of this paper to examine this suggestion using two different active/inactive composites; one containing an inactive metal (Cu) matrix and the other an inactive ceramic (Li_2O) matrix. In both cases the Li active metal is Sn. These composites were chosen because they both have higher capacities than graphite and cycle data is available for these materials having micron-sized particle/grains/phases and thus, a direct comparison can be made if reducing these features to the nano-scale from the micron-scale does improve cycle life.

2. EXPERIMENTAL

2.1 Metal Matrix Composite Preparation

A Cu_6Sn_5 alloy was chosen for this study. It has been shown as Li is added to Cu_6Sn_5 it eventually decomposes to a Li-Sn alloy (active) surrounded by a Cu matrix

(inactive) (Kepler et al., 1999; Larcher et al., 2000) Nano-scale Cu_6Sn_5 powders were synthesized by a chemical method, which involved reducing a methanol solution of $CuCl_2$ and $SnCl_2$ (1.2:1 volume ratio) with $NaBH_4$ in a 14M NaOH solution under constant stirring at room temperature. Twice the amount of the $NaBH_4$ solution was added to the methanol solution containing the Cu and Sn ions to ensure complete reduction of the metal ions. Upon addition of the $NaBH_4$ solution a black precipitate was observed immediately. The black precipitate was washed with distilled water and filtered until the pH of the filtrate was the same as that of the distilled water. The precipitate was then dried at 100°C under vacuum.

2.2 Ceramic Matrix Composite Preparation

The active (Sn)/inactive ceramic (Li_2O) matrix composite was formed by the in-situ electrochemical reduction of SnO by Li_3N according the reaction given below:

$$2\,Li_3N + 3\,SnO \rightarrow 3\,Sn + 3\,Li_2O + N_2\uparrow \qquad (1)$$
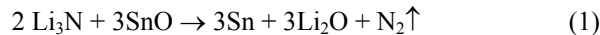
Li_3N and SnO powders were combined in a jar mill under an argon atmosphere of less 0.5 ppm moisture/oxygen. The jar was sealed and the materials were milled continuously at ambient temperature for five days. Upon opening the vessel under an inert atmosphere, the contents appeared to be pressurized presumably due to the formation of nitrogen gas in accord with Equation 1.

2.3 Material Characterization

Powders from both approaches were characterized by x-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Powders for TEM were prepared by dispersing them in methanol and while in an ultrasonic bath a drop of the suspension was placed on a Ni grid covered with an amorphous carbon film.

The cycle life of the powders were evaluated in half-cells at room temperature. Positive electrodes were prepared by mixing 85-wt. % alloy powders, 5-wt.% carbon and 10-wt.% polyvinylidene fluoride dissolved in N-methylpyrrolidinone. The mixture was coated onto a Cu substrate. Metallic lithium was used as the negative electrode. The electrolyte solution was 1M $LiPF_6$:ethlylene carbonate/dimethyl carbonate/diethyl carbonate (5:4:1 by volume). The cells were cycled at a constant current density of 0.1 mA/cm^2 between 0.0 to 1.0 V. After cycling the structure of the alloys was investigated using x-ray diffraction.

3. RESULTS AND DISCUSSION

Figure 1 is an x-ray diffraction pattern of the Cu_6Sn_5 powders after precipitation. From Figure 1, it can be observed that the precipitate was single-phase Cu_6Sn_5. No other Cu-Sn phases or pure component (Cu or Sn) peaks were exhibited in the x-ray diffraction pattern. The average crystallite size calculated using the Scherrrer formula was 10 nm. X-ray microanalysis on particles that were cold-mounted and polished revealed the Cu and Sn were uniformly distributed with a Cu:Sn of about 1:1, which is in good agreement with the desired Cu:Sn of 1.2:1 for the Cu_6Sn_5 alloy. SEM analysis revealed the particles exhibited an equiaxed morphology with all particles less than 100 nm. The average particle size determined using the line intercept method on more than 200 particles, was estimated to be about 40 nm. TEM confirmed that all particles were nano-scale (<100 nm). Figure 2 is a TEM photomicrograph of some nano-scale Cu_6Sn_5 powders. It shows equiaxed particles with a size between 30 to 40 nm.
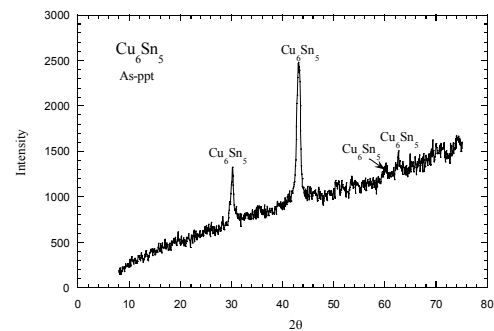

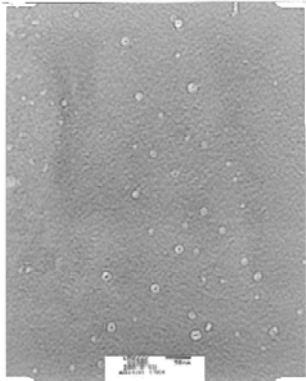Figure 1. X-ray diffraction pattern of the as-precipitated material.

Figure 2. Transmission electron photomicrograph of some nano-scale Cu_6Sn_5 powders.

Figure 3 shows the x-ray powder diffraction pattern of the Li_3N reduced SnO. The diffraction peaks match the pattern for tin metal power also shown in Figure 3, revealing that the SnO has been reduced to tin metal and confirming the reaction of Equation 1. From Figure 3, there is one unidentified peak in the pattern for the chemically reduced SnO at $2\theta = 37.8°$. This peak is not present in the powder patterns for tin, tin oxide, lithium oxide, lithium nitride, or any of the lithium-tin alloys and may be contamination from ceramic particles worn from the jar mill apparatus. The broad region of enhanced x-ray intensity near the beginning of the milled powder pattern is indicative of an amorphous phase and is believed to be amorphous Li_2O consistent with the reaction of Equation 1. Amorphous Li_2O has also been identified in electrochemically reduced tin oxides (Goward et al., 1999).

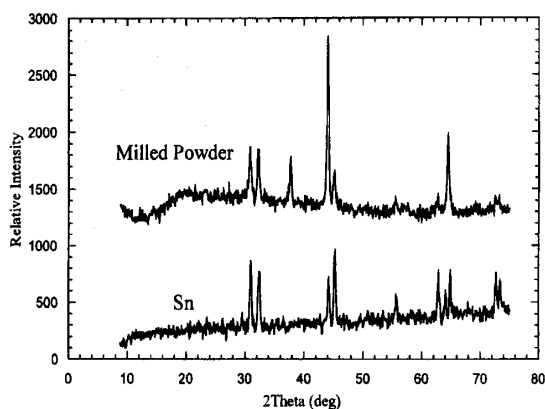Figure 3. X-ray powder diffraction pattern of SnO reduced by Li_3N and Sn metal powder.

Figure 4 shows an SEM backscattered image of the tin and lithium oxide composite. The light colored tin particles vary somewhat in size but most of the particles appear to be on the order of 100 nm or less. Apparently, there are still enough large tin particles to account for the rather narrow x-ray intensity peaks in Figure 3. The tin particles appear to be fairly round in shape and uniformly distributed in the Li_2O matrix.
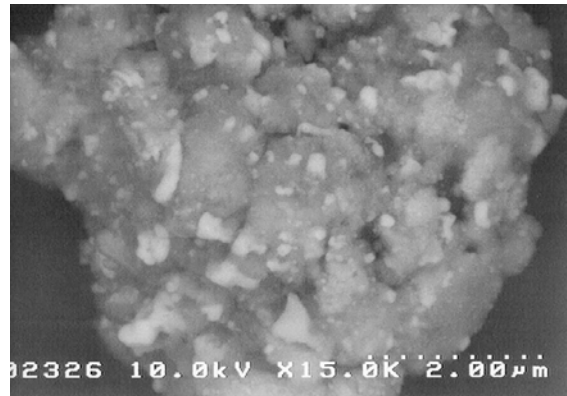

Figure 4. SEM backscattered image of the Sn and Li_2O composite formed by milling SnO and Li_3N.

The voltage versus time profile for the first two cycles of the nano-scale Cu_6Sn_5 alloy are shown in Figure 5. From Figure 5 two important points are noted. Firstly, the discharge curve for the first cycle is longer than that for the second cycle. The extra length of the discharge curve for the first cycle compared to the second cycle is most likely associated with irreversible Li loss (i.e., Li_2O formation) as a result of the reduction of metal oxides (i.e., metal oxide→metal + Li_2O, upon initial Li titration) that are formed when the powders were handled in air during subsequent processing steps after precipitation and also from the reduction of the electrolyte solvent to form a solid electrolyte interphase on the particle surface. The second point is that the shape of the discharge curve is different from that observed for the micron-sized Cu_6Sn_5 powders that were prepared by melting, when discharged at a similar current density. From Figure 5 it can be seen that there is a lack of well-defined plateaus in the second cycle discharge curve. In contrast micron-sized Cu_6Sn_5 powders, prepared by melting, exhibit a well-defined plateau around of 0.4 volts in the discharge curve. A similar result has been observed in another metal-based composite system, where the effect of particle size on discharge performance was evaluated (Crosnier et al., 2001). In Sn-based metallic composites it was found that as the particle size decreased, that well-defined plateaus observable in coarse powders (<45 μm) were impossible to distinguish in the finest powders (<0.2 μm). These results are in good agreement with the results for the Cu_6Sn_5 alloy, which also show that as the particle size is

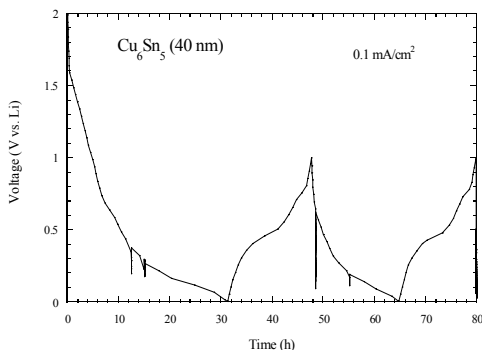reduced, in this case to the nano-scale sized powders disappear.

Figure 5. The first and second cycle charge/discharge curves for the Li/Cu_6Sn_5 cell.

Figure 6 shows the first discharge and charge cycle of the nano-scale active (Sn)/inactive ceramic (Li_2O) matrix composite formed by the in-situ electrochemical reduction of SnO by Li_3N. Also shown is the charge/discharge behavior of untreated SnO.
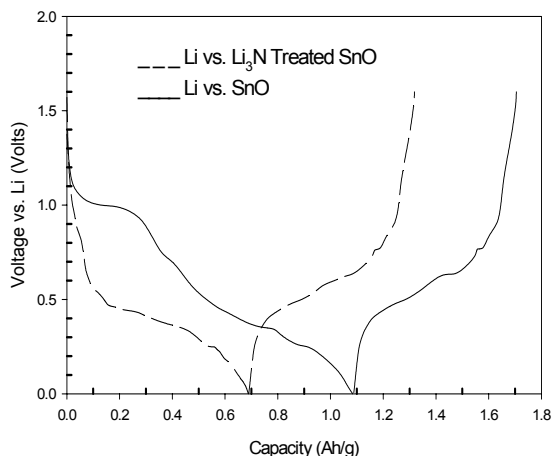

Figure 6. Comparison of first cycle discharge and charge curves for a nano-scale Sn-Li_2O composite electrode and a SnO electrode at 0.1 mA/cm^2.

From Figure 6 the curves are similar except the in-situ formed material has much less irreversible capacity loss as expected. In particular, the plateau at around 1 V in the Li/SnO discharge representing the irreversible Li loss

associated with the following reaction (2) is not present in the discharge curve of the in-situ formed nano-composite.

$$2Li^+ + SnO + 2e^- \rightarrow Sn + Li_2O. \qquad (2)$$

The volumetric capacity of the nano-scale Cu_6Sn_5 alloy (≈ 40 nm) versus cycle number is plotted in Figure 7. Also shown in Figure 7 is data for the melted (< 38 μm) (K epler et al., 1999) and mechanical alloyed (<1 μm) (Xia et al., 2001) Cu_6Sn_5 materials. The current density for the melted and nano-scale materials was 0.1 mA/cm^2. It was 0.25 mA/cm^2 for the first 5 cycles, then 0.5 mA/cm^2 for the remaining cycles of the mechanical alloyed material. From Figure 7 it can be observed that the extrapolated capacity approaches zero at about 45-50 cycles for the melted alloy and 80-85 cycles for the mechanical alloyed material. In contrast, at 100 cycles the nano-scale Cu_6Sn_5 powders still have a significant amount of reversible capacity. This result shows that a large improvement in capacity retention of the Cu_6Sn_5 alloy is obtained when the particle size is reduced to the nano-scale range. The volumetric capacity of the nano-scale Cu_6Sn_5 alloy at 100 cycles ($\approx$1450 mAh/mL) is almost twice the theoretical capacity of graphite ($\approx$850 mAh/mL) (Kepler et al., 1999).
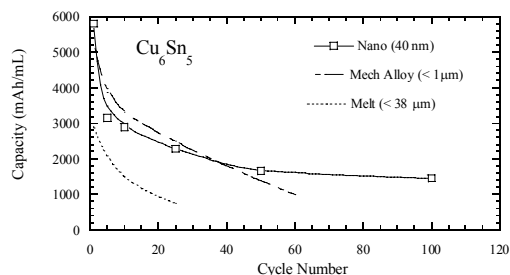

Figure 7. Volumetric capacity versus cycle number for the nano-scale, melted and mechanical alloyed Cu_6Sn_5 materials cycled in the voltage range 0.0 -1.0 V (nano-scale and melted) and 0.0-1.5 V (mechanical alloyed).

Preliminary cycle life testing of the in-situ formed nano-scale Sn-Li_2O composite has shown an improvement over a similar composite prepared by simply mixing micron-sized Sn and Li_2O powders.

4. CONCLUSIONS

The results of this study reveal a significant improvement in the cycle life of active/inactive composites anodes, that are be used in Li-ion batteries, was achieved when the structural features (particle/grain/phase size) are reduced from the micron-scale to the nano-scale range (<100 nm).

ACKNOWLEDGEMENTS

REFERENCES

Crosnier, O., Devaux, X., Brousse, T., Fragnaud, P. and Schleich, D.M., "Influence of Particle Size and Matrix in Metal Andes for Li-ion Cells", *J. Power Sources*, Vol. 97-98, pp. 188-190 (2001).

Goodenough, J. B., "Design Considerations", *Solid State Ionics*, Vol. 69, pp. 184-189 (1994).

Goward, G. R., Leroux, F., Power, W.P., Ouvrard, G., Domowski, W. T., Emami, T. and Nazar, L.F., *Electrochem. and Solid State Lett.*, Vol. 2, pp. 367-369 (1999).

Hamlin, R., Au, G., Brundage, M., Hendrickson, M., Plichta, E., Slane, S. and Barbaraello, J., "US Army Portable Power Programs", *J. Power Sources*, Vol. 22-24, pp. 97-98 (2001).

Huggins, R. A. and Nix, W. D., "Decrepitation Model for Capacity Loss During Cycling of Alloys in Rechargeable Electrochemical Systems", *Ionics*, Vol. 6, pp. 57-63 (2000).

Keppler, K. D., Vaughey, J. T. and Thackeray, M. M., "Copper-Tin Anodes for Rechargeable Lithium Batteries: An Example of the Matrix Effect in an Intermetallic System", *J. Power Sources*, Vol. 81-82, pp. 383-387 (1999).

Larcher, D., Beaulieu, L. Y., MacNeil, D. D. and Dahn, J. R., "In Situ X-Ray Study of the Electrochemical Reaction of Li with η-Cu_6Sn_5", *J. Electrochemical Soc.*, Vol. 147, pp. 1658-1662 (2000).

Scrosati, B., "Recent Advances in Lithium Ion Battery Materials", *Electrochimica Acta*, Vol. 45, pp. 2461-2466 (2000).

Wolfenstine, J., "Critical Grain Size for Microcracking during Lithium Insertion", *J. Power Sources*, Vol. 79, 111-113 (1999).

Xia, Y., Sakai, T., Fujieda, T., Wada, M. and Yoshinga, H., "Flake Cu-Sn Alloys as Negative Electrode Materials for Rechargeable Lithium Batteries", *J. Electrochemical Soc.*, Vol. 148, pp. A471-A481 (2001).