Dealloying at High Homologous Temperature: Morphology Diagrams

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Dealloying under conditions of high homologous temperature, TH, (or high intrinsic diffusivity of the more electrochemically reactive component) is considerably more complicated than at low TH since solid-state mass transport is available to support this process. At low TH the only mechanism available for dealloying a solid is percolation dissolution, which results in a bicontinuous solid-void morphology for which nanoporous gold serves as the prototypical example. At high TH there is a rich set of morphologies that can evolve depending on alloy composition and the imposed electrochemical conditions, including negative or void dendrites, Kirkendall voids and bi-continuous porous structures. We report on a study of morphology evolution upon delithiation of Li-Sn alloys, produced by the electrochemical lithiation of Sn sheets. Electrochemical titration and time of flight measurements were performed in order to determine the intrinsic diffusivity of Li, D Li, as a function of alloy composition, which ranged from ~5 × 10⁻¹² to ~4 × 10⁻¹² cm²s⁻¹. The activation energy for D Li was measured in the temperature range 30–140 °C and found to be 37.4, 37.9 and 22.5 kJ/mole, respectively for the phases Li₂Sn, Li₅Sn and Li-Sn.17 Morphology evolution was studied under conditions of fixed dealloying potential and fixed current density and our results are summarized by the introduction of dealloying morphology diagrams that reveal the electrochemical conditions for the evolution of the various morphologies.

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Today electrochemical dealloying processes are used to design nanostructures for a variety of functions encompassing electrocatalysis2–5 and biosensors6–9 with additional applications being explored such as actuation10–11 and structural composites.12–14 To date, the targeted nano-scale morphologies include bi-continuous structures such as nanoporous gold (NPG) formed by a percolation dissolution mechanism15–18 and so-called skin or core-shell nanoparticle structures, formed by a passivation-like process.2 Several of these architectures are employed in the fabrication of Pt-based alloy nanoparticle electrocatalysts for fuel cell applications,1,3,19 Since the solid-state transport processes available to support selective dissolution are temperature dependent one should expect the resulting morphologies to be similarly dependent on temperature. For example, in a noble metal alloy such as Ag-Au at 300 K (i.e., low homologous temperature) the diffusivity of each of the components is of order 10⁻¹¹ to 10⁻¹² cm²s⁻¹ which is about 20 orders of magnitude too low to contribute to dealloying processes over technologically relevant time scales. Consequently, percolation dissolution is the only mechanism available for dealloying resulting in the well-studied morphology of NPG. However, at higher homologous temperature, TH, we should expect additional sets of dealloying morphologies to evolve. Here our use of the term high TH is meant to designate that the solid-state mobility of the component that is selectively dissolved is of order 10⁻¹² cm²s⁻¹ or larger.

In order to address these issues we have been studying the behavior of Li-Sn alloys. These alloys were chosen since they have a rich history, with abundant thermodynamics, kinetic and structural data available. Additionally, since these alloys can be fabricated at ambient temperature by electrochemical processing it is relatively straightforward to access a range of alloy compositions necessary to examine morphology evolution. A significant difference between the more-studied noble metal alloys and Li-Sn is also in the nature of the equilibrium phase diagrams. Li-Sn displays multiple stoichiometric intermetallic phases not all of which are accessible at ambient temperature. Previous work from our group on dealloying in this system identified several morphologies that evolve upon de-lithiation including bicontinuous morphologies and Kirkendall voiding.21 In this study we use planar Sn films and sheets to examine both morphology evolution and various aspects of the kinetics of dealloying including the measurement of the intrinsic Li diffusivity as a function of alloy composition and temperature. While there have been a number of published studies of the ambient temperature Li diffusivity in these alloys, as shown in Table I, these results vary by as much as 5 orders of magnitude and consequently we decided to perform our own measurements. Diffusion measurements were performed using three different techniques; potentiostatic intermittent titration (PITT),22 galvanostatic intermittent titration (GITT)23 and a “time of flight” measurement using the technique developed by Devananthan and Stachurski (DS).24 Our results are discussed in terms of dealloying morphology diagrams that we introduce which facilitates describing morphology evolution under conditions of low and high TH.

Previous Work Examining Morphology Evolution at High TH

There are relatively few studies of morphology evolution by electrochemical dealloying in systems for which solid-state diffusional processes are significant. Harrison and Wagner conducted what they called an “incomplete” 800 C dealloying study for Ag-Au alloys of composition 88, 65 and 44 at% Ag in molten AgCl.25 While some type of porosity was apparently observed for the 88% alloy, no definitive statements could be made for the behavior of the 65 at.% alloy and the 44 at.% alloy which only showed grain boundary penetration. There were no images of the dealloyed Ag-Au morphologies presented in this work. Kaiser examined the selective dissolution of In from In₀.₃Sn₀.₇Oₓ, β-InSn and γ-InSn.26 In the case of β-InSn (containing ~90 at% In) he reported a polarization curve nearly identical to that of pure In. The occurrence of porosity formation was reported and attributed to a Kirkendall mechanism. Dealloying of In from both In₀.₃Sn₀.₇Oₓ and γ-InSn (containing ~20 at% In) was solid-state mass transport controlled as Kaiser was able to fit an indium concentration profile in a dealloyed solid to an error function and obtained a room temperature diffusivity for In of 5 × 10⁻¹² cm²s⁻¹.

While there have been a few recent reports discussing morphology evolution in Li alloy systems most of the commentary related to porosity evolution on dealloying is vague and often confused with cracking and fracture issues that these anode reservoirs suffer from owing to the large volume expansions these systems undergo during lithiation. We only know of several reports in the literature connecting porosity evolution in these systems to dealloying processes. In recent work, Cui’s group considered nano-pore evolution by alloying/dealloying cycles of Li in ZnO nano-rods, Sn nano-wires and Ag nano-wires.27 In ZnO, pore formation in the size range of 1–8 nm was attributed to a Kirkendall process while no specific mechanisms were discussed in regard to Si and Ag. TEM images (Figure 5 of their Supporting Information) of de-lithiated Ag showed encased nano-voids; similar to what some researchers have observed in NPG or...
cycling of Pt-alloy nanoparticles.29 Liu et al. considered pore formation on alloying/dealloying cycles of Li in Ge nanowires.29 They attributed porosity evolution to a dealloying process by a mechanism analogous to that for NPG, however, there were no clear images of bi-continuous morphologies in the TEM images that they presented. Chao et al. examined the microstructural evolution of Sn and Sn-Sb anode reservoirs during lithiation/de-lithiation cycling using in situ X-ray microscopy and observed the formation of porosity and cracking of micron-size particles.30 The image resolution was poor and the morphology seemed to consist of isolated pores. Guo et al. used lithiation/de-lithiation cycling to produce nanoporous Pt and RuO2.31 Porosity evolution was confirmed using nitrogen BET, but the detailed morphology of the porous structures observed in TEM was unclear. Chen and Sieradzki reported on the formation of bi-continuous structures upon delithiation of Sn anode reservoirs.21 Depending on Sn particle size and dealloying rate, they observed Kirkendall voids in dealloyed Sn particles as well as bi-continuous structures. Chen and Sieradzki also examined the dealloying behavior of Mg from Mg-Cd alloys at homologous temperatures in the range of 0.53–0.69 containing 65, 45 and 10 at.% Mg.21 Dealloying of the 45 and 65 at.% alloys yielded bi-continuous structures while negative dendrites were reported for dealloying the 10 at.% Mg-Cd alloy.

Experimental

Sample preparation: Tin foils (ESPI metals, 5N purity) were cold rolled to 0.001'' (25.4 μm) and stored at room temperature for three months before the experiments described below. GITT and PITT diffusion measurements were performed on electrodeposited Sn layers. These Sn layers were electrodeposited onto Cu foils following Ivey’s procedure.25 The native oxide on the Cu foils was cleaned by dipping into concentrated sulfuric acid for 5 seconds followed by rinsing with nanopure water. This cleaning procedure was repeated 3 times prior to electrodeposition. The electropolishing cell was in a standard three-electrode configuration with platinum wire as the reference and counter electrodes and Cu foil as the working electrode. The Cu foil was partially covered by Kapton tape leaving only an area of 0.25 cm² immersed in the electrolyte and facing the counter electrode. The electrolyte contained 0.22 mol/L stannous chloride dihydrate (SnCl2•2H2O) and 0.31 mol/L tri-ammonium citrate (HOCO(NH2)3) (CH3(NH2)2CO2H). Electropolishing was performed at a current density of 10 mA/cm² for 1200 s and 5 mA/cm² for 800 s to control the thickness of the Sn layer to ~7 μm and ~2 μm, respectively. A SEM (Nova 200 Nano-Lab system) was used to measure the thickness of the electrodeposited Sn layers.

PITT and GITT Measurements: A 3-neck round bottom flask containing 10 mL of 1 M LiClO4 in polypropylene carbonate (PC) was used as the electrolyte. Li foil was used as the counter and reference electrodes. Electrodeposited Sn layers on Cu foil served as the working electrode. Prior to initiating a PITT or GITT experiment, the working electrode was maintained at voltage of 1 V until the current density was below 10 μA/cm². Galvanostatic activation cycles in the voltage range 1 V–50 mV were sequentially performed at current densities of 250 μA/cm², 250 μA/cm² and 100 μA/cm². Without galvanostatic activation cycles, the GITT procedure consisted of pulses at a current density of 250 μA/cm² for 50 s, followed by a relaxation period of 100 s at both ambient temperature and elevated temperature. For the PITT measurements with galvanostatic activation cycles, potential steps of 10 mV were applied and the current was measured as a function of time. The potential was stepped to the next 10 mV increment either when the current reached 10 μA/cm² or if time exceeded 5000 s.

Devanathan-Stachurski measurements: As described in the original work by Devanathan and Stachurski, the electrochemical cell consisted of two cylindrical glass compartments sealed at the bottom by two size 12 O-ring joints, between which a Sn foil of thickness of 25.4 μm and active area of 0.1963 cm² was sandwiched. The Sn foil served as shared working electrode for both compartments. Each compartment carried two pieces of Li foils serving as reference and counter electrodes. The cathodic side of the Sn foil was potentiostatically lithiated at voltage of 400 mV vs. Li/Li⁺, while the anodic side of the Sn foil was maintained at a fixed voltage corresponding to the open circuit potential of Sn insuring that Li could be oxidized to Li⁺. Morphology evolution: Potentiostatic lithiation of 25.4 μm thick Sn sheets was performed by maintaining the working electrode at prescribed potential until the current density was below 10 μA/cm². Galvanostatic delithiation was performed at prescribed current densities in the voltage range of 0.4–2.5 V.

All electrochemical measurements and morphology evolution experiments were conducted inside an ultrahigh-purity argon-purged MBraun LABMaster glove box using either a Gamry series-G or BioLogic SP-150 potentiostat. All potentials mentioned in this work are referred to the Li⁺/Li electrode.

Focused ion-beam milling (FIB) and SEM: Fully delithiated Sn foils were immersed in acetonitrile for 12 h to dissolve the SEI layer.

Table I. Summary of existing literature values of the intrinsic Li diffusivity, Dli, in Li-Sn alloys.

| X in LiₓSn | D (cm²/s) | technique | Temperature (K) | direction | Cite |
|-----------|-----------|-----------|----------------|-----------|-----|
| 0.7       | 6–8×10⁻⁸  | galvanostatic | 298.15         | lithiation| 43  |
| 2.33      | 3–5×10⁻⁷  | galvanostatic | 298.15         | lithiation| 43  |
| 1         | 2.24–4.1×10⁻⁶ | potentiostatic | 688.15         | lithiation| 44  |
| 2.33–4.4  | 2.57–75.9×10⁻⁵ | potentiostatic | 688.15         | lithiation| 44  |
| full range | 10⁻¹⁵–10⁻¹⁰ | GITT       | 253            | both      | 45  |
| full range | 10⁻¹⁴–10⁻⁹  | GITT       | 273            | both      | 45  |
| full range | 4×10⁻¹³–4×10⁻¹⁰ | GITT    | 333            | both      | 45  |
| full range | 3×10⁻¹⁰–6×10⁻¹⁴ | GITT    | 293.15         | lithiation| 46  |
| full range | 6×10⁻¹³–3×10⁻¹³ | GITT       | -              | lithiation| 47  |
| full range | 4×10⁻¹⁵–4×10⁻¹² | GITT       | -              | delithiation| 47  |

Table II. Summary of Dli (cm²/s) calculated from GITT and PITT measurements in single-phase Li-Sn alloys.

| Phase          | GITT delithiation | PITT delithiation |
|----------------|-------------------|-------------------|
| LiₓSn          | 1.2×10⁻¹¹         | 1.9×10⁻¹²          |
| LiSn           | 1.9×10⁻¹¹         | 2.1×10⁻¹³          |
| LiₓSn (x>2.33) | 2.1×10⁻¹¹         | 4.6×10⁻¹³          |
and then transferred to the SEM chamber. Partially delithiated Sn foils were wiped clean and then immediately transferred to the SEM chamber in sealed bag filled with Ar. SEM and FIB milling was conducted in a dual-beam Nova 200 Nano Lab system at a 52° tilt angle.

**Diffusion Measurements**

To quantitatively understand the effect of Li diffusion on morphology evolution of dealloying, the composition-dependent intrinsic diffusion coefficient, $D_{Li}$, of Li in Li-Sn alloys was measured by GITT, PITT, and a time of flight technique based on the Devanathan-Stachurski cell. In this work, $D_{Li}$ was calculated from GITT measurements using Equation 1:

$$D_{Li} = \frac{4}{\pi} \left( \frac{1}{V_M Z_{Li} F A} \right)^2 \left[ \left( \frac{dE}{ds} \right) / \left( \frac{dE_t}{d\sqrt{t}} \right) \right]^2,$$

where $V_M$ is the molar volume of the sample, $I$ is the applied current, $Z_{Li}$ is the charge number, $F$ is Faraday’s constant, $A$ is the area of the electrode, $dE/ds$ is the slope of steady-state cell potential ($E_s$) vs. stoichiometric change ($\Delta$$\delta$) of Li$_{1-\delta}$Sn, and $dE_t/d\sqrt{t}$ is the slope of transient cell potential vs. $\sqrt{t}$ for the first 36 s. of each current-on period. $D_{Li}$ was calculated from PITT measurements using Equation 2:

$$D_{Li} = \pi L \frac{1}{\Delta Q} \left( \frac{\sqrt{t}}{\Delta Q} \right)^2,$$

where $L$ is the thickness of the Sn layer (here $L = 2 \mu$m), $\Delta Q$ is the charge accumulated during each potentiostatic step of 5000 s in duration. $D_{Li}$ was calculated in the time of flight measurement from Ref. 24.

$$D_{Li} = \frac{L^2}{6t_{lag}}.$$

where $t_{lag}$ is the time lag, which is the time at which the current reaches 0.63 of the steady-state anodic current density.

The results for $D_{Li}$, as a function of potential, $E$ obtained at ambient temperature from GITT and PITT measurements for the lithiation and delithiation directions are compared in Figures 1A and 1B and summarized in Table II. Similar to results of other researchers, the large dips in the diffusivity were found in the phase transformation regions since the current was consumed by both new phase formation and Li diffusion (PITT) or because the electrochemical potential is constant in the two-phase co-existence regions (GITT). Since the diffusivity in the two-phase coexistence regions are inaccurate, only those in the single-phase regions are taken into consideration hereafter. These figures show that the measured values of $D_{Li}$ from PITT and GITT measurements for lithiation and delithiation were in reasonable agreement. Differences in $D_{Li}$ determined from PITT and GITT measurements were less than a factor of 100 in the lithiation direction. Not including the data for the Li$_2$Sn for $x > 2.3$, the differences in diffusivities calculated from PITT and GITT measurements were less than a factor of 6. Considering both the GITT and PITT measurement results, the diffusivities are of order $10^{-13}$ - $10^{-10}$ cm$^2$s$^{-1}$ in the lithiation direction and $10^{-12}$ - $10^{-10}$ cm$^2$s$^{-1}$ in the delithiation direction. One typical current response of Devanathan-Stachurski cell measurements is shown in Figure 1C. The $D_{Li}$ obtained from three separate experiments in the Devanathan-Stachurski cell was $1.7 \times 10^{-15} \pm 5 \times 10^{-14}$ cm$^2$s$^{-1}$, which is in good agreement with the GITT and PITT results.

As shown in Figure 2A, GITT measurements were conducted at temperatures of 30, 51, 80, 100, 110, 120 and 140°C in order to determine the activation energy of $D_{Li}$. Figure 2B is an Arrhenius plot of the data fit to $D_{Li} = D_{Li0} \exp(-\Delta E_a/RT)$ and the results are summarized in Table III. Our result for the temperature dependent behavior of the intrinsic Li diffusion coefficient $D_{Li}$ requires some additional commentary. At ambient temperature, and at 400 mV it requires $\sim$72 hours to fully lithiate the 25 $\mu$m-thick Sn sheet and using a simple $s^2 \sim D_{Li}t$ estimate for $D_{Li}$ yields an average compositional value of the intrinsic Li diffusivity $\sim 10^{-11}$ cm$^2$s$^{-1}$. The DS time-of-flight measurements are not included in the fits for the pre-exponential and the activation energies.

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**Figure 1.** Ambient temperature measurements of the intrinsic Li diffusivity, $D_{Li}(E)$. A. $D_{Li}(E)$ determined from lithiation titrations, GITT (black) and PITT (red) measurements. B. $D_{Li}(E)$ determined from de-lithiation titrations GITT (black) and PITT (red) measurements. C. Devanathan-Stachurski cell result showing chronocoulometry at 0.400 V Li$^+/Li$ for lithiation (red) and the evolution of the current density on the anodic side of the membrane (black).

**Figure 2.** Temperature dependent GITT results for $D_{Li}(E)$. A. $D_{Li}(E)$ for temperatures ranging from 30–140°C. B. The data in the single-phase regions fit to an Arrhenius plot. The circled points were not included in the fits for the pre-exponential and the activation energies.
measurement for $D_L$ is also a compositionally averaged number that yielded $1.7 \times 10^{-11}$ cm$^2$/s, which is in good agreement with our simple estimate. Both of these numbers are also in reasonable agreement with both the GITT and PITT values.

Typically at ambient temperature, the solid-state mobility of the host material in Li alloys such as Sn or Al is believed to be too small to make a significant contribution to the interdiffusion coefficient formally defined as, $D = (X_{Sn}\sqrt{D_{Li}} + X_{Li}\sqrt{D_{Sn}})$, where the $D_j$ correspond to the intrinsic diffusivities, $X_i$ the mole fraction and $\sqrt{V_i}$ the partial molar volume of the components. The intrinsic diffusivities, are defined by, $D_i = D_i^* \left[1 + \left(\frac{\partial \ln \gamma_i}{\partial \ln X_i}\right)\right]$, where $D_i^*$ is the tracer diffusion coefficient and $\gamma_i$ is the activity coefficient of components in the binary alloy and the bracketed term is called the thermodynamic factor. Apparently the self-diffusivity of Sn$^{2+}$ at ambient temperature is of order $10^{-18}$ cm$^2$/s so that we suspect that $D_{Sn}$ likely does not significantly contribute to $D$. If we consider an equation of the form, $\overline{D}_{Li} = D_{Li} \exp(-Q/LT)$, in order for Arrhenius behavior to be observed for any particular single-phase composition, both the activation energy and the pre-exponential factor should remain constant over the temperature range of interest. Hilliard considered these factors and showed that for negative deviations from ideal solution behavior, i.e., (tendency toward ordering as in the Li-Sn intermetallics) variations of these quantities would be within experimental scatter while for positive deviations from ideality (tendency for phase separation) the effects could be large enough to significantly alter behavior. As shown in Figure 2B, Arrhenius behavior was observed at voltages of 0.440, 0.580 and 0.680 V corresponding respectively to the compositions of Li$_2$Sn$_5$, Li$_2$S and Li$_2$Sn$_5$.

**Morphology Evolution**

Owing to the fragility of fully lithiated Sn sheets, samples were potentiostatically alloyed only to a voltage of 400 mV vs. Li$^+/$/Li to form the phases Li$_2$Sn$_5$, Li$_2$S and Li$_2$Sn$^5$. The fragility results from diffusion-induced stresses and micro-cracking of the 25 mm-thick Sn sheets used in this portion of our work. These cracks appeared mainly toward the middle of the Sn sheet and did not obscure our ability to identify the smaller length scale morphologies that evolve upon de-lithiation. As a note, we observed no such cracking in the electrodeposited 2 mm-thick electrodeposited films used for the determination of the Li diffusivities. It is difficult to determine whether in addition to Li$_2$Sn$_5$, higher concentration Li phases such as Li$_2$Sn$_2$, Li$_1$Si$_2$N, Li$_2$N$_3$, Li$_2$O$_3$, and Li$_2$O$_5$ formed since (as shown later in Figure 4) the ambient temperature lithiation/delithiation voltage vs. Li concentration behavior for Li$_2$Sn for $x > 2.33$ behaves as if the system was single-phase.

Clearly, not all of the intermetallic phases that appear on the equilibrium Li-Sn phase diagram are accessible by electrochemical lithiation at 300 K.

Figure 3A shows linear sweep voltammetry (LSV) data as a function of sweep rate for planar Sn sheets lithiated to 400 mV. The waves in the polarization curves correspond to delithiation of Li$_2$Sn phases initially present and those that may be evolving on the electrode surface during potential scanning. For diffusion-controlled processes the current maximum in the waves is proportional to the square root of the scan rate. Accordingly, the current density, $i$, has been scaled by the square root of the voltage scan rate, $i^* = i/\sqrt{\delta V/\delta t} = i/\sqrt{\nu}$, in order to identify the waves in the LSV associated with diffusion-limited dealloying from those that are not. The data shows that for a sweep rate of $\sim 0.3$ mV s$^{-1}$ there was a single broad wave present at $\sim 1.2$ V. However, at sweep rates lower than 0.087 mV s$^{-1}$, three waves are apparent that we associate with dealloying of Li$_2$Sn ($x \geq 2.33$), Li$_2$S and Li$_2$Sn$_5$. The peak currents of waves 2 and 3 are proportion to $\nu^{1/2}$, while that of wave 1 is not. Waves 2 and 3 likely correspond to solid-mass transport limited delithiation of the Li$_2$S and Li$_2$Sn$_5$ phases. We associate wave 1 with dealloying of the Li$_2$Sn ($x \geq 2.33$) phase(s) and the corresponding voltage to the critical potential for bi-continuous porosity evolution. One can see that wave 1 shifts to higher potentials with increasing sweep rate displaying a shift of $+17$ mV for sweeps of 0.17 and 0.30 mVs$^{-1}$. This shift is consistent with the association of wave 1 with an irreversible process such as percolation dissolution.

The width of wave 1 at half-maximum is $\sim 100$ mV, so based on the LSV behavior we estimate $E_{crit}$ is 600 $\pm$ 50 mV. In order to test this hypothesis, we conducted fixed voltage dealloying experiments for samples lithiated to 400 mV and examined the resulting morphology and chronoamperometry. Figures 3B–3E show the morphologies obtained at 530, 600, 700 and 750 mV. At 700 and 750 mV we observed the formation of a bi-continuous morphology typical of percolation dissolution and the corresponding chronoamperometry shows that the current density maintained a relatively constant value $\sim 2$ mA cm$^{-2}$ for $\sim 800$ s until it began a steep decay following $\sim \nu^{-1}$ behavior that we associate with secondary dealloying occurring from ligaments formed during the initial 800 s. At 530 and 600 mV the morphology shows the evolution of a roughened surface that we associate with layer-by-layer dissolution of finite-size Li-rich (Li$_2$Sn; $x \geq 2.33$) surface domains. As shown in Supplementary Figure S1, at 600 mV the chronoamperometry displays an approximate $\nu^{-1/2}$ decay for the first 500 s followed by a steeper decay.
Given that the critical potential lies in two-phase coexistence voltage region of LiSn/Li7Sn3, we tried to ascertain if dealloying of the LiSn phase, at high enough potentials could result in percolation dissolution and a corresponding bi-continuous morphology. Accordingly, we lithiated Sn sheets at 600 mV vs. Li+/Li and subjected the resulting two-phase Li2Sn5/LiSn microstructure to galvanostatic dealloying at 40 mA cm⁻². Supplementary Figure S2 shows the corresponding negative dendrite morphology. These experiments are consistent with the LSV data and revealed that for the conditions employed, the Li2Sn5 and LiSn phases do not dealloy by a percolation dissolution mechanism.

Figure 4 shows morphology and chronopotentiometry results for galvanostatic delithiation of samples lithiated to 400 mV. For low enough dealloying rates, we expect the chronopotentiometry to result in at least four regions or stages of behavior: Region 1, corresponding to dealloying of the single-phase-like behavior of high concentration Li phases (LiₓSn, x ≥ 2.33); Region 2, corresponding to a voltage plateau resulting from dealloying within two-phase LiSn/Li7Sn3; Region 3 corresponding to a voltage plateau resulting from dealloying within two-phase Li2Sn5/LiSn and Region 4 corresponding to dealloying within two-phase Li2Sn5/Sn. At higher dealloying rates (above ~40 μA cm⁻²) several or all of these regions become convoluted. Based on the LSV and chronoamperometry results, as discussed above, we can expect the formation of bicontinuous structures so long as the dealloying potential achieves a value of 550 mV (lower bound of E_crit) prior to delithiation of the parent phase to the LiSn composition. Otherwise dealloying will be supported by solid-state diffusion and the corresponding morphologies that will form are negative dendrite structures and/or Kirkendall voids. Figures 4A and 4B show samples dealloyed at 40 and 4 mA cm⁻² and Figure 4C shows the corresponding chronopotentiometry demonstrating that the dealloying voltage achieved values of 550 mV within 1 and 10 s respectively at these current densities. Figures 4D–4F show results obtained at 400 μA cm⁻². The FIB cross-sections show a bi-continuous structure with ligament diameters ~1 μm with a substructure within the ligaments. As shown in Figure 4E, this substructure corresponds to a smaller length scale bi-continuous structure. We can understand the evolution of this based on the chronopotentiometry (Figure 4F) showing that the Region 1 voltage was below 500 mV. During this stage, delithiation was supported by Li-diffusion to the alloy/electrolyte interface, since the potential was not large enough for a percolation dissolution process to operate. However, the total charge associated with dealloying in this region was ~0.03 of the total lithiation charge of ~6 C. Within Region 2, the voltage plateau at ~555 mV was of ~36,000 s in duration after which ~0.50 of the lithiation charge remained. Region 3 delithiation was characterized by a voltage plateau at ~710 mV that lasted for ~18,000 s (after which ~0.25 of the lithiation charge remained). This suggests that the larger length-scale bi-continuous structure evolved in the second stage after which the remaining lithium was partitioned into LiSn and Li7Sn3. The ligaments comprising this porous structure...
Figure 5. Dealloying morphology diagrams at low and high $T_f$. A. The behavior noble-metal alloys such as Ag-Au at ambient temperature. B. The ambient temperature behavior of Li-Sn alloys. In each of these diagrams the black curve is the metal/metal-ion equilibrium potential of the less-noble component in the alloy and the red curve is the composition--dependent critical potential. In A the dotted blue vertical line corresponds to the dealloying threshold or parting limit while in B the line corresponds to the threshold composition for percolation dissolution. In these diagrams the abbreviations PD, SVC ND, and KV respectively represent percolation dissolution, surface vacancy clusters, negative dendrites and Kirkendall voids.

Dealloying Morphology Diagrams

A useful way to facilitate a discussion of our results is by constructing dealloying morphology diagrams. Figure 5A shows a generic diagram displaying the morphological evolution behavior expected at low $T_f$ of a $A_pB_{2-p}$ alloy ($p$ is the mole fraction of component A) which forms a continuous series of solid solutions and where the A component is selectively dissolved. The behavior of Ag-Au alloys at ambient temperature is the prototypical example of this. The black--colored curve is the equilibrium potential of the more electroactive component and the red-colored curve shows the composition dependent thermodynamic critical potential, $V_{crit}$. The dashed blue vertical line at $p = p^*$ corresponds to the dealloying threshold or parting limit for the alloy, below which it is not possible to selectively dissolve the more reactive component. The only mechanism for dealloying the sample throughout its volume is percolation dissolution. In order for this to occur the potential needs to be large enough to result in vacancy cluster injection into terrace surface sites. The approximate size, $\xi$, of the mean diameter of the injected clusters is $(1+p)a/(1-p)$ where $a$ is the nearest neighbor spacing in the alloy. During this process the mean composition at the interface between the dealloyed and the un-dealloyed parent phase is virtually identical to the original alloy composition. For potentials larger than $V_{crit}$, the sample will form a bicontinuous structure similar to NPG. At lower potentials and for compositions above $p^*$, surface dealloying occurs and dissolution of A-atoms proceeds in a layer-by-layer process from low-coordinated kink sites at surface steps without the creation of new surface area. Owing to surface step fluctuations, A-atoms in terrace sites eventually find their way to kink sites from which they dissolve. Eventually, this leads to a surface highly enriched in the B component and passivation. Another mechanism for surface passivation occurs at compositions below $p^*$ and potentials higher than $V_{crit}$ for which surface dealloying occurs by a vacancy injection mechanism. A-atoms clusters larger than the mean cluster size, $\xi$, are dissolved (forming surface vacancy clusters) and consequently dissolution is limited to finite penetrations since such large A atom-clusters do not percolate through the solid. As discussed below, for high $T_f$, dissolution within this potential-composition regime results in the evolution of negative dendrite morphologies.

Morphology evolution on dealloying at low $T_f$ of a 2-phase $\alpha/\beta$ microstructure depends on the volume fraction of the phases as well as their composition. Suppose the $\alpha$-phase is rich enough in the A component to allow for percolation dissolution at a sufficiently high potential, while the $\beta$-phase composition does not. In order for dealloying of the $\alpha$--phase to occur throughout the sample volume it is clear that this phase must percolate through the solid. If this is the case then the dealloyed $\alpha$-phase morphology will resemble that which occurs in a single-phase system, however, the bi-continuous morphology resulting from percolation dissolution will be spatially confined to regions previously occupied by the $\alpha$-phase domains. During dealloying the $\beta$-phase will be essentially passive. A more interesting situation can arise in two-phase systems if the composition of both phases allows for percolation dissolution. At a sufficiently high potential bi-continuous porosity would evolve in each of the phases although the length scales (e.g., mean ligament diameter) of the porous structures would be different owing to compositional effects. Since the spatial distribution of these dealloyed morphologies should correlate with the initial microstructure of the parent phase alloy, a multitude of dealloyed bi-continuous microstructures could evolve.

Figure 5B illustrates the dealloying morphology diagram we constructed for the Li-Sn system. The black curve is the equilibrium potential of Li in the alloy referenced to the activity of Li in the electrolyte. The flat regions of this curve correspond to two-phase coexistence regions for which the activity of Li is the same in each phase. We estimated the critical potential in the single-phases, Li$_2$Sn, LiSn and Li$_2$Sn (x $\geq$ 2.33) from the equation,

$$V_{crit}(p) = V_{equil}(p) + \frac{4\gamma_{el} \Omega_{Li}}{F} \frac{1 - p}{(1 + p)^a},$$  

where, $\gamma_{el} \approx 0.6 \text{ Jm}^{-2}$, is the Sn/electrolyte interfacial free energy, $\Omega_{Li} \approx 1.5 \times 10^{-2} \text{ m}^3$, is the molar volume of Li in the alloy, $F$ is Faraday’s constant and $a$ is the nearest neighbor distance in the structure. We note that, as discussed earlier, the Li titration charge/discharge behavior for Li$_x$Sn (x $\geq$ 2.33) is single-phase like and this is the composition range connected to percolation dissolution. The solid red-colored curve is the compositionally dependent thermodynamic critical potential for
bi-continuous porosity formation. This curve has been extended into the region of negative dendrite formation since surface vacancies have contributed to this morphology for the production of Li-dendrites. The large differences in composition among Li$_2$Sn, LiSn and Li$_2$Sb resulted in large differences in the corresponding $V_{rel}$ values that were spliced together in a manner paralleling the Li$^+$/Li$^0$ equilibrium potential. The vertical red-colored dashed line at ~0.52 mole fraction Li corresponds to a percolation dissolution threshold, $\rho_{PD}$. The percolation dissolution regime is similar to that in Figure 5A and is cutoff at a compositional threshold, $\rho_{PD}$, which does not represent a conventional parting limit for the alloy. For Li compositions lower than $\rho_{PD}$ and below the dashed extension of the critical potential curve, de-lithiation is supported by solid-state mass transport since the dealloying potential is too low to result in vacancy injection. Clearly, $\rho_{PD}$ does not correspond to a parting limit since de-lithiation below this composition occurs. Another key difference between Figures 5A and 5B is that there is no passivation region in Figure 5B. At compositions below $\rho_{PD}$ and above the compositionally dependent critical potential curve there is a morphology region that we have termed negative or void dendrites that form by vacancy injection resulting from dissolution of atoms from terrace sites. In this region dealloying is rate-limited by the solid-state mass transport of Li and the evolution of this morphology is isomorphic to dendrite formation in electrodeposition. Between the critical potential and the equilibrium potential curves we observe Kirkendall voids. Within this region the electrochemical potential is too low to allow for dissolution of Li from highly coordinated surface terrace sites and so no significant increase in the area of the solid/electrolyte interface occurs. In a two-phase coexistence region such as Li$_2$Sn/LiSn, morphology evolution will depend on the volume fraction of the phases. In this case there is an additional morphology evolution that can occur in addition to Kirkendall voiding. Assume the volume fraction of the parent phases are such that the LiSn phase is in the form of non-percolating "island" domains within a sea of Li$_2$Sn. For this situation dissolution of Li from LiSn would result in sinusoidal-like surface roughness with a mean wavelength and amplitude corresponding respectively to the mean separation and diameter of the Li$_2$Sn domains.

Conclusions

Titration measurements and a time-of-flight technique were used to measure the compositionally dependent Li intrinsic coefficient, $\Delta V_{Li}$, which at ambient temperature in the delithiation direction ranged from $10^{-12}$ to $10^{-10}$ cm$^2$ V$^{-1}$ s$^{-1}$. Over the temperature range of 30–140 °C, we found the activation energies for Li diffusion in the phases Li$_2$Sn, LiSn and Li$_2$Sb to be respectively 37.4, 37.9 and 22.5 kJ/mol. We described the various dealloyed morphologies that can form in the Li-Sn system and have defined the potentiostatic and galvanostatic composition space, but owing to solids-state mass transport other dealloying morphologies can evolve. These behaviors were summarized in dealloying morphology diagrams that we introduced herein.

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