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The Effect of Grain Size on Mechanical Instability in Single-Phase Li-Alloy Anodes

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Abstract

We derived a critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle single-phase alloys. The predicted critical grain size is less than the unit cell size for a majority of single-phase alloys. We conducted indentation fracture toughness measurements to confirm the prediction. The critical crack length determined from fracture toughness data was in excellent agreement with the predicted critical grain size for microcracking. This result suggests that the model for predicting the critical grain size for microcracking during Li charging into brittle single-phase alloys is correct. The results of this study suggest that decreasing the particle and/or grain size is not a practical approach to solving the mechanical instability problem of single-phase Li alloys that are intended to be used as anodes in Li-ion batteries.

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Introduction

The use of Li alloys (e.g., Li_xM , where M could be Al, Bi, Sn, Si, and Ga) as anodes in Li batteries leads to improved safety and faster cycling rates compared to pure Li [1–5]. One disadvantage of Li alloys as anodes, compared to pure Li, is a reduction in specific energy and energy density. In addition, another problem with Li-alloy electrodes is mechanical instability. Mechanical instability refers to the observation that when Li is inserted/removed during charging/discharging, this leads to microcracking/crumbling of the alloy. Some potential solutions to solve the mechanical instability problem include [6–9] (1) incorporating the alloys within a ductile Li-ion-conducting metal or polymer matrix or (2) decreasing the alloy particle and/or grain size. Decreasing the particle and/or grain size is also important from an electrochemical viewpoint because this can lead to faster cycling rates [10]. How small must the grain size be for the Li alloys to exhibit mechanical stability during lithium charging/discharging? Are grain sizes of Li-alloy particles produced using new nanophase (particle sizes between 10 and 100 nm) techniques small enough?

The purpose of this report is to (1) derive, using an energy balance, a critical grain size below which microcracking does not occur in single-phase Li alloys and (2) confirm experimentally, using the basic concepts of fracture toughness, that the theoretical predictions are indeed correct.

Theoretical Prediction

Determination of the critical grain size below which microcracking does not occur for the Li alloys as a result of volume expansion during Li charging is based on an energy criterion. The energy criterion is based on the concept that the strain energy (generated due to a volume difference between phases) released when microcracks form must equal or exceed that required for the creation of new fracture surfaces. This criterion has been successfully applied to explain crack formation in brittle materials, microcracking due to thermal shock, and thermal expansion anisotropy [11–13].

Start with a single particle composed of fine equiaxed grains. The total energy of this system, U_{tot} , is given as follows [11–13] :

$$U_{tot} = U_0 - U_{\text{strain}} + U_{\text{surface}} , \quad (1)$$

where U_0 is the energy of the unmicrocracked particle, U_{strain} is the strain energy per unit volume, and U_{surface} is surface energy per unit area. The following discussion assumes that microcracking (1) is due to tensile stresses generated as a result of volume expansion and (2) occurs along grain boundaries. Assuming a dodecahedral grain morphology of grain size d , equation (1) reduces to [13]

$$U_{tot} = U_0 - 7.66NU_{strain}d^3 + 20.65N\gamma d^2 , \quad (2)$$

where N is the number of grains relieving their elastic strain energy by microcracking and γ is the surface energy. The critical grain size d_{crit} which we calculate by differentiating equation (2) and equating it to zero, is given as

$$d_{crit} = 1.79\gamma/U_{strain} . \quad (3)$$

The importance of equation (3) is that a material with a grain size smaller than d_{crit} will not exhibit microcracking, whereas if the grain size is greater than d_{crit} , it will exhibit microcracking. Assuming only elastic behavior, the strain energy is

$$U_{strain} = \sigma^2/2E , \quad (4)$$

where σ is the stress and E is the elastic modulus. For the case of a volume change, the stress is given as follows [14]:

$$\sigma = \frac{E}{3(1-2\nu)} \frac{\Delta V}{V_0} , \quad (5)$$

where ΔV is the volume change, V_0 is the initial volume, and ν is Poisson's ratio. Substitution of equation (5) into equation (4) and combining with equation (3) yields the following equation for the critical grain size as a function of volume change:

$$d_{crit} = \frac{32.2\gamma(1-2\nu)^2 V_0^2}{E\Delta V^2} . \quad (6)$$

We can use equation (6) to determine how small a grain size is required so that Li alloys (e.g., Li_xM , where $M = Al, Bi, Sn, Si$, and Ga) that are to be used as anodes will exhibit no microcracking during Li charging. A material with a grain size less than d_{crit} (eq (6)) will not exhibit microcracking as a result of tensile stresses generated by a volume expansion.

What is the critical grain size of an Li alloy that is to be used as an anode in Li batteries? Take $Li_{4.4}Sn$, for example. This binary alloy has the highest Li capacity in the Li-Sn system [7]. The volume change, $\Delta V/V_0$, from Sn to $Li_{4.4}Sn$, is 2.59 per atom of Sn [7,15]. Determination of the critical grain size also requires that E , ν , and γ be known. Unfortunately, a review of the literature did not reveal the values of E , ν , and γ for $Li_{4.4}Sn$. The average E for 20 other intermetallic alloys is close to 200 GPa [16]. The surface energy for brittle materials is typically between 0.3 and 1.2 J/m² [17]. Using $E = 200$ GPa, $\gamma = 0.75$ J/m², $\nu = 0.33$ (a typical value for a crystalline solid), and $\Delta V/V_0 = 2.59$, we can determine the critical grain size below which microcracking will not occur during Li charging of Sn to $Li_{4.4}Sn$. Substituting these values into equation (6) yields a predicted $d_{crit} \approx 0.002$ nm. It is important to note that this grain size (0.040 nm) is about 12 to 13 times smaller than the size of an Sn unit cell (≈ 0.5 nm). A similar

calculation for $\text{Li}_{4.4}\text{Si}$ ($\Delta V/V_o = 3.12$ [7]) yields a predicted $d_{\text{crit}} \approx 0.0014$ nm. These results suggest that it is almost impossible to obtain a grain size fine enough to prevent microcracking during Li charging of a single-phase material. We believe that this is primarily a result of the strain energy generated by large tensile stresses due to the volume change that cannot be accommodated by plastic deformation because of the brittle nature (significant fraction of covalent or ionic bonding) of the material; hence, microcracking occurs.

Experimental Confirmation

Fracture toughness K_{IC} is an intrinsic material property and, for the case of a brittle material, is related to the applied stress σ and the critical crack size c_{crit} by the following relation [14,18,19]:

$$K_{IC} = \sigma (\pi c_{\text{crit}})^{1/2} . \quad (7)$$

When $\pi (\sigma)^{1/2} > K_{IC}$, brittle fracture occurs. Thus, the critical crack size corresponds to the largest crack size the material can tolerate without exhibiting brittle fracture for a given value of applied stress. From equation (7) we observe that if K_{IC} and σ are known, this allows for a determination of the critical crack size. The value of σ , tensile stress generated due to the volume expansion as a result of Li charging, is given by equation (5). We will determine K_{IC} for $\text{Li}_{4.4}\text{Sn}$ using an indentation technique [20–23]. Since both K_{IC} and σ are known, it is then possible to determine c_{crit} for $\text{Li}_{4.4}\text{Sn}$. If the previous theoretical predictions are correct, then $c_{\text{crit}} \approx d_{\text{crit}}$.

An $\text{Li}_{4.4}\text{Sn}$ alloy was chosen as representative of a typical brittle single-phase Li-alloy anode material. We prepared the $\text{Li}_{4.4}\text{Sn}$ alloy by mixing the appropriate amounts of Li (rod; Foote Co.) and Sn (powder; Aldrich Co.) in an Mo crucible. We then heated the Li-Sn mixture at 800 °C for 0.5 hr in a glove box having an oxygen concentration and moisture level of less than 1 ppm to form a molten alloy. The molten alloy was rapidly quenched onto a stainless steel cooling plate. We crushed and ground several of the smaller solid pieces in the glove box using a mortar and pestle. These powders were sealed in capton for x-ray diffraction studies. Some of the larger chunks were mounted and polished for fracture toughness measurements. The samples were cold mounted in the glove box. They were rough polished by SiC paper with mineral oil as the lubricant. Final polishing was done with 1.0- and 0.3- μm Al_2O_3 powder suspended in mineral oil. The samples were indented immediately after polishing. We kept to a minimum the time that the samples were exposed to the ambient atmosphere to prevent a reaction with the moisture and oxygen in the air. If such reactions occurred, the sample was not indented but repolished so that the reaction layer was removed before indentation.

We made measurements of room-temperature fracture toughness using the indentation technique [20–23]. For fracture toughness, a total of five indents per sample were made at 5 kg with a Vickers indenter. The indentation crack lengths were measured immediately after unloading. Fracture toughness was evaluated by the following relation for median cracks [20]:

$$K_{IC} = C_v (P/C_o^{3/2}) (E/H)^{1/2} , \quad (8)$$

where $C_v (= 0.016)$ is a material-independent constant for a Vickers-produced radial median crack, H is the measured hardness, P is the load, and C_o is the crack dimension. Hardness was measured at different indentations than those used for the fracture toughness determination. Crack propagation was examined by optical microscopy.

Figure 1 shows a typical Vickers indentation in the $\text{Li}_{4.4}\text{Sn}$ alloy. A crack emanating from a corner of the indent can be seen; the length of the crack is about 500 μm .

The values of H , P , and C_o determined from the indentation measurements are listed in table 1. K_{IC} for $\text{Li}_{4.4}\text{Sn}$, determined from equation (8) on the basis of the data in table 1 and $E = 200 \text{ GPa}$ [24], is $0.8 \pm 0.2 \text{ MPa}\cdot\text{m}^{1/2}$. K_{IC} values for the ideal brittle material, glass, are close to unity [18–23]. Thus, the K_{IC} results confirm that $\text{Li}_{4.4}\text{Sn}$ is a very brittle material.

The volume change, $\Delta V/V_o$, from Sn to $\text{Li}_{4.4}\text{Sn}$ is 2.59 per atom of Sn [7,15]. Substituting this value into equation (2) with $E = 200 \text{ GPa}$ and $\nu = 0.25$ yields a value of $\sigma = 2.1 \times 10^5 \text{ MPa}$. Substituting $K_{IC} = 0.8 \text{ MPa}\cdot\text{m}^{1/2}$ and $\sigma = 2.1 \times 10^5 \text{ MPa}$ into equation (7) and rearranging yields c_{crit} for $\text{Li}_{4.4}\text{Sn} \approx 0.005 \text{ nm}$. We can compare the $c_{\text{crit}} \approx 0.005 \text{ nm}$ value to the critical grain size, $d_{\text{crit}} \approx 0.002 \text{ nm}$, that was predicted for $\text{Li}_{4.4}\text{Sn}$. From the comparison it can be observed that c_{crit} for $\text{Li}_{4.4}\text{Sn}$ is in excellent agreement with the predicted d_{crit} for $\text{Li}_{4.4}\text{Sn}$. This result suggests that the model for predicting the critical grain size for microcracking during Li charging into brittle single-phase Li alloys is correct.

Figure 1. Typical Vickers indentation in $\text{Li}_{4.4}\text{Sn}$. A crack emanating from a corner is shown. (Magnification = 200 $\times$.)

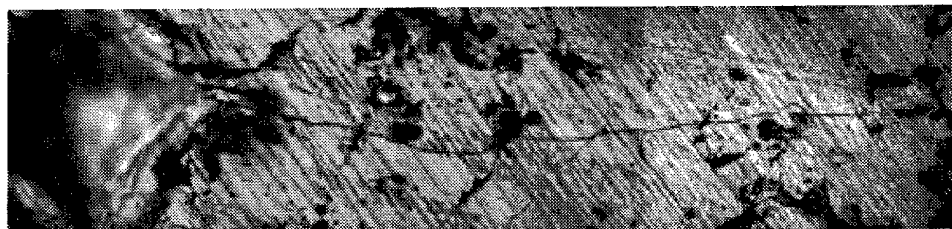


Table 1. Experimental values for $\text{Li}_{4.4}\text{Sn}$.

Parameter	Value
P (kg)	5
H (GPa)	25.8 ± 1.5
C_o (μm)	322 ± 27

Conclusions

It is important to note that both the model and experimental data reveal a grain size below which fracture will not occur that is less than the unit cell size for a majority of brittle single-phase alloys. This suggests that decreasing the particle and/or grain size alone will not solve the mechanical instability problem in brittle single-phase Li alloys that are to be used as anodes in Li-ion batteries. More likely solutions to solve the mechanical instability problem involve a composite approach that would include (1) incorporating the Li alloys within a ductile metal or polymer matrix or (2) surrounding the alloys within a matrix that places them under compressive stresses, which prevents microcrack formation.

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