Critical grain size for microcracking during lithium insertion

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Abstract

A critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys was derived. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or grain size is not a practical solution to solve the mechanical instability problem of Li-alloys. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Microcracking; Grain size; Li-alloys; Anodes

1. Introduction

The use of Li-alloys (e.g., Li_xM where M = 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]. A disadvantage of Li-alloys compared to pure Li as anodes 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]: (i) incorporate the alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) decrease the alloy particle and/or grain size. Decreasing the particle and/or grain size is also important from an electrochemical viewpoint. Decreasing the particle or grain size can lead to faster cycling rates [10]. How small a grain size is required 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 10–100 nm) techniques small enough?

It is the purpose of this paper to attempt to answer the above questions by determining a critical grain size below which microcracking and hence, disintegration of the Li-alloy anodes does not occur during Li charging.

2. Discussion

Determination of the critical grain size below microcracking does not occur for the Li-alloys as a result of volume expansion during Li charging is based on an energy criterion. The basic concept of the energy criterion is 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. The energy 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]:

$$U_{tot} = U_0 - U_{strain} + U_{surface} \tag{1}$$

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: (i) is due to tensile stresses generated as a result of volume expansion and (ii) occurs along grain boundaries. Assuming a dodecahedal grain morphology of grain size, d, Eq. (1) reduces to [13]:

$$U_{tot} = U_0 - 7.66 N U_{strain} d^3 + 20.65 N \gamma d^2 \tag{2}$$

where N is the number of grains relieving their elastic strain energy by microcracking and γ is the surface en-

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ergy. The critical grain size, d_{crit}, is calculated by differentiating Eq. (2) and equating it to zero is given as follows:

$$d_{crit} = 1.79\gamma/U_{strain} \tag{3}$$

The importance of Eq. (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 given as follows:

$$U_{strain} = \sigma^2/2E \tag{4}$$

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]:

$$\sigma = \frac{E}{3(1-2\nu)} \frac{\Delta V}{V_o} \tag{5}$$

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

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

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

What is the critical grain size of a Li-alloy that is to be used as an anode in Li batteries. For example, take $Li_{4.4}Sn$. This binary alloy has the highest Li capacity in the Li–Sn system [7]. The volume change, $\Delta V/V_o$, 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 to 1.2 J/m^2 [17]. Using $E = 200$ GPa, $\gamma = 0.75$ J/m^2, $\nu = 0.33$ (a typical value for a crystalline solid) and $\Delta V/V_o, = 2.59$, the critical grain size below which microcracking will not occur during Li charging of Sn to $Li_{4.4}Sn$ can be determined. Inserting these values into Eq. (6) yields a predicted $d_{crit} \approx 0.002$ nm. If the value of the surface energy is off by a factor of 2 and the elastic modulus is off by a factor of 10 the predicted critical grain size is still less than 0.040 nm. It is important to note that this grain size (0.040 nm) is about 12–13 times smaller than the size of a Sn unit cell (≈ 0.5 nm). A similar calculation for $Li_{4.4}Si$ ($\Delta V/V_o = 3.12$ [7]) yields a predicted $d_{crit} \approx 0.0014$ nm. These results suggest that it is almost impossible to obtain a fine enough grain size to prevent mircocracking during Li charging of a single-phase material. It is believed this is primarily a result of the strain energy generated by large tensile stresses due to the volume change which cannot be accommodated by plastic deformation due to the brittle nature (significant fraction of covalent or ionic bonding) of the material and hence, microcracking occurs. The above predictions are in agreement with experimental electrochemical results, which reveal that it is almost impossible to electrochemically insert Li into fine grain pure metals such as Sn to form Li–Sn alloys without the alloys suffering cracking/disintegration [15,18]. It should be noted that even if a sacrifice in capacity is made in order to reduce the amount of volume expansion, the predicted critical grain size is still less than the size of a unit cell for most of the Li-alloys. For example, Li charging of Sn to form LiSn ($\Delta V/V_o = 0.53$) instead of $Li_{4.4}Sn$ only increases the critical grain size by a factor of about 25 to about 0.05 nm. This grain size is still much smaller than the size of the Sn unit cell. The above predictions and their agreement with the experimental observations emphasize that it is highly unlikely produce a fine enough grain size in an intrinsically brittle single-phase material to prevent microcracking as a result of a volume expansion due to Li charging no matter what processing technique is used, including new nanophase techniques.

The results suggest that decreasing the particle and the grain size is not a practical solution to solve the mechanical instability problem of Li-alloys. More likely potential solutions to solve the mechanical instability problem include: (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix as previously suggested [6–9] or (ii) surrounding the alloys within a matrix which places them under compressive stresses to prevent microcracking formation. This suggestion may explain why SnO and SnO_2 can be cycled where as metallic Sn cannot [15,18,19]. It has been observed that as Li is initially titrated into SnO or SnO_2, it decomposes to Li_2O and Sn. Upon further Li addition a series of Li–Sn alloys form with increasing Li content until a final alloy composition of $Li_{4.4}Sn$ is reached [15,19,20]. It is likely that the Li_2O surrounding the Li–Sn alloys supplies a residual compressive stresses that prevents the Li–Sn alloys from suffering mechanical deterioration during repeated charging/discharging. This same reasoning may also explain why $Li_2MnO_4/Na_{0.7}MnO_2$ composites exhibit better capacity retention during cycling in the 3 V region compared to single phase Li_2MnO_4 [21].

3. Conclusions

A critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys was derived based on energy

considerations. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or the grain size is not a practical solution to solve the mechanical instability problem associated with Li-alloys. More likely potential solutions to solve the mechanical instability problem include: (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix, or ii) surrounding the alloys within a matrix which places them under a compressive stress.

Acknowledgements

References

[1] K.M. Abraham, Electrochimica Acta 38 (1993) 1233.
[2] Z. Takehara, K. Kanamura, Electrochimica Acta 38 (1993) 1169.
[3] R.A. Huggins, J. Power Sources 22 (1988) 341.
[4] R.A. Huggins, J. Power Sources 26 (1989) 109.
[5] A. Anani, S. Crouch-Baker, R.A. Huggins, J. Electrochem. Soc. 134 (1987) 3098.
[6] M. Maxfield, T.R. Jow, S. Gould, M.G. Sewchok, L.W. Shacklette, J. Electrochem. Soc. 135 (1988) 299.
[7] B.A. Boukamp, G.C. Lesh, R.A. Huggins, J. Electrochem. Soc. 128 (1981) 725.
[8] J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1997) 109.
[9] J. Yang, M. Winter, J.O. Besenhard, Solid State Ionics 90 (1996) 281.
[10] K.M. Abraham, D.M. Pasquareillo, E.M. Willstaedt, J. Electrochem. Soc. 145 (1998) 482.
[11] D.P.H. Hasselman, J. Am. Ceram. Soc. 46 (1963) 535.
[12] J.P.A. Tillet, Proc. Phys. Soc. London, Ser. B 69 (1956) 47.
[13] J.J. Cleveland, R.C. Bradt, J. Am. Ceram. Soc. 61 (1978) 478.
[14] M.W. Barsum, Fundamentals of Ceramics, McGraw-Hill, New York, 1997, p. 502.
[15] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2045.
[16] K. Tanaka, M. Kiowa, Intermetallics 4 (1996) S29.
[17] I. LeMay, Principles of Mechanical Metallurgy, Elsevier, New York, 1981, p. 218.
[18] T. Brousse, R. Retoux, U. Herterich, D.M. Schleich, J. Electrochem. Soc. 145 (1998) 1.
[19] C.-K. Huang, J.S. Sakamoto, M.C. Smart, S. Surampudi, J. Wolfenstine, in: D.S. Ginley, D.H. Doughty, T. Takamura, Z. Zhang, B. Scrosati (Eds.), Materials For Electrochemical Energy Storage and Conversion II-Batteries, Capacitors and Fuel Cells, Vol. 496. Materials Research Society, Warrendale, PA, 1998, p. 519.
[20] J. Wolfenstine, J. Sakamoto, C.-K. Huang, J. Power Sources 75 (1998) 181.
[21] J. Kim, A. Manthiram, Electrochem. Solid-State Lett. 1 (1998) 201.