A Mathematical Model of Volume Expansion and Fracture in Lithium-ion Battery Electrodes

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Introduction

Particle fracture and electronic isolation of active electrode material is a possible failure mechanism in lithium-ion batteries. Volume changes in electrode particles during Li insertion and deinsertion create stresses which may induce cracking. This is particularly evident in lithium alloys, which undergo volume changes of up to 300% of the non-lithiated electrode material.[1] Thomas[2] has suggested that cracking of alloys and subsequent growth of a passivating film (the solid electrolyte interphase) on the newly formed surface leads to isolation of active material from the conducting matrix.

Fracture has been observed in intercalation compounds as well. Ohzuku *et al.*[3] and Sawai *et al.*[4] have observed fracture of Li_yMnO_2 particles with an acoustic emission measurement technique. Their results indicate a higher rate of fracture at higher intercalation rates, especially during the first discharge, and little or no cracking during deintercalation. The former observation can be explained by the high degree of lattice strain experienced by an insertion material with a large concentration gradient, which corresponds to high insertion rates.

Mathematical Model

In the present work, we introduce a continuum model that describes the volume expansion of a spherical insertion material, as well as the strain and stress distributions that arise from lithium intercalation. As shown in Figure 1, the outer shell of the particle will expand as lithium is inserted, resulting in a strain differential between the inner and outer regions of the sphere. This strain differential, which increases with the rate of intercalation, gives rise to stress within the particle. If the stress surpasses the yield stress of the material, the particle will fracture.

As a first approximation, we assume that the electrode particle is disordered and that lithium diffusion and lattice expansion/contraction are isotropic. Figure 2 shows the radial and tangential stress profiles for a 5-μm graphite particle that has been charged to an average state of charge of 0.6 at a rate of 0.1 mA/cm^2 (on an initial particle surface area basis). Figure 3 shows the effect of charge rate on the maximum radial and tangential stresses after a fixed amount of lithium has been intercalated. It is clear that higher charge rates lead to increased stress at the edge of the particle.

Winter *et al.*[5] suggest that cracking in alloy particles will be avoided by selecting a small enough particle size. We postulate that this critical size increases as we decrease the charge/discharge rate requirements for a given application. One could conceive of a porous electrode reaching this state naturally as it is cycled, with the particles cracking until they are below the critical size.

Acknowledgement

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References

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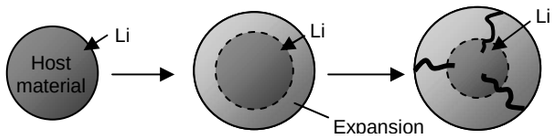

Figure 1. Expansion and cracking of an electrode particle during lithium intercalation.

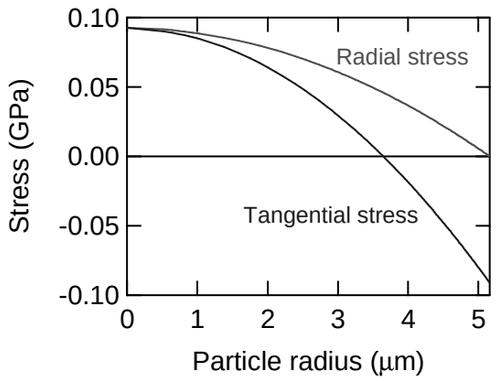

Figure 2. Stress profiles in a graphite particle after it has been charged with lithium at 0.1 mA/cm^2.

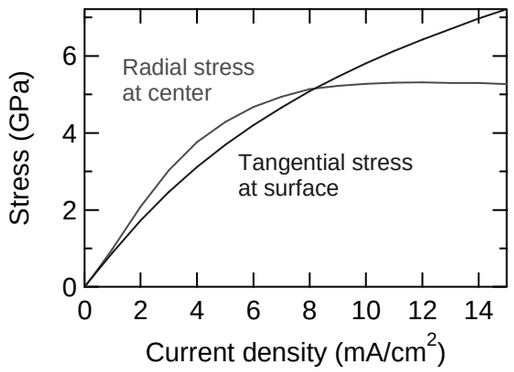

Figure 3. Maximum tangential stress (at the edge of the particle) and radial stress (at the center) once the particle has been charged to an average state of charge of 0.6. The elastic modulus and Poisson's ratio are assumed to be 200 GPa and 0.3, respectively.