Intergranular cracking of polycrystalline particles during electrochemical cycling of Lithium-ion batteries

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Abstract

With the electrification of vehicles and the widespread use of portable digital devices, lithium-ion batteries are experiencing significant growth. Since lithium and cobalt mineral resources are limited and under pressure, it is essential to maximize the lifespan of these devices. For these batteries, the migration of lithium ions from the negative electrode to the positive electrode enables the flow of electrons in the circuit. Therefore, electrode materials have been selected based on their ability to store and release Li+ ions under the influence of an external voltage. The positive electrode studied here is manufactured from micron-sized polycrystalline particles of lithium, nickel, manganese, and cobalt oxide (NMC). These crystals have a layered structure in which lithium atoms can intercalate. While this layered structure is advantageous for storing atoms, it results in anisotropic volume changes during the charging and discharging cycles of the battery. This phenomenon is believed to be the cause of cracking in the positive electrode polycrystalline particles. Indeed, the cracks appear to localize at the grain boundaries as a consequence of the strain mismatch between the grains of differing crystal orientations (Mao et al., 2024). This intergranular fracture is considered one of the key factors behind battery aging and the reduction of capacity over charge/discharge cycles, particularly at high charge rates (Xia et al., 2018).
To understand this phenomenon, it is necessary to establish a link between the microstructure and the damage mechanisms in these particles through multiphysics numerical simulations. There are several examples from the literature which use a model coupling mechanics, diffusion, and damage to simulate this phenomenon at the microstructure scale, using a finite element model (Allen et al., 2021)(Singh et al. 2022) or discrete element method (Sun et al., 2022). In (Allen et al., 2021) and (Sun et al., 2022), synthetic microstructures are used which might influence the simulated results compared to the real microstructures. In (Allen et al., 2021), a synthetic microstructure is generated based on statistics from experimental data for the grain morphology and particle shape, but an assumption is made that the grains are randomly oriented. However, according to (Quinn et al., 2020), there seems to be a texture of the grain orientation which is probably relative to the particle center. Moreover, this texture

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is expected to influence the performance and fracture of the particle and should therefore be integrated in the simulation. In addition, in the previously cited models the material properties data used, like the elasticity coefficients, are taken from density functional theory (DFT) simulations without being compared to experimental measurements.

In this work, a finite element model coupling mechanics, diffusion, and damage is developed. A linear elasticity assumption is made, similarly to the existing models of the literature. For damage, a phase-field model is used. The originality of this work, compared to existing literature, lies in feeding and validating this model through detailed characterizations of the microstructure, and mechanical property measurements. Initially, the model uses as an input a mesh generated from an electron backscatter diffraction (EBSD) map of a particle and elasticity coefficient data obtained from Resonant Ultrasound Spectroscopy (RUS) measurement on a single crystal. Ultimately, the developed model is applied for the simulation of optimized microstructures to mitigate this degradation phenomenon.

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