

Electrochemical Shock in Cubic Spinel

William H. Woodford, W. Craig Carter, and Yet-Ming Chiang

Department of Materials Science and Engineering,
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

“Electrochemical shock” – the electrochemical cycling induced mechanical degradation of electrochemical active materials—contributes to impedance growth in lithium-ion batteries [1-3]. The root cause of electrochemical shock is the shape change during lithium (de)intercalation, which is often large and/or anisotropic. The challenge of designing electrochemical shock resistant electrodes and operating conditions offers an opportunity for new microstructure design criteria.

We present *in-situ* acoustic emission measurements and corroborating micromechanical models which demonstrate and explain C-rate independent electrochemical shock cubic spinel materials. Unlike layered and olivine materials, which have anisotropic shape changes, the cubic spinels undergo isotropic strains as composition is varied. However, these materials, such as LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ undergo first-order phase-transformations between two cubic phases. The linear misfit strains between the coexisting cubic phases are $\sim 1\%$, which is sufficient to drive fracture of particles on the micron scale. This is analogous to the coherency-stress fracture which occurs in LiFePO_4 [4], but the misfit strain is isotropic in the spinels.

First-cycle, slow charge acoustic emission measurements, shown in Figure 1 demonstrate that coarse LiMn_2O_4 particles, with typical particle sizes of 2-4 μm are subject to electrochemical shock, even during C/50 charging. The observed acoustic emission is highly concentrated in the two-phase region. Finer particles, around 1 μm , are not subject to this C-Rate-independent electrochemical shock. These experimental results are in good agreement with micromechanical modeling which incorporates the phase-transforming nature of LiMn_2O_4 . Figure 2 shows an electrochemical shock map, which summarizes the particle sizes and C-Rates at which electrochemical shock is—and is not—possible in this material. The solid red line is the failure line for materials cycled through the two-phase region, and this line is essentially C-Rate-independent. The dashed black line is the failure line for cycling only through the single-phase region. Even to very fast charge rates $>1000\text{C}$, the two-phase coherency stresses are the dominant electrochemical shock mechanism. Analogous experimental and computational results are obtained for the high-voltage spinel system $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

C-Rate-independent electrochemical shock in these spinel materials can be averted by controlling the particle size and/or by identifying chemical modifications which reduce the misfit strain between the coexisting cubic phases.

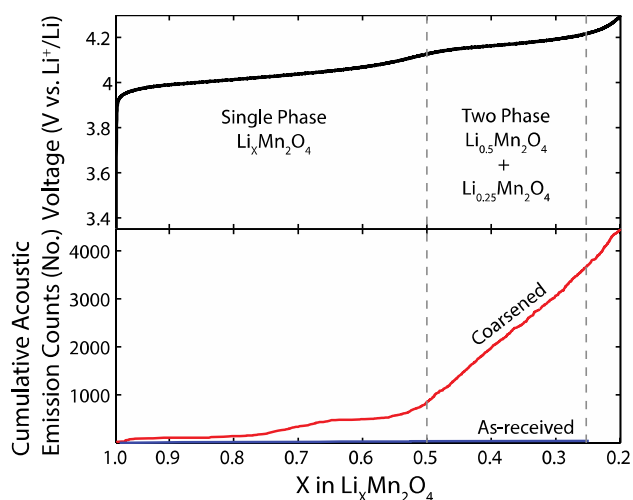


Figure 1: Half-cell voltage and cumulative acoustic emission counts measured during first cycle C/50 charge of LiMn_2O_4 ; the as-received material has typical particle size of $\sim 1 \mu\text{m}$ while the coarsened particles are $\sim 2\text{-}5 \mu\text{m}$.

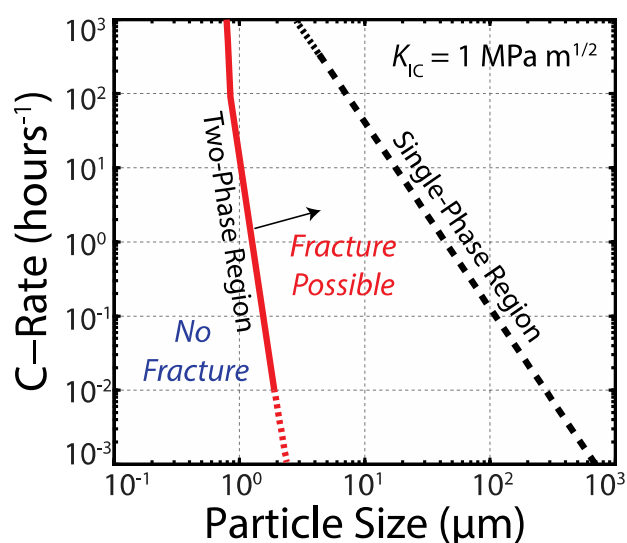


Figure 2: Electrochemical shock map for LiMn_2O_4 , accounting for both concentration gradient stresses and coherency stresses, assuming a fracture toughness of $K_{IC} = 1 \text{ MPa} \cdot \text{m}^{1/2}$. Also shown is the hypothetical failure line for single-phase-only cycling of LiMn_2O_4 . Across a wide range of practical particle sizes and C-Rates, the dominant electrochemical shock mechanism is two-phase coherency stresses, rather than concentration-gradient stresses.

References:

- [1] W.H. Woodford, Y.-M. Chiang, and W.C. Carter, *J. Electrochem. Soc.*, **157**(10), A1052-A1059 (2010).
- [2] P. Arora, R. E. White, M. Doyle, *J. Electrochem. Soc.*, **145**(10), 3647-3667 (1998).
- [3] Y. Ito and Y. Ukyo, *J. Power Sources* **146**, 39–44 (2005)
- [4] Y. Hu, X. Zhao, and Z. Suo, *J. Mater. Res.*, **25**(6) 1007-1010 (2010).

Acknowledgments:

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Award No. DE-SC0002633 and by the National Science Foundation Graduate Research Fellowship Program (WHW).