Supporting Information

Electrochemistry Coupled Mesoscale Complexations in Electrodes Lead to Thermo-Electrochemical Extremes

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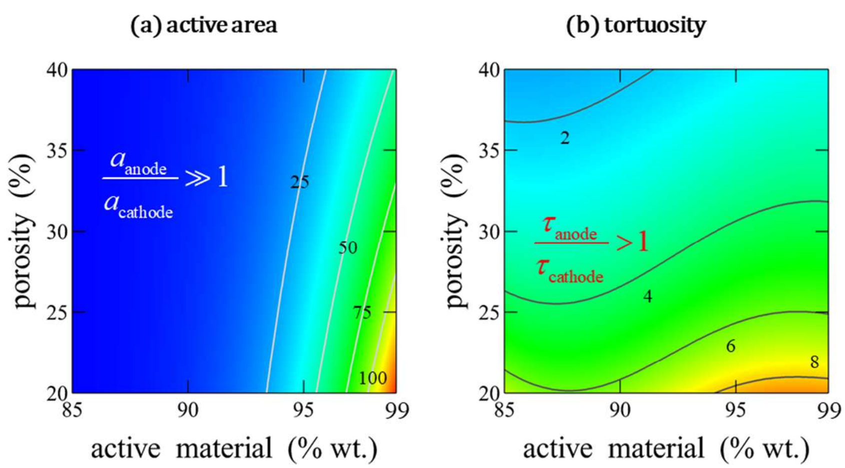
S1. Microstructural Comparison – Platelet Graphite vs. Spherical NMC

As outlined in the manuscript, active material particles have different shapes at the anode and cathode. This dissimilarity results in effective properties and in turn contribute to the difference in the physicochemical evolution of the two electrodes. The particle geometries have been recognized from imaging studies[1-3] and the associated microstructural difference have been hypothesized[4-5]. Given the requirement for cumbersome tests for such investigations, a sufficiently detailed description of composite electrode structures and the corresponding effective property trends has not been hitherto resolved. A major shortcoming of such studies is improper (often absent) treatment of secondary solids that exacerbates the complexations in microstructural responses. Previously authors' have reported comprehensive trends for spherical NMC structures[6], while here similar relationships (Table 1) are derived for platelet-type graphite anode from pore-resolved calculations.

Figure S1 graphically compares the two types of electrodes in terms of their active area (i.e., active material – pore interface) and pore phase tortuosity. The contours are appropriately labeled to assist visualization. Individual particle volumes are kept identical for a fair comparison. The sphere is the most compact shape for a given volume and hence platelet graphite has a much higher area (Figure S1 (a)). This difference manifests as different scales of interfacial effects. On the other hand, the pore network resulting in a platelet structure is much distorted and equivalently the tortuosity is higher than spherical microstructure (Figure S1 (b)). Tortuosity differences alter electrolyte transport behavior.



<u>Figure S1</u>: A comparison of anode and cathode microstructures in the form of (a) active area and (b) tortuosity ratio indicate that a platelet graphite has the much higher active area, but also results in more server pore network resistances. Active particles in both these electrodes have identical volumes. Label denote the respective ratios.

The difference in particle shapes also alter the intercalation dynamics (e.g.,[7]) since the intercalation direction changes accordingly, for example, a platelet particle experience the most dominant intercalation along the thickness coordinate. Subsequently, other associated phenomena such as the mechanical degradation also changes[8-9]. Zhang et al.[9] explicitly analyzed the effect of particle shape on intercalation induced stresses and concluded that particles with a smaller size and larger aspect ratio result in reduced stresses.

References

(1) Ebner, M.; Geldmacher, F.; Marone, F.; Stampanoni, M.;Wood, V. X□Ray Tomography of Porous, Transition Metal Oxide Based Lithium Ion Battery Electrodes. *Adv. Energy Mater.* **2013**, *3*, 845-850.

(2) Shearing, P.; Howard, L.; Jørgensen, P. S.; Brandon, N.;Harris, S. Characterization of the 3-Dimensional Microstructure of a Graphite Negative Electrode from a Li-Ion Battery. *Electrochem. Commun.* **2010**, *12*, 374-377.

(3) Taiwo, O. O.; Finegan, D. P.; Eastwood, D. S.; Fife, J. L.; Brown, L. D.; Darr, J. A.; Lee, P. D.; Brett, D. J.;Shearing, P. R. Comparison of Three□Dimensional Analysis and Stereological Techniques for Quantifying Lithium□Ion Battery Electrode Microstructures. *J. Microsc.* **2016**, *263*, 280-292.

(4) Ebner, M.; Chung, D. W.; García, R. E.;Wood, V. Tortuosity Anisotropy in Lithium□Ion Battery Electrodes. *Adv. Energy Mater.* **2014**, *4*, 1301278.

(5) Billaud, J.; Bouville, F.; Magrini, T.; Villevieille, C.;Studart, A. R. Magnetically Aligned Graphite Electrodes for High-Rate Performance Li-Ion Batteries. *Nat. Energy* **2016**, *1*, 16097.

(6) Mistry, A. N.; Smith, K.;Mukherjee, P. P. Secondary-Phase Stochastics in Lithium-Ion Battery Electrodes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 6317-6326.

(7) Chen, C.-F.;Mukherjee, P. P. Probing the Morphological Influence on Solid Electrolyte Interphase and Impedance Response in Intercalation Electrodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9812-9827.

(8) Chen, C.-F.; Barai, P.;Mukherjee, P. P. An Overview of Degradation Phenomena Modeling in Lithium-Ion Battery Electrodes. *Current Opinion in Chemical Engineering* **2016**, *13*, 82-90.

(9) Zhang, X.; Shyy, W.;Sastry, A. M. Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles. *J. Electrochem. Soc.* **2007**, *154*, A910-A916.