Title: In-depth understanding on lithium metal degradation mechanisms through mathematical modelling and simulation

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Introduction:

Current commercial lithium ion batteries are composed of two intercalation electrodes (anode and cathode) which are porous structures with the capability to intercalate lithium, which gets dissolved and diffuses in the liquid electrolyte covering those porous structures [1,8].

One of the hot topics in battery research right now is the substitution of the porous intercalation anode by a lithium metal foil to increase significantly the volumetric and gravimetric energy density, as future electric vehicle applications demand. However, one of the main problems of using lithium metal anodes is the solid electrolyte interface (SEI) that develops on top of the fresh lithium (by a side reaction of some electrolyte solvents) and the heterogeneous lithium deposition underneath leading to dendrite formation which results in an irreversible loss of lithium and possible short-circuits. This last problem seems inevitable to avoid with liquid electrolytes [4] and it is a strong safety constraint, which constitutes a major drawback.

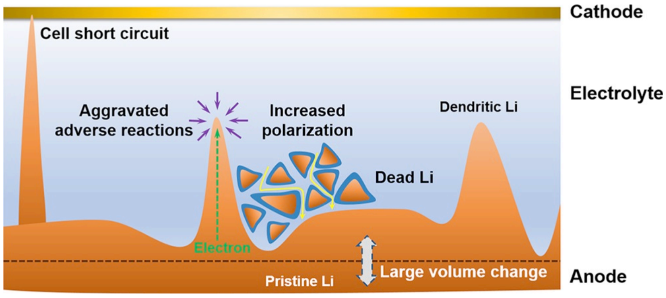

Figure 1: Failure (short circuit) and degradation (dead lithium) mechanisms on lithium metal batteries. Extracted from [2]

A mechanistic understanding and a mathematical model capable to reproduce this degradation and failure mechanisms could pave the way for the design of future lithium metal based batteries.

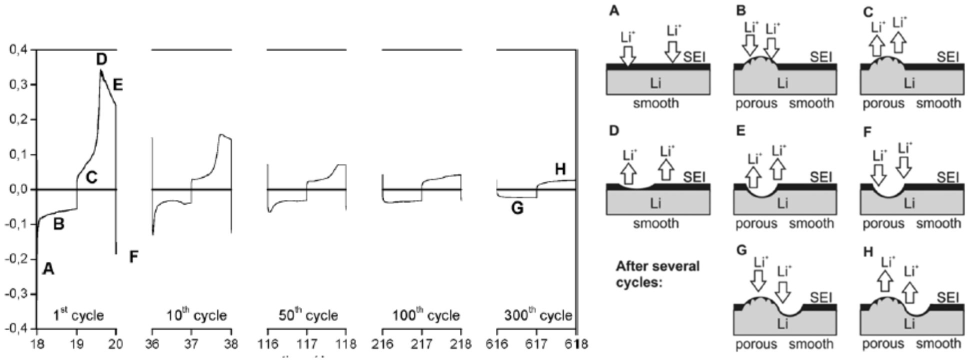

Figure 2: Mechanistic relationship hypothesis between voltage response to cycling and heterogeneous lithium stripping/plating. Extracted from [3]

One can find in [2] a review on lithium metal degradation and failure mechanisms. More specifically in [3], a physical relationship between voltage responses and, degradation and failure mechanisms during cycling of a symmetric lithium metal cell has been suggested.

Objectives:

The main objective of this work is to develop a physically based model capable to explain the voltage response of lithium foil symmetric cells with different electrolytes, as suggested in Figure 2.

To achieve this goal, we propose to extend the existing models by including heterogeneous lithium stripping and plating and solid-electrolyte interface growth and cracking.

Work plan:

Starting from a one-dimensional basic model (having as variables lithium concentration in the electrolyte and ionic potential) we plan to increase model complexity progressively:

1. In a first step, solid-electrolyte interface growth and diffusion of solvent through it [5,9] will be implemented over a one dimensional model, extending the SEI growth mechanisms for intercalation electrodes into foil electrodes and considering expansion/contraction of lithium anode during stripping / plating.

2. As with the previous model it will not be possible to capture heterogeneities, model will be extended to two-dimensions. At this point, we consider to use both a reference domain and / or a phase field approach [9-12] in order to handle the domain evolution.

3. Finally, mechanical effects will be included to account for the solid-electrolyte interface and dendrite formation [4].

We propose to implement the developed models within the finite element platform FENICS [7]. In all cases, we will try to fit model parameters to replicate experimental voltage measurements for different electrolytes.

Requirements:

It is advised to have some knowledge on mathematical modelling of multi-physic problems, numerical simulation or Python programming language.

Bibliography:

[1] J. Newman and K. E. Thomas-Alyea. *Electrochemical Systems*. John Wiley & Sons, 2004.

[2] G. Bieker, M. Winter and P. Bieker. *Electrochemical in situ investigations of SEI and dendrite formation on the lithium metal anode*. Phys.Chem.Chem.Phys., 2015, 17, 8670.

[3] Xin-Bing Cheng, Rui Zhang, Chen-Zi Zhao, Qiang Zhang. *Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review*. Chem. Rev. 2017, 117, 15, 10403-10473.

[4] R. M. McMeeking, M. Ganser, M. Klinsmann, F. E. Hildebrand. *Metal electrode surfaces can roughen despite the constraint of a stiff electrolyte*. J. Electrochem. Soc. 2019, 166, 6, A984-A995.

[5] C. Delacourt, M. Safari. *Simulation-based Analysis of Aging Phenomena in a Commercial Graphite/LiFePO4 Cell.* J. Electrochem. Soc. 2011, 158, 12, A1436-A1447.

[7] M. S. Alnaes, J. Blechta, J. Hake, A. Johansson, B. Kehlet, A. Logg, C. Richardson, J. Ring, M. E. Rognes, G. N. Wells. *The FEniCS Project Version 1.5*. Archive of Numerical Software, vol. 3, 2015.

[8] G. L. Plett, Battery Management Systems, Volume I: Battery Modeling., vol. 1, Artech House, 2015.

[9] X.-G.Yang,Y.Leng, G.Zhang, S. Ge, and C.-Y.Wang, Modeling of lithium plating induced aging of lithium-ion batteries: Transition from linear to nonlinear aging, Journal of Power Sources, 360 (2017), pp. 28–40.

[10] E. Meca, A. Münch, B. Wagner. *Thin-film electrodes for high-capacity lithium-ion batteries: influence of phase transformations on stress*. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences, 472, 2193, 2016.

[11] L. Chen et al. *Modulation of dendritic patterns during electrodeposition: A nonlinear phase-field model.* Journal of Power Sources, 300, 376-385, 2015.

[12] D. R. Ely, A. Jana, R. E. García. *Phase field kinetics of lithium electrodeposits.* Journal of Power Sources, 272, 581-594, 2014.

[13] V. Yurkiv, T. Foroozan, A. Ramasubramanian, R. Shahbazian-Yassar, F. Mashayek. *Phase-field modeling of solid electrolyte interface (SEI) influence on Li dendritic behaviour*. Electrochimica Acta 265 (2018) 609-619.