A fresh look on liquid-electrolyte-Li/S-batteries: non-equilibrium thermodynamics based modeling of transport and reactions

Andreas F. Hofmann and Arnulf Latz
German Aerospace Agency (DLR)
Institute of Technical Thermodynamics
Stuttgart and Helmholtz Institute Ulm (HIU)
Albert-Einstein-Allee 11, 89069 Ulm, Germany

Lithium-Sulfur (Li/S) cells are promising candidates for a next generation of cost-effective high energy density batteries for mobile and stationary applications. At present, Li/S cells using liquid electrolytes still suffer from poor cycleability, capacity loss under high current densities and self-discharge. Furthermore, the underlying chemical mechanisms of the general discharge/charge behavior as well as Li/S-specific phenomena like the (polysulfide) shuttle are not yet fully understood.

Mathematical modeling and simulation of the operation and degradation of Li/S cells generates deeper understanding of the involved principles and mechanisms. Insights gained from modeling can then be used to advise experimentalists in the construction of better functioning cells and thus advance the field in general.

Here we present a general approach for modeling liquid electrolyte transport with more than one anion species based on non-equilibrium thermodynamics (based on [1, 2]). Strong interactions between anions and cations maintain local charge neutrality at all times and we therefore consistently describe the transport of only complexes with no net charge. To that end, we introduce adequate substitutions in the entropy production term, which additionally allows us to reduce model complexity by eliminating explicit descriptions of the conducting-salt anion and the solvent molecule concentrations.

Before surface reactions can take place, the transported uncharged complexes are broken up and charged species are formed at electrolyte-electrode interfaces which subsequently adsorb to the electrode surface. The transfer of charged chemical species from the liquid electrolyte to the solid electrode is thus modeled via a simple double-layer description including explicit kinetics for desolvation and adsorption reactions (see Fig.1). In our description, the adsorption of the desolvated ions to the electrode surface is the only process influenced by the potential difference between electrolyte and electrode.

Using this general modeling approach, we describe a liquid-electrolyte, solid-lithium-anode Li/S cell with a basic set of electrochemical reactions (Fig. 1, following [3]), allowing for simulations of the general operation as well as degradation mechanisms commonly found in liquid electrolyte Li/S batteries (poor cycleability, low cycling efficiency, self-discharge - all related to the polysulfide "shuttle-effect" - see, e.g., [4,5]).

All reactions are described as surface reactions on the solid electrode with kinetic descriptions based on [6]. From the described reaction rates, electron-source terms are derived to explicitly describe cell current density.

The model is transiently solved for the 1D case and results of simulations for various operating conditions are shown and common Li/S battery degradation mechanisms are investigated.

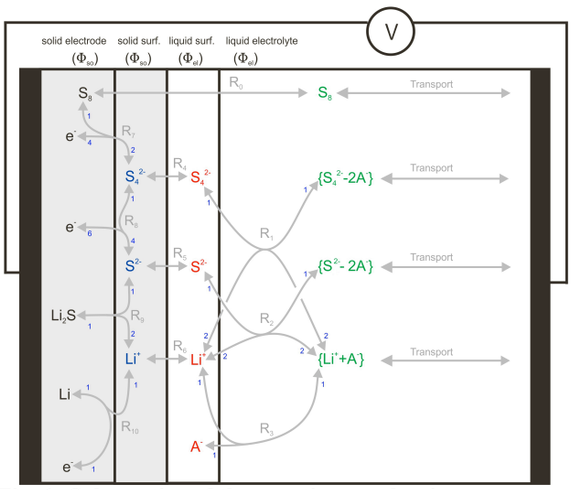

Fig. 1: Schematics of the reaction mechanism at one electrode (without loss of generality the cathode here). At the other electrode, equivalent reactions are modeled. At each electrode, we consider four different layers: the solid electrode (chemical species in black), the surface of the solid electrode (chemical species in dark blue), the "surface" (i.e. the double layer region) of the liquid electrolyte (chemical species in red), and the bulk liquid electrolyte (chemical species in green). Φ_{so} and Φ_{el} are the electrical potential in the solid and the electrolyte, respectively. Light blue numbers indicate the stoichiometric coefficients of the respective reaction.

References:

1. Latz, A and Zausch, J, *Thermodynamic consistent transport theory of Li Ion batteries,* Journal of Power Sources 196, 3296 – 3302, 2011
2. Latz, A., Zausch, J., *Thermodynamic derivation of Butler Volmer model for intercalation in Li ion batteries,* preprint , 2013.
3. Hofmann, A. F., Fronczek, D. N., Bessler. W. G., *Simulating the polysulfide shuttle effect: a thermodynamically consistent, fully reversible, numerical Li/S-battery model,* in preparation.
4. Mikhaylik, Y. V., Akridge, J. R., *Polysulfide Shuttle Study in the Li/S Battery System*, Journal of the Electrochemical Society, 151 (11), A1969-A1976, 2004
5. Zhang, S. S., *Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems and solutions*, Journal of Power Sources, 231, 153-162, 2013
6. Baird, J. K., *A Generalized Statement of the Law of Mass Action,* Journal of Chemical Education, 76 (8), 1146-1150, 1999