

Electrosorption in lithium-sulfur batteries: modeling of solvation and adsorption at nanostructured cathodes

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Since the energy density of lithium-ion batteries is reaching its ceiling so that improvements are just of minor nature, researchers have moved their focus to systems beyond lithium-ion. One of the most promising candidates besides the lithium-air technology for future energy storage both for automotive and stationary applications are lithium-sulfur batteries. The use of sulfur as an active material offers many benefits compared to lithium-ion systems. First of all sulfur is expected to deliver a specific capacity as high as 1675 Ah kg^{-1} for a complete electrochemical conversion reaction with lithium. The rather low operation potential of such a cell is more than offset by such high specific capacity, which leads to a theoretical energy density of around 2600 Wh kg^{-1} , a value approximately 4-5 folds higher than for current lithium-ion cells [1]. Further sulfur is naturally abundant, low in price, non toxic and owns an intrinsic overload protection [2].

Despite all advantages of lithium-sulfur batteries and ongoing research over many decades a commercialization has not succeeded. Occurring problems are a high selfdischarge-rate, low charging efficiency and a short cycle life. All challenges in operating lithium-sulfur cells are correlated with lithium polysulfides, which are intermediate reduction products when lithium reacts with sulfur [3]. These lithium polysulfides, particularly those with longer chain length, are soluble in common liquid electrolytes. So after being formed at the cathode and the dissolution process, polysulfides are moving through the electrolyte to the anode, where they are further reduced, then moving back to the cathode generating a redox shuttle. Insoluble Li_2S and Li_2S_2 precipitate on the anode. This reduces the available active sulfur and results in corrosion and polarization of the anode. Recent approaches to overcome these issues are for one protecting the anode from reacting with lithium polysulfides or for another hindering the movement of lithium polysulfides with MPLs or a structuring of the cathode [4].

To adress the latter, we present a thermodynamically consistent continuum model for nanostructured sulfur carbon composite cathodes. The ideal case is investigated, where all lithium polysulfides are confined within carbon particles. Particular emphasis is put to the adsorption of Li ions on the carbon particle surface and the preceding removal of the solvation shell. We use a consistent mathematical description of charge accumulation at the interface to cover the influence of the electrochemical double-layer. This double-layer model is derived from fundamental thermodynamic and electrostatic laws. No structural properties of the double-layer are presumed. Therefore, the double-layer model gives insight into the underlying mechanisms at the electrode-electrolyte interface. This model is applied to our previous work [5], where an unexpected transport of lithium ions against a concentration gradient into the particles was observed. We investigate the interaction between the osmotic pressure inside the particles due to the transport of lithium ions and surface processes like adsorption and desolvation. This allows to connect surface effects with the overall performance of lithium-sulfur cells.

References:

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