

at least keep up with the consumption by electrochemical reduction. This increase is fueled by both the dissolution of solid sulfur and the subsequent reduction of S_{2-x} species producing shorter, but also more numerous molecules. Once no more sulfur dissolves into the electrolyte (or only at comparatively low rates, see above), the total concentration of polysulfides levels off. The continuous precipitation of Li_2S from the electrolyte is balanced by the progressive reduction of longer S_{2-x} species down to S_{2-4} . Later during the discharge, when less longer species are available, most reduction products precipitate immediately, reducing the total amount of dissolved polysulfides. 5.23 contains the most relevant information about the liquid electrolyte system, which is also confirmed by various experimental characterization techniques, see e.g. Ref. Hence, there is a constant flow of sulfur in its highest oxidation state into the electrolyte, stabilizing a steady-state equilibrium, which in turn results in a constant cell voltage. In that situation, the voltage decreases continuously as does the average oxidation state of the dissolved S_{2-x} polysulfide species. Therefore, each electron extracted from the system directly lowers all concentrations simultaneously, in the end precipitating 1/16 molecule of S_8 per electron. The shorter polysulfides are very short lived; they are fully reduced to S_{2-} and rapidly precipitate as solid Li_2S . Depending on the discharge cutoff voltage, the total concentration may either become as low as [that of a fully charged cell or remain close to the plateau level. As indicated by the solid lines in Fig. [P4