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Modelling transport-limited discharge capacity of lithium-sulfur cells

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ABSTRACT

Lithium-sulfur (Li-S) battery could bring a step-change in battery technology with a potential specific energy density of 500 - 600 Wh/kg. A key challenge for further improving the specific energy-density of Li-S cells is to understand the mechanisms behind reduced sulfur utilisation at low electrolyte loadings and high discharge currents. While several Li-S models have been developed to explore the discharge mechanisms of Li-S cells, they so far fail to capture the discharge profiles at high currents. In this study, we propose that the slow ionic transport in concentrated electrolyte is limiting the rate capability of Li-S cells. This transport-limitation mechanism is demonstrated through a one-dimensional Li-S model which qualitatively captures the discharge capacities of a sulfolane-based Li-S cell at different currents. Furthermore, our model predicts that a discharged Li-S cell is able regain some capacity with a short period of relaxation. This capacity recovery phenomenon is validated experimentally for different discharge currents and relaxation durations. The transport-limited discharge behavior of Li-S cells highlights the importance of optimizing the electrolyte loading and electrolyte transport property in Li-S cells.

1. Introduction

Lithium sulfur (Li-S) battery is emerging as a prime candidate for post lithium-ion battery technologies due to its high practical specific energy density of 500 - 600 Wh/kg [1,2]. Despite their presently limited cycle life, the superior specific energy density of Li-S cells already allows for niche applications, such as in the high-altitude unmanned air vehicle, Zephyr [3]. A key challenge in further enhancing the energy density of Li-S batteries is to identify the mechanisms behind the limited sulfur utilization, especially at higher discharge rates. To this end, a majority of Li-S literature have been focused on improving the sulfur utilization through materials research, whereas relevant studies from a mathematical modeling perspective have been rare.

The discharge of a Li-S cell produces various intermediate polysulfide species that are soluble in typical aprotic solvents. It is generally believed that the dissolution of these polysulfide species into the electrolyte, and their subsequent diffusion away from electrochemically active surfaces, contribute to a major degradation mechanism as well as sulfur-utilization limitation [4,5]. In light of this loss mechanism, numerous strategies have been proposed to encapsulate polysulfides in the cathode, including optimization of the cathode nanomorphology (as reviewed in [6,7]), doping of polysulfide-adsorption sites [8,9], and coating of polysulfide blocking or adsorption layers [10,11]. However, most of these experimental studies are carried out with vast excess of electrolyte [12], not taking into account the fact that the electrolyte-to-sulfur mass ratio has a major influence on the sulfur utilisation [13–15]. In order to achieve high energy-density at cell level, the mass ratio between electrolyte and sulfur should be limited to below 3 [12]. In such cases, the electrolyte is highly concentrated, and the solubility and transport of the various species could be limiting the sulfur utilisation.

While several physics-based models have been developed for Li-S cells [16–26], they fail to capture the utilization of sulfur at different discharge currents, e.g. the rate capability. Kumaresan et al [17] developed the first 1D Li-S model that describes electrochemical reactions, precipitation and dissolution reactions, and ionic transport during discharge based on the Nernst-Plank equations. The model is able to qualitatively capture the discharge behavior of a Li-S cell at low currents. Sensitivity analysis of the Kumaresan model by Ghaznavi and Chen [20–22] indicates that at high discharge currents, the model predicts a capacity reduction in the high-plateau region while the change in low-plateau capacity is negligible. However, experimental Li-S cell discharge curves exhibit an opposite trend whereby increasing the discharge current reduces the cell's low-plateau capacity significantly but not its high-plateau capacity [27,28]. The same mismatch between the

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experimental and modelled discharge behavior is also present in other similar Li-S models [18,19].

In analysing the sensitivity of the Kumaresan model with respect to the diffusion coefficients of ions, Ghaznavi and Chen [22] noticed that the modelled low-plateau capacity would decrease when the effective ionic diffusion coefficients were reduced. With an effective lithium ion diffusion coefficient on the order of 10^{-12} m^2s^{-1}, the dissolving Li^+ ions build up a large concentration gradient in the separator which requires high concentrations of polysulfide anions in the separator to maintain charge neutrality. Based on the Kumaresan model [17], the high concentration of polysulfides in the separator would lead to the precipitation of Li_2S_2, Li_2S_4, and Li_2S_8. These precipitates would eventually block the separator/anode interface and cause a reduced discharge capacity. However, there has been no direct experimental evidence for the existence of any solid discharge product other than Li_2S in Li-S cells [29]. The modelled discharge profiles with low ionic diffusion coefficients were also not compared to experiments.

Recently, Danner et al [26] introduced a particle-scale model for Li-S cells in which polysulfides are confined only within nanostructured sulfur/carbon (S/C) particles. The model predicts the existence of a ‘transport overpotential’ caused by the transport of Li^+ ions against a concentration gradient into the S/C particles. This Li^+ ion concentration gradient, arising from the high concentrations of polysulfide anions confined within the S/C particles, leads to localized Li_2S precipitation during discharge which could cause pore-blocking and reduced sulfur utilisations at high sulfur loadings. This transport-limitation at the particle-scale is similar to the transport limitation scenario at the cell-scale predicted by the Kumaresan model with low ionic diffusion coefficients [22]. However, Danner et al noted that this transport-limitation effect was absent when modelling conventional cathodes where polysulfides were not confined.

This study presents a more detailed investigation into the discharge behavior of Li-S cells subjected to transport limitation. We show that with effective ionic diffusion coefficients on the order of 10^{-12} m^2s^{-1}, a modified Kumaresan model [17] is able to capture the rate capability of a 3.4 Ah Li-S pouch cell containing conventional composite cathodes. The reduction of low-plateau capacity at high discharge currents is explained by trapping of polysulfides in the separator as result of the slow transport of Li^+ ions through the separator. Based on this transport-limitation mechanism, the model predicts that a discharged Li-S cell is able to regain some capacity after a short period of relaxation. We validate this capacity recovery effect by comparing modelled and experimental recoverable capacities at different discharge currents and after various durations of relaxation.

2. Discharge modelling and experiments

2.1. The Li-S model

We employ the relatively well-studied Li-S model developed by Kumaresan et al [17] to investigate the discharge behaviour of Li-S cells. The model formulation, implementation, and parameters are summarized in Appendix A. Two major modifications to the Kumaresan model are made in order to capture the high-rate discharge behaviour of measured Li-S cells: First, we prohibit the precipitation of polysulfides (Li_2S_2, Li_2S_4, and Li_2S_8) other than Li_2S in the model, since Li_2S is the only experimentally detected solid discharge product in Li-S cells. Secondly, we reduce the effective ionic diffusion coefficients in the Kumaresan model by two orders of magnitudes to around 10^{-12} m^2s^{-1}, which was shown to cause transport limitation in the model [22]. The diffusion coefficients of dissolved polysulfides are not well-established in the literature due to the difficulties in isolating an individual polysulfide species that could rapidly disproportionate or associate. The diffusion coefficient of dissolved S_8 was estimated with rotating ring-disk electrode measurement to be on the order of 10^{-10} m^2s^{-1} in a dilute electrolyte containing mixtures of 1,2-dimethoxyethane and 1,3-dioxolane solvents [30]. The same quantity was estimated to be on the order of 10^{-12} to 10^{-11} m^2s^{-1} in a concentrated electrolyte containing a tetraglyme solvent based on steady-state cyclic voltammetry measurements using an ultramicroelectrode [27]. The Li-S cell under study contains sulfolane solvent which is known to exhibit an order of magnitude higher viscosity than most ether-based solvents [31], and is therefore likely to possess lower ionic diffusion coefficients as well.

The effective ionic diffusion coefficients in Li-S cells depend on the electrolyte composition, ionic concentrations, as well as the porosity and tortuosity of electrodes. In the present model, however, we take the simplifying assumption that ionic diffusion coefficients are independent of the electrolyte composition and ionic concentrations, so that the standard Nernst-Planck equations for dilute solution can be applied to describe ionic transport in Li-S cells. We note that all existing Li-S models utilize dilute solution theory to describe ionic transport, even though it was found to be inaccurate in calculating the electrolyte resistance which is concentration-dependent [23]. This limitation is due to a lack of measured polysulfide transport properties, as well as the complexity of concentrated-solution theory (e.g. Maxwell-Stefan formulation) which would render the resulting Li-S model intractable. In addition, we employ the empirical Bruggeman relation (Eq. A22) frequently applied in both lithium-ion and Li-S battery models to describe the dependence of effective diffusion coefficients on the electrode morphology. However, we note that the Bruggeman relation with an exponent of 1.5 is derived for porous morphology made up of isotropic spheres [32], which is quite different from the carbon/sulfur composite morphology in which sulfur (or Li_2S) is dispersed in the pores of carbon matrix. Consequently, the model does not accurately capture the effect of carbon/sulfur morphology on ionic diffusivity. More complex approaches are required to adequately characterise the morphology-diffusivity relation, which may include image based modelling with 3D microstructure data obtained from tomography experiments [33].

2.2. Discharge measurements

A Li-S pouch cell (OXIS Energy Ltd) with a rated capacity of 3.4 Ah at 0.2 C was used to calibrate and validate the discharge curves generated by the model. The cell contains multiple layers of lithium foil anode, polymeric separator, and carbon/sulfur composite cathode filled with sulfolane solvent. Constant current discharges were performed at 30 °C with a Bio-Logic VMP3 potentiostat at 0.2C, 0.5C, and 1C discharge rates to a cut-off voltage of 1.5V. Two sets of capacity recovery experiments were conducted. In the variable discharge-rate tests, the cell was first discharged at a constant current of different magnitudes (0.2C, 0.5C, and 1C). The cell was then disconnected for 5 hours, before it was discharged again at 0.2C. In the variable rest-duration tests, the cell was discharged at 1C followed by a relaxation period of different lengths (10 minutes to 4 hours). It was then discharged again at 1C.

3. Results and discussion

The simulated discharge profiles at 0.2C, 0.5C and 1C rates are compared with the measured curves in Fig. 1. The model captures the reduction of low-plateau capacity at high discharge currents, which was not possible with previous Li-S models in the literature.