

# NUMERICAL MODELLING OF LI-S CHEMISTRY

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**Abstract:** This work presents a custom electrochemical model of a lithium-sulfur cell implemented into Ansys Fluent software. The model was used to analyse cyclic voltammetry at differently sized particles, which represented porous cathodes. The results indicate that the cyclic voltammetry response of the whole porous sulfur cathode could be solved as a response of a single particle, which might lead to a simplification of numerical simulations and in result, to accelerating their optimizing process.

**Keywords:** Li-S battery, electrochemistry, numerical modelling, Ansys Fluent, cyclic voltammetry

## 1 INTRODUCTION

Lithium-Sulfur batteries are seen as a candidate for the new generation of batteries because of their low cost, high theoretical capacity of  $1672 \text{ mAh} \cdot \text{g}^{-1}$  and associated energy density of  $2600 \text{ Wh} \cdot \text{kg}^{-1}$ . This means that practical Li-S battery system should allow for approximately twice the gravimetric energy density of conventional Li-ion batteries [1].

However, the practical application of Li-S batteries is inhibited by complex redox reactions of sulfur, which results in a large number of soluble intermediates with different properties. Furthermore, the poor electronic conductivity of both elemental sulfur  $\text{S}_8$  and  $\text{Li}_2\text{S}$ , as well as continuous dissolution and precipitation of solid species coupled with polysulfide shuttle leads to major challenges to the advancement of Li-S cells [2]. While there is an extensive focus on experimental research [3] on the general properties, the discharge/charge behaviour and microstructure of Li-S cells, the research on numerical models is quite limited [1,4].

This paper focuses on the numerical investigation of sulfur reactions by cyclic voltammetry as its results bring better information about the behaviour of electrochemical reactions and their properties. A custom electrochemical model based on the work of Kumaresan *et al.* [4] was implemented into commercially available software Ansys Fluent. The CV responses a porous electrode was investigated. The influence of the size of porous particles was studied more closely.

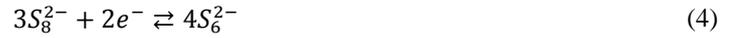
## 2 LI-S BATTERY

The usual Li-S cell is made of composite sulfur cathode based on solid elemental sulfur, conductive carbon and a binder, metallic lithium foil anode and an aprotic electrolyte such as 1,2-dimethoxyethane (DME):1,3-dioxolane (DOL) [4] with lithium salts usually consisting of  $\text{LiNO}_3$  or lithium bis-trifluoromethylsulfonfyl imide (LiTFSI) or their mixture. These salts decrease diffusion and migration of polysulfides into the electrolyte. Interestingly, it was found that lithium salts have no significant effect on the electrochemical performance of Li-S batteries as the behaviour strongly depends on the used solvent [5]. The course of electrochemical reactions is dependent the applied solvent and chemical properties of cathode. As stated in [6], the selection of the solvent strongly influences the stability of polysulfides, which consequently affect the chemical equilibrium between various polysulfides, which makes numerical simulations even more complicated [6]. The overall electrochemical reaction occurring in the Li-S cell can be described as [7]:



However, this reaction does not describe the complete mechanism of the creation of polysulfides during reduction and oxidation. These reactions are responsible for the characteristic two plateau discharge/charge curves. The high plateau is usually situated at 2.3 V – 2.4 V and is controlled by the reduction of longer chain polysulfides. The second plateau is situated at 2 V – 2.1 V and is controlled by the creation of  $Li_2S_2$  and  $Li_2S$  [8].

The model used in this work is based on the reaction mechanism presented by Kumaresan *et al.* [4] The cell at its initial state is fully charged and so the cathode consists of solid sulfur  $S_{8(s)}$ , which is being dissolved into liquid sulfur  $S_{8(l)}$ . During the discharge, the  $S_{8(l)}$  is gradually reduced into shorter chain polysulfides. The reverse process occurs during charging which results in longer chain polysulfides. These electrochemical reactions can be described as:



Depending on the concentration of  $Li^+$  ions and polysulfide chains several dissolution/precipitation reactions can be considered. These reactions are described in [4]. However, experimental studies have shown that all lithium sulfides except  $Li_2S_2$  and  $Li_2S$  are substantially soluble in the electrolyte, so they were not considered in this work, as they would not influence the results significantly [9].

## 2.1 CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) provides valuable information for initial electrochemical research on new systems. Fundamental studies on the electrochemical redox reactions of elemental sulfur on flat electrodes (e.g. glassy carbon, gold, platinum) in nonaqueous media have been extensively investigated. However, these studies do not capture the reaction behaviour in the batteries, as they differ in used electrodes and electrolytes. Additionally, studies of the fundamental mechanism rarely consider effects of the cathode, anode and structure, which greatly affect the redox process and battery performance. In such cases, the translation of the information between fundamental and application studies is difficult. Li-S batteries performance can be significantly influenced by electrode parameters such as sulfur loading and content, material of the current collector and the binder, battery parameter such as the electrolyte and its amount, separator and the amount of lithium, the assembling process and ultimately testing conditions [7, 10].

## 3 NUMERICAL MODEL

The numerical model used in this work is based on Nernst-Planck equations, which describe the flux of all ionic species and the Laplace equation describing the potential in the electrode as the potential in the electrolyte was considered to be 0 V. The reaction kinetics are defined by the concentration-

dependent Butler-Volmer equation. The numerical model is closely described in [9]. The final equations used are:

$$\frac{\partial c_i}{\partial t} - \nabla \cdot (D_i \nabla c_i) = 0 \quad (8)$$

$$\nabla \cdot (-\sigma_s \nabla \varphi_s) = 0 \quad (9)$$

$$\mathbf{j}_{far} = j_0 \left[ \left( \frac{c_A}{c_{ref}} \right)^\gamma e^{\left( \frac{\alpha_a F \eta}{RT} \right)} - \left( \frac{c_B}{c_{ref}} \right)^\gamma e^{\left( \frac{\alpha_c F \eta}{RT} \right)} \right] \quad (10)$$

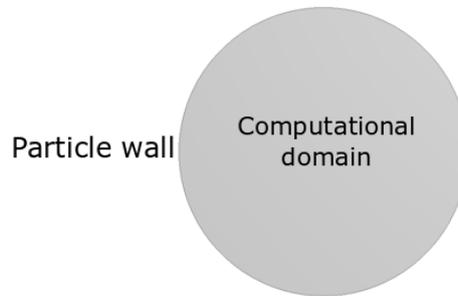
$$\eta = \varphi_s - E_{eq} \quad (11)$$

Where  $c_i$  is the molar concentration [ $\text{mol} \cdot \text{m}^{-3}$ ],  $t$  is time [s],  $D_i$  is the diffusion coefficient [ $\text{m}^2 \cdot \text{s}^{-1}$ ],  $\varphi_s$  is the electrode potential [V],  $\sigma_s$  [ $\text{S} \cdot \text{m}^{-1}$ ] is the electrical conductivity,  $j_0$  is the exchange current density,  $c_A, c_b$  is the molar concentration of reduced and oxidized species [ $\text{mol} \cdot \text{m}^{-3}$ ],  $\alpha_a, \alpha_c$  is the anodic and the cathodic transfer parameter [-],  $\gamma$  is the dimensionless power of species [-],  $\eta$  is the overpotential, which is defined as a potential difference across electrode-electrolyte interface [V] and  $E_{eq}$  is the reduction potential [V].

Ansys Fluent offers a possibility of coupling with Microsoft Visual Studio, which can be used to create custom macros or models based on C++ language. The implementation is described more closely in [9].

#### 4 SIMULATION

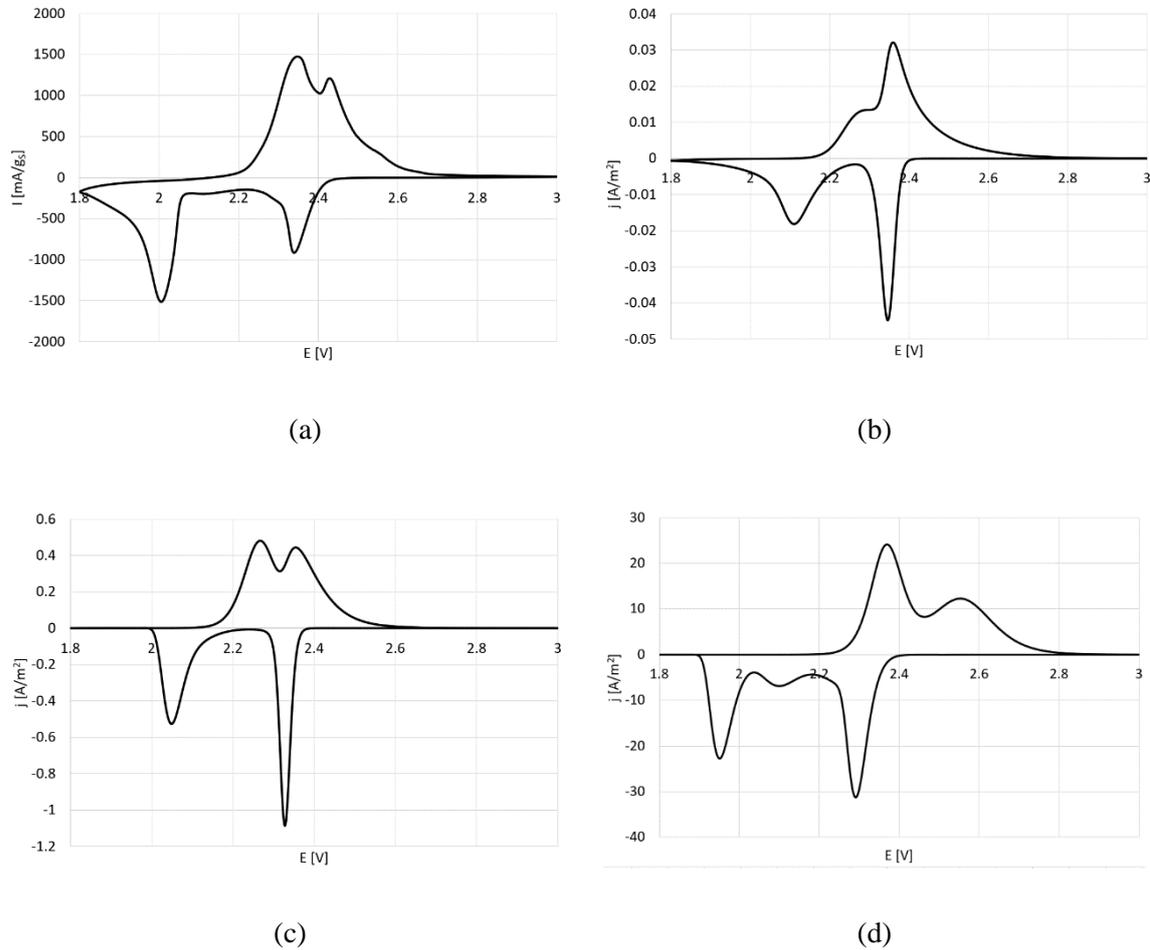
The numerical model presented above was used to study CV of Li-S cells. As it is difficult to experimentally obtain the characteristic parameters of the reactions and polysulfides, they were taken from [4]. The dissolution/precipitation reaction of  $\text{Li}_2\text{S}$  was not considered as the reaction is a chemical and not an electrochemical one, it only depends on the concentration of species and the time. This means that in the CV study, there is only a short amount for the precipitation reaction to occur, as the  $\text{S}^{2-}$  is created only at the end of the cathodic scan [9]. Additionally, the cathode cannot be considered as a planar electrode which slightly increases the complexity of the problem. As described in [11], the porous cathode can be described by a single particle. Figure 1 shows the illustration of such geometry. Initially, the computational domain is uniformly filled with  $19 \text{ mol/m}^3$  of  $\text{S}_{8(0)}$ . CV responses of particles with different radii were modelled and investigated (50 nm, 5  $\mu\text{m}$  and 500  $\mu\text{m}$ ). The boundary condition for the electrode potential was set to a triangle sweeping signal with a scan rate of 0.1 mV/s, with a potential range of 1.8 V – 3 V, with a starting point at 3 V.



**Figure 1:** Illustration of the computational domain for a porous particle [9].

## 5 RESULTS

The numerical results were compared to an experimentally obtained CV of a Li-S cell (Figure 2 (a)). Its characteristics are described more closely in [9]. The results of simulations are also shown in Figure 2. General reaction mechanism is the same for all cases and corresponds with the measured voltammogram. The main difference lies in the amplitude and the position of the peaks. The simulations start with a cathodic scan, during which, two peaks are clearly noticeable. The first peak represents the reduction of the elemental sulfur  $S_{8(l)}$  to  $S_8^{2-}$  and  $S_8^{2-}$  to  $S_6^{2-}$ . The second prominent peak describes the simultaneous reductions of  $S_4^{2-}$  to  $S_2^{2-}$  and  $S_2^{2-}$  to  $S^{2-}$ . These peaks are corresponding with the two plateaus during the discharge process. The reduction of  $S_6^{2-}$  to  $S_4^{2-}$  is not visible in most cases. Similarly, during the anodic scan, two peaks are noticeable. However, their positions and shape are different as they consist of slightly different combination of reactions. The first peak at the lower potential consists of combination of oxidation of  $S^{2-}$  to  $S_2^{2-}$  and  $S_2^{2-}$  to  $S_4^{2-}$  and  $S_4^{2-}$  to  $S_6^{2-}$ , while the second peak consist of oxidation of  $S_6^{2-}$  to  $S_8^{2-}$  and  $S_8^{2-}$  to  $S_{8(l)}$ . As the radius of the particles decreased, the peaks of individual reactions were more separated and more noticeable. For the particle with the radius of 50 nm, the peak representing the reduction of  $S_6^{2-}$  to  $S_4^{2-}$  has become visible.



**Figure 2:** Resulting voltammograms – experimental (a) [9], numerical with a radius of 500  $\mu\text{m}$  (b), numerical with a radius of 5  $\mu\text{m}$  (c), numerical with a radius of 50 nm (d).

## 6 CONCLUSION

The presented results show that the custom electrochemical model is able to model CV of Li-S cells. By comparing the shapes of voltammograms, the modelling of the whole porous cathode might be

replaced by a single particle. This assumption leads to a significant simplification of the solution. Additionally, it might be possible to predict the size of the pores in the cathode. As the radius of particles decreased, the resulting CV has become more similar to the experimental measurement. The peaks of the individual reactions have become more separated and their position has been moved towards lower potentials during the reduction and towards higher potentials during the oxidation. From these simulations, it is possible to predict the size of the pores of the real cathode to be somewhere between 50 nm and 5  $\mu\text{m}$ , pointing towards radii of hundreds of nm as reported in [9]. Unfortunately, only qualitative comparison could be carried out, as the data was measured through the capacity, while the simulations were measured through the current density. In order to properly match the shape of voltammograms it would be necessary to measure the reaction rates and parameters of the exact cathode. Nevertheless, these simulations bring interesting insight to the reaction mechanism of Li-S cells, as it is possible to predict the influences of individual parameters.

## ACKNOWLEDGEMENT

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