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Capacity fading in lithium/sulfur batteries: A linear four-state model

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HIGHLIGHTS

- We introduce a model for the analysis of capacity fading curves of Li/S cells.
- The model describes the discharge process as a Markov chain.
- This approach describes a broad variety of different systems.
- A direct comparison of different concepts of Li/S batteries is enabled.

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ABSTRACT

Lithium/sulfur batteries represent a promising class of energy storage systems. Their drawback still preventing major technical applications is the fading of capacity with the number of cycles. Here we introduce a linear four state model that is capable of describing the majority of the capacity fading curves of recently presented Li/S battery systems with different cathode materials (*e.g.* carbon, metal oxide and metals). Our approach models the discharge process as a Markov chain and consists of only four states that belong to three phases. The living phase comprises a stable and unstable state. The sleeping phase is converted into the living stable state and the dead phase represents the irreversible loss of living phase during the charge/discharge process. Despite its inherent simplicity this approach describes a broad variety of different systems. It gives detailed insights into the fading mechanisms of lithium sulfur cells. Moreover, it represents an easy-to-use tool for the quantitative assessment of a given system in terms of three figures of merit.

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1. Introduction

Lithium/sulfur (Li/S) batteries are discussed as a cost efficient key technology for future applications in portable electronic devices, electromobility and as a backup storage system for the reliable use of renewable energies [1–3]. Because of their high theoretical electrochemical capacity C_{ec}^{max} of 1675 mAh g^{-1} Li/S batteries represent in principle an efficient energy storage system. Moreover, the abundance and low-cost of their raw materials are important advantages of this battery concept. Hence, Li/S batteries have become the subject of an intense research with several publications per week. However, the pronounced capacity fading with increasing cycle number has prevented so far a broad technical application of this system [4].

The decrease of the capacity with cycling is a well known problem for all types of batteries. Especially lithium-ion batteries have been the subject of intense research in order to elucidate the various reasons for the loss of capacity during usage. Thus, many models have been presented that deal with capacity fading of lithium-ion batteries [5–14]. In the review of Arora et al. [5] several causes for capacity fading processes were described in detail. Capacity fading models of Li-ion batteries focus on many parameters like temperature [11,7], growth of a solid electrolyte interface (SEI) layer [12,10,14], active material degradation [6,12,7] and solvent reduction [8]. Similar mechanisms of capacity fading may also be operative in Li/S batteries. However, up to now no model has been introduced that quantitatively analyzes the fading of capacity of Li/S batteries with the number of charge/discharge cycles. Evidently, a modeling of capacity fading in Li/S systems would be highly

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desirable inasmuch it would lead to a quantitative comparison between different materials or chemical processing routes.

Here, we introduce a linear four state model that can be used to analyze to the majority of the published capacity fading curves Fig. 1 gives a survey of typical fading curves where the capacity is plotted as the function of the number of cycles. First of all, ordinary battery aging (curve a)) occurs in every real battery system and determines the long-term stability of the system. In addition to this curve b) and d) describe a film formation period at the electrodes and an additional activation of material, respectively. Curve c) represents a superposition of all processes. The model developed here allows us to analyze the complex processes in Li/S batteries leading to these characteristic fading curves. Based on the model we present three figures of merit that characterize a given Li/S battery.

Our model is based on a Markov process [15], that describes the evolution of the fractions f_i of the system in each state after one charge/discharge cycle, given the present composition. This theory is widely applied to model processes in structural biology [16,17], to optimize the power management of devices and electric vehicles [18–20] or to solve optimization problems in energy supply [21]. It was also previously used to describe a battery's degradation process in the context of implementing optimal power management schedules for devices and electric vehicles. These models typically assume a specific chemical system, and then model degradation based on this assumption [18,22]. Our aim is different. What we are about to show is that a large variety of cathode materials, differing both in terms of chemical composition as well as the specific route followed for their synthesis, show degradation properties that can be described within a unifying framework using a simple Markov model. Since the parameters' in this model can be linked to known physicochemical degradation processes and materials properties, our model aims to provide a qualitative and quantitative tool to evaluate how various design choices might eventually affect a battery's life. To the best of our knowledge, no previous simple and general model was shown to achieve such goal.

The linear four state model developed here is applied to the three typical Li/S systems that differ with regard to their cathode material. Specifically, the cathode of the respective systems is made from either carbon [23,24], a metal oxide composite [25,26], or a metal composite [27]. Metals and metal oxides have been introduced in order to achieve a successful confinement of polysulfides. The strongest adsorption (chemisorption) of sulfur occurs on metal surfaces followed by metal oxides. This fact is reflected by the effect of poisoning of catalysts by sulfur [28]. On the other hand, carbon surfaces exhibit only weak interaction with sulfur (physisorption).

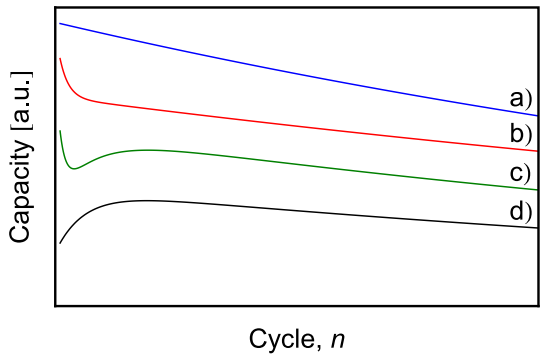

Fig. 1. Capacity fading of lithium/sulfur batteries: The capacity of a Li/S system is plotted as the number of discharge/charge cycles. Here we plot four typical fading curves that apply to practically all published data. The model developed here allows us to discern the different decay channels in Li/S systems.

We demonstrate here that the confinement of the polysulfides can directly be correlated to parameters deriving from our model.

2. Model

The model which is shown in Fig. 2 consists of only four states that belong to three phases. First, the living phase comprises a stable f_{liv1} and unstable f_{liv2} state. Both fractions contribute to the electrochemical capacity of the battery. Second, a sleeping phase f_s that is converted into the living stable state with increasing cycle number. Third, a dead phase f_d that represents the irreversible loss of living phase which cannot contribute to the charge/discharge process anymore. Transitions between these four states are governed by three conditional transition probabilities $k_{liv1\to d}$, $k_{liv2\to d}$ and $k_{s\to liv1}$.

The majority of the capacity curves presented are normalized with respect to the mass of sulfur that is employed in the Li/S battery. Therefore the maximum capacity during the discharge is limited to $C_{ec}^{max} = 1675\ mAh\ g^{-1}$ of sulfur. The fraction of living phase f_{liv} in our model can be regarded as the part of sulfur and lithium-ions that participate in the sulfur reduction process (i.e., in the battery's discharge) (Eq. (1)). Therefore the measured battery capacity is the product of f_{liv} and C_{ec}^{max}.

$$\begin{aligned} &S_8 + 2Li \to Li_2S_8 \\ &Li_2S_8 + 2Li \to Li_2S_n + Li_2S_{8-n} \\ &2Li_2S_n + (2n-4)Li \to nLi_2S_2 \\ &Li_2S_n + (2n-2)Li \to nLi_2S \\ &Li_2S_2 + 2Li \to 2Li_2S \end{aligned} \tag{1}$$

If high amounts of one reaction partner in the sulfur reduction process (Eq. (1)) are irreversibly fixed in other chemical compounds (*e.g.* SEI-layer, the passivation layer, insoluble salts) f_{liv} decreases. The unusable or inaccessible amounts of Li and S are assigned to the dead phase f_d of the battery. Finally, the sleeping phase f_s represents a state that can be converted into the stable living phase during cycling.

The majority of Li/S cells exhibit a sharp decay in electrochemical capacity at the beginning of the cycling process [5]. This process has been attributed to the film formation of *e.g.* a SEI layer or an electrode passivation layer during the early cycling periods [5]. Formation of these films are caused by electrolyte decomposition and unwanted side reactions of the polysulfide or lithium-ions in the vicinity of both electrodes' surfaces. After all available electrode surfaces are coated, this reaction stops. In order to account for this process, we assume that there are two living phases, namely f_{liv1} and f_{liv2}. Here the latter represents the amount of living phase necessary for the initial film formation, which transforms to the dead phase f_d with a conditional transition probability $k_{liv2\to d}$. This fraction cannot contribute to the electrochemical capacity

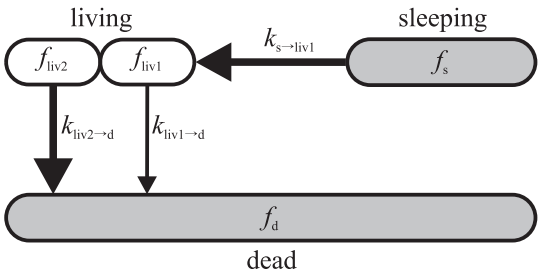

Fig. 2. Linear four state model describing the transition of different phases during cycling of Li/S batteries.

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