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Multi-temperature state-dependent equivalent circuit discharge model for lithium-sulfur batteries

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ABSTRACT

Lithium-sulfur (Li-S) batteries are described extensively in the literature, but existing computational models aimed at scientific understanding are too complex for use in applications such as battery management. Computationally simple models are vital for exploitation. This paper proposes a non-linear state-of-charge dependent Li-S equivalent circuit network (ECN) model for a Li-S cell under discharge. Li-S batteries are fundamentally different to Li-ion batteries, and require chemistry-specific models. A new Li-S model is obtained using a 'behavioural' interpretation of the ECN model; as Li-S exhibits a 'steep' open-circuit voltage (OCV) profile at high states-of-charge, identification methods are designed to take into account OCV changes during current pulses. The prediction-error minimization technique is used. The model is parameterized from laboratory experiments using a mixed-size current pulse profile at four temperatures from 10 °C to 50 °C, giving linearized ECN parameters for a range of states-of-charge, currents and temperatures. These are used to create a nonlinear polynomial-based battery model suitable for use in a battery management system. When the model is used to predict the behaviour of a validation data set representing an automotive NEDC driving cycle, the terminal voltage predictions are judged accurate with a root mean square error of 32 mV.

1. Introduction

To increase an acceptance and a demand of electric vehicles (EV's) among the public, there is a need to overcome range anxiety [1]. Since the range of EVs is strongly connected to their energy storage, there is a request for a low cost and safe operating battery with high specific energy. Potentially fulfilling these requirements, the lithium-sulfur (Li-S) chemistry is a prospective replacement of the current lithium-ion (Li-ion) battery technology [2,3]. However, Li-S batteries still suffer from fast degradation and high self discharge [4], which leads the modelling community to be focused on elucidating the complex inner mechanisms governing the cell behaviour. Despite being essential for Li-S technology uptake, operational models and on-line diagnostic tools, capable of predicting and controlling the batteries performance in operation are lacking in the literature. Recently, commercial Li-S cells have become available (e.g. those supplied by OXIS Energy [5], Sion Power, Polyplus), offering the opportunity for application oriented research. In the framework of electric mobility this translates into investigating the cell's performance under the power and temperature demands of an EV [6]. For established battery chemistries, models have been developed, providing varying levels of insight into the cells' internal processes, at varying computational cost [7]. Since the computational power of a typical electronic control unit (ECU) or battery management system (BMS) is limited, simple low-complexity battery models are often needed for application oriented purposes. Examples of such simplified models are equivalent electrical circuit networks (ECN), which reproduce the transient behaviour of a battery with a circuit of electrical components,

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including resistors, capacitors and a voltage source [8]. The structure of these models is often independent of the cell chemistry, and as such they are not able to give insight into the cell's physical, chemical and electrochemical processes [9]. However, for Li-ion batteries, they have been successfully used for estimating the internal states, such as state of charge (SoC) and measures of battery health such as increase in resistance and decrease in effective capacity [10] (In this paper, only SoC will be considered in detail). Usually they have relatively low computational effort and use easily available measurements like current and terminal voltage. For Li-S batteries ECN models of varying accuracy and complexity have been developed in Ref. [11–14]. These models have been developed for the purpose of analyzing impedance spectroscopy data, such that they describe the cell at a fixed SoC. Because of this they are unsuited to describe performance during cycling. For an OXIS Li-S cell a first operational model including two parallel resistor-capacitor (RC) pairs, has been developed recently with good prediction of the charging process [15]. Furthermore, a comparison of ECN topologies for Li-S batteries in terms of accuracy, and a parameter identification for a three RC model for the same kind of cell were presented in Ref. [16]. In this paper, we introduce the complete framework for developing a Li-S battery model with one RC element, suitable for BMS use, and evaluate its accuracy. Thereby our approach follows the development of a standard ECN model for Li-ion batteries; parametrizing the circuit by fitting pulse discharge data. In order to investigate the temperature dependence of the various circuit parameters for the OXIS Li-S cell, here the parametrization is done for four different temperatures. Also, some of the open questions regarding the suitability of this approach to parametrize the unique properties of Li-S cells are discussed. Therefore we, after a brief introduction into the general requirements for a Li-S battery model (Section 2), (i) use a robust parameter estimation technique developed for Li-S cells, accounting for OCV differences before and after a current pulse (Section 3–4), (ii) apply a novel mixed current pulse test procedure to explore current-dependencies of the model parameters (Section 5), and (iii) identify the cell parameters at four different temperatures (Section 6). The validation of a simplified model is done in Section 7 and Section 8.

2. From Li-ion to Li-S modelling

In the literature, there are many examples of established Li-ion battery models [9,17]. The purpose of one kind, the ECN models, is to predict the output voltage, the available capacity and the degradation at relatively low computational cost [8]. These models are successful enough to be widely used in applications. The main reason for their success is that the intercalation-based chemistry of the Li-ion battery offers a relatively consistent and predictable performance when operated within its limits of charge, temperature and current rates [10]. This is not the case for the Li-S batteries, because they are based on conversion reactions rather than on intercalation. Sulfur reacts with lithium ions when reduced from elemental state S_8, via the intermediates Li_2S_8,Li_2S_4,Li_2S_2, to lithium sulfide Li_2S [18] (Fig. 1), offering theoretically a capacity of 1672 mAh g-1 [19].

However, the practical capacities currently achieved are significantly lower [9,19], mainly due to poor sulfur utilisation and fast degradation [20]. High order polysulfides are highly soluble and reactive [21] in organic electrolytes, while low order polysulfides tend to be insoluble and form an electrically insulating precipitate [4]. The details of the reduction path during discharge are still a matter of ongoing research and are probably more complex [22]. The discharge curve exhibits two regions [23] (Fig. 2): a high plateau at about 2.35 V open circuit voltage (OCV), characterized by the presence of a majority of high order polysulfides in solution (Li_2S_8, Li_2S_6), and a low plateau at around 2.1 V OCV, where lower order chains have been identified (Li_2S_4, Li_2S_3, Li_2S_2), including Li_2S which can precipitate out [24]. With the growing amount of insulating Li_2S_2 and Li_2S, the practical discharge stops at about 1256 mAh g^{-1}, indicated by the increasing cell resistance [25,26]. While charging, the oxidation of low order polysulfides forms high order chains. However, they do not all become elemental sulfur. Highly soluble, high order polysulfides diffuse to the anode and, in contact with its surface, are reduced to lower order chains. These can diffuse back to the cathode, where they are oxidised back to longer chains. This phenomenon, called the polysulfide shuttle [27], can act as overcharge protection [19], but is also responsible for self discharge and poor coulombic efficiency, and associated with capacity fade [27,28].

To identify requirements and challenges towards a fully operational low order Li-S battery model, some Li-ion approaches are listed and examined for their suitability for the Li-S chemistry.

2.1. Voltage curve

The OCV of Li-ion batteries can be measured after some rest time and is sensitive to the SoC [10] and weakly influenced by temperature [29]. Therefore it is usually represented by a variable voltage source with a function or lookup table over SoC, which simplifies the SoC estimation for those batteries [30]. Li-ion has a known predictable and reproducible temperature dependence on OCV. However, lithium sulfur due to the presence of multiple species and multiple reactions between those species has a highly variable and state dependent temperature dependence on OCV, where the state dependence can be a function of the history of the cell going back many cycles. Attempts to model the OCV [31] have been made, but are yet to include the full temperature dependence, which would be necessary to accurately reproduce this effect. Furthermore, in the low plateau, the OCV is not an indication for the SoC since it will always return to about 2.15 V, when given enough

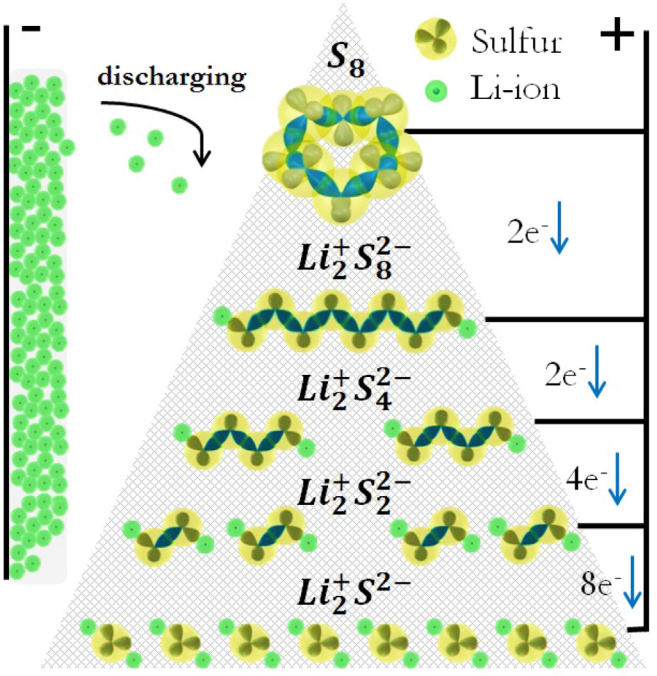

Fig. 1. Work principle of Li-S battery.