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Kalman-variant estimators for state of charge in lithium-sulfur batteries

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HIGHLIGHTS

- Li-S batteries differ to Li-ion batteries, and require specific state of charge estimation.
- We discuss the limitations of standard SoC estimation methods with Li-S.
- A set of applicable state-of-charge estimators for Li-S batteries is developed.
- The extended Kalman Filter (KF), unscented KF and Particle filter are applied.
- The performance of the applied recursive Bayesian filters is evaluated.

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ABSTRACT

Lithium-sulfur batteries are now commercially available, offering high specific energy density, low production costs and high safety. However, there is no commercially-available battery management system for them, and there are no published methods for determining state of charge *in situ*. This paper describes a study to address this gap. The properties and behaviours of lithium-sulfur are briefly introduced, and the applicability of 'standard' lithium-ion state-of-charge estimation methods is explored. Open-circuit voltage methods and 'Coulomb counting' are found to have a poor fit for lithium-sulfur, and model-based methods, particularly recursive Bayesian filters, are identified as showing strong promise. Three recursive Bayesian filters are implemented: an extended Kalman filter (EKF), an unscented Kalman filter (UKF) and a particle filter (PF). These estimators are tested through practical experimentation, considering both a pulse-discharge test and a test based on the New European Driving Cycle (NEDC). Experimentation is carried out at a constant temperature, mirroring the environment expected in the authors' target automotive application. It is shown that the estimators, which are based on a relatively simple equivalent-circuit–network model, can deliver useful results. If the three estimators implemented, the unscented Kalman filter gives the most robust and accurate performance, with an acceptable computational effort.

1. Introduction

Compared to today's widespread lithium-ion (Li-ion) battery technologies, lithium-sulfur (Li-S) offers increased specific energy storage capability [1]. A greater battery capacity is often advantageous, particularly in applications such as electric vehicles, where it can mitigate consumer concerns about driving range. Li-S batteries also have significant benefits in terms of their wide operational temperature window and safety [2]. The fact that sulfur is abundant and environmentally friendly is also attractive for large-scale cost-driven consumer applications. Commercialization has been hindered by the limitations of early-stage Li-S technologies such as quick degradation and limited sulfur utilization [3]. In recent years, considerable effort has been put into the exploration of Li-S's inner cell mechanisms, resulting in enhanced understanding [4]. Commercial cells are now available from suppliers such as OXIS Energy [5] and Sion Power [6]. Although today's cells may not fulfil every aspect of high automotive demands, they do open the opportunity for practical application oriented research.

In order to use a battery in a practical application, it is necessary

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to have an appropriate battery management system (BMS). A key function of the BMS is determining the remaining usable capacity of the battery, i.e. estimation of the state of charge (SoC). This is important for many reasons: the more accurately SoC is known, the greater the proportion of a battery that can be potentially utilized without fear of overcharging and over-discharging; for consumers, it is often helpful to know how much battery life remains.

In the automotive sector in particular, there has been much research on accurate and robust SoC estimation techniques for Li-ion batteries, aimed at meeting the demanding requirements of the automotive traction battery. Here, the batteries operate in an environment with varying power loads, different operation temperatures, noisy and crude measurements, and high safety requirements [7]. For systems with limited computational power, the SoC of a Li-ion battery can be estimated through the use of equivalent–circuit-networks (ECNs) [8,9], which simulate the voltage response of the battery. Due to their simplicity they are not able to give any insight into the inner cell reactions. However, in practice this does not matter: when operated within their specified limits—in terms of state-of-charge, temperature and current rates—performance of intercalation-based lithium-ion batteries is consistent and predictable [10–13]. This behaviour and the fact that the nonlinear relationship between open-circuit voltage (OCV) and SoC is monotonic means that it is relatively straightforward to determine a Li-ion battery's SoC [14].

For Li-ion batteries, there are many viable techniques for estimating SoC *in situ*. The simplest is to measure the open-circuit voltage and relate it through a nonlinear function or lookup table to the SoC. However, this method needs the battery to be in resting condition which limits the applicability for electric vehicles while driving. For improved robustness, OCV-based estimation is combined with other methods [15]. For a given value of SoC, ECN models can be used to predict terminal voltage output from a known dynamically-changing input current. This can be used to estimate SoC with a good compromise between accuracy, robustness and simplicity. A powerful approach is the use of 'observers' or 'state estimators' which combine model-based estimation with actual measurements using principles derived from control theory, particularly the Kalman filter and its derivatives. Estimators of this kind are popular (particularly within the automotive environment) due to their ability to handle measurement noise and model inaccuracies [7]. With these estimation methods, a high battery utilization is possible, without compromising battery safety or lifetime [16].

To date, estimation techniques of this kind have not been applied to Li-S batteries. There are big differences between Li-S and the classic Li-ion chemistry. Li-ion has an intercalation based process that has a single well-known dominant reaction pathway. Li-S batteries however are more complex with multiple pathways [17], which leads to some unusual and challenging behaviour for the SoC estimation: (i) the OCV-SoC curve has two voltage 'plateaus' with different properties; (ii) the OCV-SoC curve has a large flat region, where the OCV does not change with SoC; (iii) the batteries exhibit relatively high self discharge; and (iv) the usable capacity and power exhibit sensitivity to the applied current profile. Until recently, there have been no models of a Li-S cell suitable for use in a battery management algorithm. Recent developments have been made, and there are now published ECN models of Li-S batteries during discharge that are valid for a range of temperatures [18]. However, the use of these models for the estimation of SoC, remains unexplored. As initial step towards a full BMS system for Li-S batteries, this study examines SoC estimation techniques for their applicability to Li-S batteries.

In this paper, Sec. 2 introduces Li-S batteries and their properties. Sec. 3 explores the applicability of state-estimation techniques used for lithium-ion, noting the limitations with OCV measurement and 'Coulomb counting' and concluding that a more sophisticated approach is required. Sec. 4 describes the filtering techniques that will be used for estimation: Sec. 4.1 describes an equivalent circuit model that will be used to implement such filters, and Sec. 4.2–4.4 introduces three such filters: the extended (nonlinear) Kalman filter (EKF), the 'unscented' Kalman filter (UKF) and the particle filter (PF). Sec. 5 describes the experimental evaluation of these. The results are presented in Sec. 6 where their performance and applicability are discussed.

This work has been conducted as part of an automotive battery project, and the batteries used in this study are kept at a well-maintained constant temperature environment. Accordingly, the work in this paper has been restricted to a constant temperature. (In future work, this could be extended to a varying temperature environment.)

The key contribution of this paper is the development and analysis of these three recursive Bayesian SoC estimators for Li-S. To the best of the authors' knowledge, no similar work has appeared elsewhere in the literature.

2. Lithium-sulfur batteries

A Li-S battery consists of a lithium metal anode and a sulfur-based cathode in electrolyte. Sulfur reversibly 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, which is the key of the high theoretical capacity of sulfur (1672 mAh g-1) [19]. The large number of different species however, lead to complex inner reactions that are still a matter of ongoing research [17]. As shown in Fig. 1, the discharge curve consists of two sections [20]: a high plateau at about 2.35 V 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 2.15 V OCV, where lower order chains have been identified (Li_2S_4, Li_2S_3) [21].

In Li-S batteries the availability of these species in the electrolyte determine the battery's behaviour. In simple words, the cathode is dissolving and participating in electrolyte [22], which causes two voltage plateaus with different behaviour (usable capacity, internal resistance, self-discharge, transient behaviour) [23,24]. As an initial step to model these effects, an equivalent circuit model was presented recently, employing the Thevenin model structure with a pulse discharge current profile and an off-line prediction error minimisation method for parameter identification [18]. The model does not explicitly consider self-discharge, but is valid for transient behaviour of the kind seen in this study. In practice, lithium-sulfur batteries do experience significant self-discharge during long

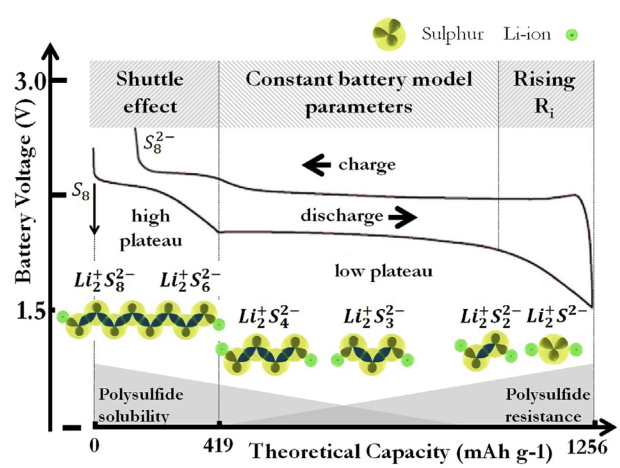

Fig. 1. Discharge/charge behaviour of a Li-S battery.