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Correlation of capacity fading processes and electrochemical impedance spectra in lithium/sulfur cells

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HIGHLIGHTS

- Correlation of capacity fading with electrochemical impedance spectroscopy.
- Distribution of relaxation times calculated with Levenberg-Marquardt algorithm.
- Identification of two capacity fading processes.
- Fast capacity fading process assigned to lithium anode.

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ABSTRACT

The capacity fading of lithium/sulfur (Li/S) cells is one major challenge that has to be overcome for a successful commercialization of this electrochemical storage system. Therefore it is essential to detect the major fading mechanisms for further improvements of this system. In this work, the processes leading to fading are analyzed in terms of a linear four state model and correlated to the distribution of relaxation times calculated with a modified Levenberg-Marquardt algorithm. Additionally, the Warburg impedance and the solution resistance are also obtained by the same algorithm. The detailed analysis of intermediate states during the first cycle gives the distinction between relaxation processes at the sulfur cathode and at the lithium anode. The influence of the polysulfides on the impedance parameters was evaluated using symmetric cells; this yields a good correlation with the results obtained from the first discharge/charge experiment. A fast and a slow capacity fading process are observed for the charge and the discharge during 50 cycles. The fast fading process can be assigned to Faradaic reactions at the lithium anode.

1. Introduction

Lithium sulfur (Li/S) batteries are a promising candidate for the due to their high theoretical gravimetric energy density of 2650 W h/kg$_{\mathrm{sulfur}}$ [1–3]. The low cost, low environmental impact, and their abundant raw materials are further important advantages that have led to intense research on this system [4]. A major drawback is the capacity fading with increasing number of cycles [5–7]. The reasons for this decrease of capacity can be found for instances in the loss of active sulfur species at the cathode (shuttle effect) [8], the drying out of the electrochemical cell by solvent decomposition [9], the formation of electrically disconnected lithium [10] and the precipitation of insoluble species at the anode that occupy active reaction sites [11]. Many studies have been published that aim at deeper insights into the processes that occur in this complex electrochemical system during charge and discharge [12–17]. An empirical model was recently presented [18] that analyses the fading curves in terms of a linear four state model.

The formation of the dynamic and complex surface layer between the liquid electrolyte and each of both solid electrodes is

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central for the cycling stability of the cell [19–21]. This solid electrolyte interphase (SEI) layer can be regarded as a mediator that controls intercalation, diffusion and the charge transfer reaction of the cations and anions. The resulting characteristic Faradaic currents at each electrode give information about the oxidation and reduction processes in an electrochemical cell. A powerful method to analyze these processes is electrochemical impedance spectroscopy (EIS). It can also be applied to many other systems like fuel cells, catalysts, electrochemical capacitors *etc.* [21–24] and it is facile to perform. It gives access to characteristics of electrochemical cells like the Warburg impedance (diffusion of ions), double layer capacity, charge transfer resistance and electrolyte resistance. Also, the various Faradaic reaction processes that occur at the SEI between liquid electrolyte and solid electrode can be investigated with this method [20,25–28]. The EIS data obtained leads to information that is often hard to interpret [29]. In particular, the decomposition of all these processes and the proper determination of all relaxation processes are difficult to achieve. The choice of several resistance-capacitance elements or constant phase elements may lead to overfitting the data [30,31].

The analysis of Li/S cells with EIS is the subject of intense research. In the work by Yuan et al. [32] and Cañas et al. [23] EIS spectra were recorded at intermediate states during the first charge and discharge that could be linked to processes in the electrolyte and at the sulfur cathode. While Deng et al. [5] highlight the important influence of agglomerates at the sulfur cathode on the capacity fading process, Xiong et al. [33] emphasize the important role of the lithium anode and suggested a multi-layer system on this metal electrode. Indication of layered structures on metallic lithium obtained by EIS was also published by Aurbach and Zabane [34,35]. All these publications make use of Nyquist plots and fittings to equivalent circuit containing constant phase or resistance-capacitance elements to investigate the charge transfer processes.

Another way to analyze the Faradaic reaction processes in battery systems is the distribution of relaxation times (DRT) method [24,25,36,37]. The application of this method clearly eases the determination and distinction of charge transfer processes. However, the determination of such DRT-functions inevitably leads to an ill-posed problem that can only be numerically solved.

In this work, we apply the Levenberg-Marquardt algorithm (LMA) that is a standard technique used to solve nonlinear least square problems [38]. The equivalent circuit model used consists of only four elements connected in series that represent the major properties of a battery like the charge transfers at both electrodes, the solution resistance, the Warburg resistance (diffusion), and the inductance of the cable connections (Fig. 1).

The main goal of this work is the correlation of the impedance spectra and the capacity fading as analyzed by the linear four state model [18]. This model allows us to decompose the capacity fading with the number of cycles into several well-distinguished processes. These processes can be subsequently correlated to the relaxation processes established by EIS.

2. Experimental

2.1. Cathode preparation and cell construction

A fraction of the EIS spectra used for this analysis was taken from a recent publication [23]. Two different types of cells were analyzed in this work. The first cells were symmetric cells consisted of two carbon electrodes separated by a Celgard® 2500 membrane. The electrodes were soaked with 14 µL of a 50 mM solution of S_8 and Li_2S_x (with x = 1–8) in tetraethylene glycol dimethyl ether (TEGDME, 99.9%, Sigma-Aldrich). The preparation procedure of the S_8 and Li_2S_x solutions is described elsewhere [39]. The carbon electrodes were composed of 90 wt% of Super P conductive carbon black (99%, Alfa Aesar) and 10 wt% of polyvinylidene fluoride (PVDF, Alfa Aesar) prepared by wet-powder spraying on Al-foil. The thickness of the carbon layer was 35 ± 2 µm.

The second type of the Li/S cells were already described elsewhere [23]. Thus, the preparation of the electrode as well as the cell assembling and electrochemical testing can be found in an earlier publication [23]. In short, the cathode consisted of 50 wt% sulfur (99.5%, Alfa Aesar), 40 wt% Super P conductive carbon black (99%, Alfa Aesar), and 10 wt% polyvinylidenefluoride (PVDF, Alfa Aesar). As electrolyte, 1 M $LiPF_6$ in TEGDME and as separator, Celgard 2500 were used.

2.2. Electrochemical testing

An electrochemical workstation (Zahner® IM6 with Thales battery software) was used to carry out the electrochemical testing of the batteries. A frequency range from 1 MHz (ω_n) to 60 mHz (ω_1) and an excitation voltage of 5 mV were applied for performing the EIS measurements. The discharge/charge procedure for the Li/S cell was performed at constant current density (300 mA g_{sulfur}^{-1}, 0.18C) within voltage range 2.8–1.5 V. EIS spectra were recorded in equidistant charge intervals of 50 mC during the first cycle [23].

2.3. Data processing

In a first step, the measured impedance spectra were corrected with the ZHIT-algorithm [40] to suppress the occurrence of artefacts that can be caused by time-dependent changes of the electrochemical system while measuring the impedance spectra.

2.4. Equivalent circuit model

The corrected EIS spectra were fitted with a linear equivalent circuit model (ECM) illustrated in Fig. 1 by using a modification of the well-known Levenberg-Marquardt algorithm (LMA). The ECM consists of four different elements in series reflecting the major processes of an electrochemical cell.

The value of R_S represents the ohmic resistance attributed to the liquid solution, collectors and cell connections. The inductance L contributes to the imaginary part of the impedance and becomes relevant at very high frequencies ω. The parameter A_W represents the ion diffusion inside an infinitely long diffusion layer (semi-infinite Warburg impedance). On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5.

The superposition of RC-elements represents the distribution of relaxation times. All charge transfer reaction at the electrodes can be expressed by a parallel circuit of a double layer capacity C_{dl} and complex Faradaic impedance Z_f that represents a net current flowing through the electrode surface. This charge transfer can be decomposed by the DRT method to obtain a relaxation time spectrum $\gamma(\tau)$. This transformed view facilitates the determination and the distinction of charge transfer reactions.

2.5. Levenberg-Marquardt algorithm

According to the ECM illustrated in Fig. 1 the measured impedance data $Z_{\text{data}}(\omega)$ can be fitted with $Z_{\text{model}}(\omega)$.

$$Z_{\text{model}}(\omega) = -\frac{A_W}{\sqrt{\omega}}(\mathrm{i}-1) + \mathrm{i}\omega L + R_S - \int \frac{\gamma(\tau)}{1+\mathrm{i}\omega\tau}\mathrm{d}\tau \tag{1}$$

The relaxation time distribution function $\gamma(\tau)$ is defined by