

Changes in internal resistance of lithium-sulfur batteries when using electrolytes based on ionic liquid [DEME][TFSI], sulfolane or TEGDME solvent

Spremembe notranje odpornosti litij-žveplovih baterij pri uporabi elektrolitov na osnovi ionske tekočine [DEME] [TFSI], sulfolana ali topila TEGDME

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Povzetek: Tehnika impedančne spektroskopije je bila uporabljena za študijo notranje upornosti litij-žveplovih akumulatorjev. Da bi razumeli vpliv različnih topil pogosto uporabljenih v elektrolitih za Li-S akumulatorje, so bili v raziskavi uporabljeni trije različni elektroliti (na osnovi ionske tekočine [DEME] [TFSI], topila sulfolan, ali topila TEGDME). Spremembe v notranji upornosti smo spremljali na več točkah praznjenja in polnjenja celic ter čez 50 ciklov delovanja. Iz impedančnih spektrov so bili preko analize in prileganja z enostavnim ekvivalentnim vezjem razločeni štirje impedančni prispevki, ki so bili pripisani elektrolitu, procesom na anodi ali procesom na katodi. Narejena je bila analiza sprememb v velikostih teh prispevkov in primerjava med različnimi uporabljenimi elektroliti

Ključne besede: litij-žveplovi akumulatorji; polisulfidi; impedančna spektroskopija; ionska tekočina; elektroliti.

Abstract: Internal resistance of lithium-sulfur batteries was investigated with impedance spectroscopy. In order to understand the effect of various common solvents for Li-S battery preparation, the electrolyte in the cells was varied (ionic liquid [DEME][TFSI], sulfolane or TEGDME solvent). The impedance changes were followed at several points during discharge and charge of the batteries and through 50 cycles of their use. The resulting spectra were analyzed and fitted, extracting information on four different impedance contribution. The contributions were assigned to the electrolyte, anode or cathode. Their change through a single cycle and through multiples cycles of battery use was evaluated as well as compared between cells employing different electrolytes.

Key words: lithium-sulfur batteries; polysulfides; impedance spectroscopy; ionic liquid; electrolytes.

1. Uvod

Lithium-sulfur (Li-S) batteries are considered an important electrochemical system for the future generation of batteries. Although their theoretical characteristics are favorable (especially in terms of high specific capacity), they are rarely realized in practice¹. The largest issue seems to be dissolution of the intermediate species formed on the cathode (polysulfides) into the electrolyte, which causes lower capacities as well as higher capacity fade and poor Coulombic efficiencies². Since the electrolyte's properties importantly influence this dissolution³, investigation of the electrolyte's performances and the reasons behind any differences is paramount.

There are several techniques one can use to evaluate the performance of battery cells and/or understand their mechanism of operation. Since internal impedance is one of the basic properties of battery cells and it influences both the voltage and the capacity of the cell, determining its size and contributions can be of significant value. Usually, this is done through the use of electrochemical impedance spectroscopy. In general, the impedance response can be divided to the contributions of the electrolyte and the impedances of both the electrodes, which contributions are from charge-transfer reactions and diffusion of active species. Usually, this is complicated due to any passivation reactions or other side reactions.⁴

In this study, we followed the impedance change in battery cells employing different electrolytes, which are commonly used in Li-S batteries - ionic liquid ([DEME][TFSI]) based electrolyte, sulfolane based electrolyte and glyme based electrolyte (TEGDME). Impedance contributions were evaluated using a simple equivalent circuit for fitting and their change was connected to the galvanostatic cycling performance of the battery cells.

2. Materials and methods

Three batteries with different electrolytes were prepared and tested for evaluation of Li-S battery internal impedance response. The electrolytes were LiTFSI (lithium bis(trifluoromethylsulfonyl) imide) salt solutions (1 M) in sulfolane:1,3-dioxolane (DOL) 1:1, TEGDME (tetraethylene glycol dimethyl ether):DOL 2:1, and [DEME][TFSI]:DOL 1:2 mixture. DOL, TEGDME, LiTFSI and sulfolane were all from Aldrich, while [DEME][TFSI] ionic liquid was from Solvionic (N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide). The ratios of the mixtures were chosen so that the viscosities of the electrolyte solutions were close to 5 mPa·s. The battery cells were constructed with 60 μ L per mg S of the electrolyte in order to avoid battery failure due to cell's dry-up. Glassy fibre separator (GF/D, What-

man) was used. Cathodes (1.5 cm²) were made in the laboratory. Preparation of the sulfur/carbon composite was done by mixing ENSACO 350G carbon (Imerys) and sulfur (Aldrich) 1:2 weight ratio. The mixture was heated to 155 °C for 5 hours under argon atmosphere. The composite was mixed with a conductivity additive (Printex XE2, Degussa) and binder (PVDF, Aldrich) in 80:10:10 wt.% ratio in N-methylpyrrolidone (Merck). The slurry was casted on aluminum foil with Doctor Blade and dried at 50 °C overnight (SP-55 EASY drier, Kambič). The active mass loading of the finished electrodes was approximately 1 mg of S per cm².

Impedance spectra were recorded in the range of 1 MHz to 10 mHz with a voltage amplitude of 10.0 mV (rms) using BioLogic VMP3 potentiostat/galvanostat with EC-lab software. The batteries were discharged at C/20 current for a period of one hour. Afterwards the current was stopped and the cells were left at OCV for 15 minutes. Impedance spectrum was recorded before C/20 current was applied again. After 1.5 V vs. Li/Li⁺ was reached, the current was reversed and the same measurement done through charge. Voltage cut-off for charge was 3.0 V vs. Li/Li⁺. 50 cycles of galvanostatic cycling with intermittent impedance measurements were conducted.

The impedance spectra measured were extracted and fitted in ZView with a simple equivalent circuit model (R_{el} -RC1-RC2-RC3). We do not claim for this equivalent circuit model to be physically explainable and directly linked to an electrolyte resistance (R_{el}) and three different processes taking place inside the cell (RC1-RC3). We used it since it was the simplest one that fit well with the measurements and could enable us to follow the change each contribution goes through with battery aging.

3. Results and discussion

The capacities and efficiencies the batteries reached are shown on Figure 1. If we compare the three tested electrolytes, we can conclude that in terms of capacity reached and its fade, sulfolane and TEGDME based electrolyte work very similar, with the latter having better efficiencies. The ionic liquid electrolyte has poor capacity, but the best Coulombic efficiency. The evolution of the impedance contributions was followed through different depths of discharge and multiple cycles of battery use. An example of a measured impedance spectrum, typical frequencies of the impedance arcs and spectrum fit using a simple equivalent circuit can be seen in Figure 2. Values of four contributions to the impedance (R_{el} , RC1, RC2 and RC3) were extracted using the fit with the equivalent circuit shown above the spectrum. The circuit chosen was arbitrary and used only as a means of following the four impedance contributions visible. The R_{el} value reflects the

resistance of the electrolyte, while the other three components do not have a direct proven correlation with a physicochemical process of battery operation (more on the origin of the contributions is discussed in continuation). In this study, we focus only on the sizes of the resistances (R_{el} , R_1 , R_2 , R_3) and merely comment on the capacitance (C) values.

Color coding on x-axis of Figure 2 also shows the graphical representation of the four resistance contributions. The sum of all resistances was usually around 1-2 k Ω , which corresponds well with the internal impedance calculated from galvanostatic experiments.

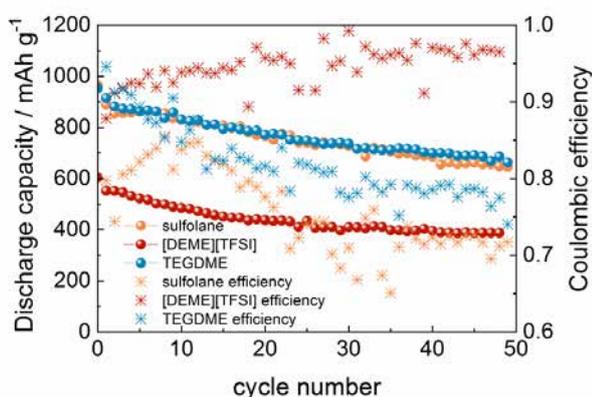


Figure 1. Specific discharge capacities (circles) and Coulombic efficiencies (stars) through 50 cycles of the experiment with intermittent impedance spectra measurements.

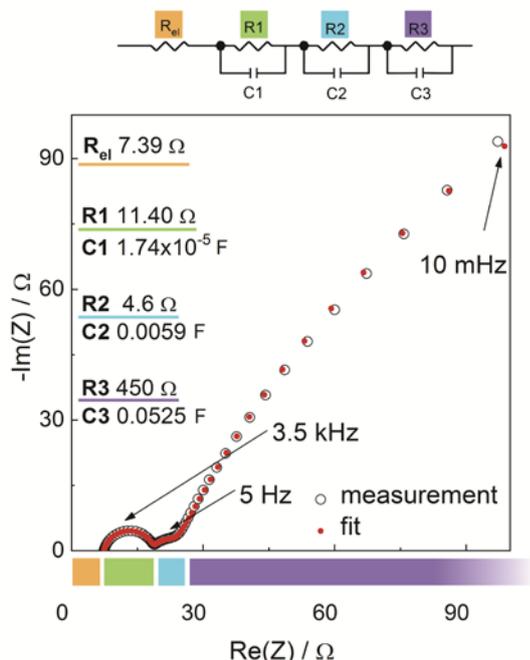


Figure 2. Typical impedance spectrum of a Li-S battery cell and its fit with the equivalent circuit shown above the graph. Color coding shows the resistance values on x-axis.

The R_{el} contribution (resistive intercept) was the only one we could unequivocally attribute to the com-

bined contribution of electrolyte and contact resistance. Since the cell setup is optimized, we have little effect on the contact resistances. Li-S batteries exhibit a distinctive curve in their electrolyte resistance response through discharge and charge of the cell.^{5,6} The same shape can be seen in the three electrolytes tested (Figure 3). The initial resistive intercept increases through the high-voltage plateau and reaches a maximum just before the precipitation of Li_2S starts in the bottom voltage plateau. In charge, a similar (reverse) thing happens, although the resistance never decreases back down to its starting value. The reason behind this curve is in polysulfide dissolution into the electrolyte, which makes it more viscous and disables the ion transport. After the amount of dissolved polysulfides decreases due to Li_2S precipitation, the resistance also decreases. Since the initial value is never reached, it is implied that some polysulfides that dissolve into the electrolyte never precipitate.

This change was monitored through the 50 cycles of the experiment. On Figure 3 shows the results for all three electrolytes. X-axis represents time, but the discharge and charge duration was both normalized. This means that with further cycling, although less capacity was reached, the data for discharge is always plotted between 0 and 1 and data for charge between 1 and 2. Y-axis and its scale for resistance is the same in the cases of sulfolane and TEGDME based electrolytes, and stretched to larger values for the ionic liquid. Blue color signifies low resistances and red higher resistances. Cycle number increases with going further into Z-axis.

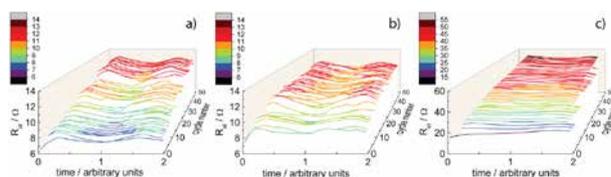


Figure 3. Resistive intercept change through 50 cycles at different DOD for three different electrolytes – (a) 1 M LiTFSI in sulfolane:DOL 1:1, (b) 1 M LiTFSI in TEGDME:DOL 2:1 and (c) 1 M LiTFSI in [DEME][TFSI]:DOL 1:2.

Results for sulfolane and TEGDME based electrolytes are again very similar (Figures 3a and 3b). The characteristic shape (two peaks) is seen through the cycles. The values first increase and level out from the starting 8 Ω to approximately 12 Ω . Sulfolane shows greater increase in values. For [DEME][TFSI] the sharp increase seen in the first cycle continues with resistances reaching just above 50 Ω by the end of the experiment.

If we move towards lower frequencies in the impedance spectrum of a Li-S battery cell, the contributions originate from the charge transfer reactions on the electrodes and diffusion of electroactive species.

The response is further complicated by passivating films and other unwanted side reactions. From the spectra alone it is difficult to extract useful information. For example – without further experiments, one cannot state even if the contribution seen in the spectrum is coming from processes occurring on the anode or on the cathode. As reported elsewhere, symmetrical cells approach 6–8 is the most useful in this case. It is therefore possible to determine, that the RC1 contribution in the battery spectrum is from the anode and the RC3 from the cathode part. In the matter of size of the contributions, the positive electrode dominates the overall response with the low frequency part being the most significant impedance contribution. Assignment of the middle frequency contribution (RC2) is a little more complex. From the symmetrical cells experiment through the first discharge it was determined that that signal is mixed with contributions from both sides.

The high frequency arc response (RC1), which we attributed to the anode 6–8, was followed through 50 cycles and is depicted on Figure 4. The representation is similar as the one for the resistive intercept, although here, the z-axis (cycle number) is reversed for better clarity.

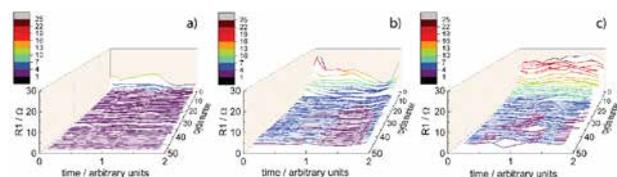


Figure 4. R1 (lithium anode contribution) change through 50 cycles at different DOD for three different electrolytes – (a) 1 M LiTFSI in sulfolane:DOL 1:1, (b) 1 M LiTFSI in TEGDME:DOL 2:1 and (c) 1 M LiTFSI in [DEME][TFSI]:DOL

The size of the anode resistance through the first discharge is a few 10 Ω. Afterwards it decreases in all three electrolytes tested (albeit with different rates) and by the end of the 50th cycle measures only a few Ω. Explanation of this phenomenon is in high surface area Li deposits (HSAL). Since the surface area of the electrode gradually increases, the resistance gets smaller. That also implies, that the anode resistance is insignificant compared to the cathode contributions after a few cycles. The double layer capacitance for this feature remains relatively constant through different DOD and further cycling and is of approximate value of 1 μF, consistent with literature reports for charge transfer contributions.⁹ This degree of size reduction is only the case when excess of electrolyte is present in the cell. If the cell dries out due to side reactions of Li anode with the electrolyte, the decrease in the anode contributions is not that pronounced.

The change of R2 contribution through cycling

in different electrolytes is shown in Figure 5. Y-axis and its scale for resistance is the same in the cases of sulfolane and ionic liquid based electrolytes, and reduced to smaller values for TEGDME. The response is different when changing the solvent. Contribution in TEGDME based electrolyte is maximum 15 Ω in size, while the resistances in the other two electrolytes reach over 500 Ω. Its shape through different DOD is also different. With sulfolane and TEGDME electrolyte, it exhibits peaks in the middle of both discharge and charge, while the resistance for the [DEME][TFSI]:DOL electrolyte increases at the end of discharge. The origin of this contribution is complex and could be either due to passivation effects on the cathode or even diffusional complications due to HSAL growth on the lithium anode. Either way, its origin exceeds the scope of this study so we cannot speculate of its meaning.

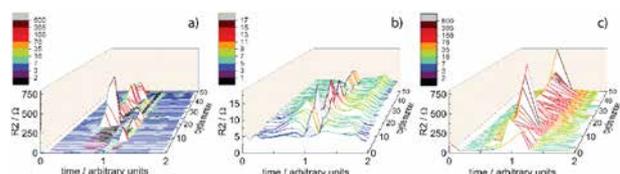


Figure 5. R2 (middle frequency resistance) change through 50 cycles at different DOD for three different electrolytes – (a) 1 M LiTFSI in sulfolane:DOL 1:1, (b) 1 M LiTFSI in TEGDME:DOL 2:1 and (c) 1 M LiTFSI in [DEME][TFSI]:DOL

The lowest frequency contribution (RC3) is similar in size in all the electrolytes, reaching over a kΩ and dominating the internal impedance Figure 6. With the ionic liquid electrolyte, the values are incomplete since at the beginning and end of discharge, the spectra showed a more blocking response and the equivalent circuit chosen for the fit was not adequate. In other studies, it has been determined that this contribution is due to diffusion of polysulfides through the separator pores¹⁰. There is little variation in this contribution with further cycling, but it does show a generally similar curve with peaks at the end of discharge (time = 1) and end of charge (time = 2) for all the electrolytes tested. This is in line with the diffusional contributions increasing at those points due to the lowest concentrations of polysulfides.

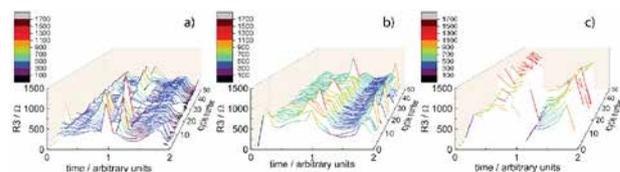


Figure 6. R3 (low frequency cathode resistance) change through 50 cycles at different DOD for three different electrolytes – (a) 1 M LiTFSI in sulfolane:DOL 1:1, (b) 1 M LiTFSI in TEGDME:DOL 2:1 and (c) 1 M LiTFSI in [DEME][TFSI]:DOL 1:2.

If the variation in impedance contributions is compared to the electrochemical performances depicted

in Figure 1, two conclusions could be made: (i) it is likely that the RC2 contribution (for which correlation to its physicochemical meaning has not been successful) causes the lower capacities achieved with the ionic liquid based electrolyte; and (ii) the difference in the Coulombic efficiencies between the sulfolane and TEGDME solvent are in all probability connected to the solubility of polysulfide species in the respective electrolytes³. The latter claim is supported by the variation in the resistive intercept (Rel). Since the values level out sooner for TEGDME solvent, polysulfide species are less soluble in the corresponding electrolyte than in the sulfolane based one.

4. Conclusions

Regardless of the electrolyte used, the impedance contribution for Li-S batteries show several similar characteristics. The resistive intercept value has a peak shape due to dissolution and precipitation of polysulfide species. The Rel value also increases with further cycling, an effect connected with permanent dissolution of polysulfides, albeit the degree of this change is different in connection to the solubility of polysulfides in different electrolytes. Secondly, the RC1 (anode) contribution significantly decreases with further cycling in all cases tested, a consequence of surface area increase due to dendritic growth, resulting in insignificant impedance contribution from the Li metal anode. Third, The RC3 contribution is the largest detected and is attributed to the cathode impedance due to diffusion of polysulfides in the separator. There is some variation in the exact shape of this contribution during charge and discharge, although in general it exhibits a peak at the beginning and end of each half-cycle. The largest difference between the electrolytes tested was detected for the (unassigned) RC2 contribution.

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