Development of High-Capacity Lithium Sulfur Batteries

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Abstract In this paper we want to show some of the most recent results obtained in our laboratory concerning the fabrication of lithium sulfur batteries. For their construction we used two different binders and two carbons with different surface areas, deposited directly on the separator. Sulfur was introduced mixed with the electrolyte in the form of polysulfide. The particular cell configuration has allowed to obtain stable specific capacities after numerous charge and discharge cycles of more than 800 and 1200 mA h/g and low cell resistances.

1 Introduction

In a rapidly changing electrical system scenario, where the energy mix sees an increasingly massive penetration of energy from renewable sources, technological solutions for the accumulation of electrical energy will progressively acquire a fundamental role. In recent years, innovative storage systems have been developed, in particular lithium-ion batteries, with a double or triple energy density compared to other previous technologies [1, 2]. Nevertheless, further technological progress and greater cost competitiveness are required for the development of storage systems for electro-mobility or stationary energy storage. To increase the energy density of the energy storage systems, it is necessary to use innovative electrochemical materials and systems. Lithium sulfur batteries (Li-S) are promising candidates to replace lithium-ion batteries because cheaper and lighter and, weight for weight, can store almost twice as much energy [3, 4]. The development of this type of battery would not only allow the development of electric vehicles but would also allow

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W. Zamboni, G. Petrone (eds.), *ELECTRIMACS 2019*, Lecture Notes
in Electrical Engineering 615, https://doi.org/10.1007/978-3-030-37161-6_53

the construction of large storage facilities to support the electricity grid. This work reports the research activities carried out in ENEA during the last year to develop lithium sulfur batteries with high energy density.

2 Materials and Methods

2.1 Preparation of the Electrode Tape

The electrodes were prepared directly on glass microfiber filters used as battery separators (Whatman® glass microfiber filters, Grade GF/A). The electrodes have been prepared with two different binders: ethylene vinyl acetate (EVA) or a self-cross-linking acrylic dispersion (CRILAT) both from Vinavil SpA. The slurry was prepared by dissolving the Byk 2061 dispersant in water, which was followed by the addition of Ketjenblack (KJB) carbon or Super P carbon. After 5 min of mixing at 2000 rpm, using the Thinky Planetary Mixer (Thinky ARE-310), the binder, the plasticizer, and finally the required amount of water were added. The resulting mixture was deposited on the support. Circular electrodes with a diameter of 10 mm were punched from the tape and used as the cathode for the electrochemical characterization.

2.2 Synthesis of Li_2S_8

Lithium sulfide (Li_2S, 99.9%, Acros Organics) and elemental sulfur (Furuuchi Chem.; 99.9%) were weighed in a 1:7 mole ratio and suspended in a 1:1 mixture of 1,3-dioxolane (DOL, 99.5%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, 99%, Sigma-Aldrich). The DOL/DME mixture was heated at 80 °C under magnetic stirring for 48 h to obtain a homogeneous dark red solution. The concentration of Li_2S_8 was 0.5 M. A solution of 1.0 M of lithium bis-trifluoromethane-sulfonyl-imide (LiTFSI) and 0.1 M of lithium nitrate ($LiNO_3$) in a 1:1 mixture of DOL/DME was used as the electrolyte. The catholyte solution was prepared by adding 10 ml of the Li_2S_8 solution to 40 ml of electrolyte: the final concentration of Li_2S_8 in the catholyte solution was 0.1 M.

2.3 Chemical-Physical Characterization

The morphology of the working electrode was studied by scanning electron microscopy (SEM). High-magnification microphotographs were obtained using a VEGA3 TESCAN SEM. The specimens were directly mounted onto a conductive double-face carbon tape, which was previously mounted on a slab. The TGA was carried out with the TA Instruments Q600 SDT analyzer in a temperature range of 20–750 °C, at a heating rate of 10 °C/min, in air flow.

2.4 Electrochemical Measurements

Electrochemical characterizations were performed with LIR2016-type coin cell, using lithium foil as a counter-reference electrode and the carbon tape as the working electrode. A Whatman glass microfiber filter (Grade GF/A) was used as separator. The separator was soaked by 30 μL of catholyte solution. The sulfur content in the catholyte was about 1.20 mg/cm^2. Cycling tests were automatically carried out with a battery cycler (Maccor 4000). Electrochemical impedance spectroscopy (EIS) was performed with a model 1260 impedance/gain-phase analyzer (Solartron Analytical) using an electrochemical workstation (Solartron Analytical 1287 electrochemical interface). All materials and cells were handled and assembled in a controlled atmosphere in a dry room (R.H. $< 0.1\%$ at 20 °C).

3 Results and Discussion

3.1 Morphological Characterization of the Electrodes

The carbon-based electrodes were morphologically characterized by SEM as shown in Fig. 1. The KJB film extends in a very inhomogeneous way and a very fragmented electrode surface is obtained. The electrode prepared with the Super P appears instead very homogeneous.

3.2 Thermal Characterization of the Electrodes

The purpose of the measurement was to determine the amount of material deposited on the glass fiber. For this reason the measurements were carried out in air, in order to induce total combustion of the carbonaceous material and the above deposited additives. Figure 2 reports the result of the TGA.

The glass fiber without any deposit (green curve) shows a weight loss of less than 2% due to moisture and impurities. The thermogravimetric curve for the KJB/EVA electrode (red curve) shows a weight loss of 0.7765 mg. The initial weight of the sample was 5.820 mg. Assuming a physiological loss of the glass fiber by 1.8%, as shown by the green curve, the contribution of the glass fiber to the total weight loss is about 0.105 mg. The KJB/EVA electrode, therefore, weighs 0.672 mg and

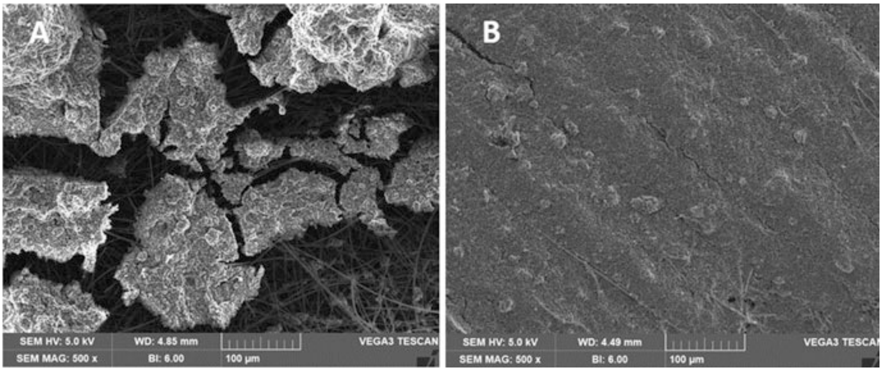


Fig. 1 SEM image of the glass fibrer coated with a layer of KJB/CRILAT (**a**) and Super P/CRILAT (**b**)

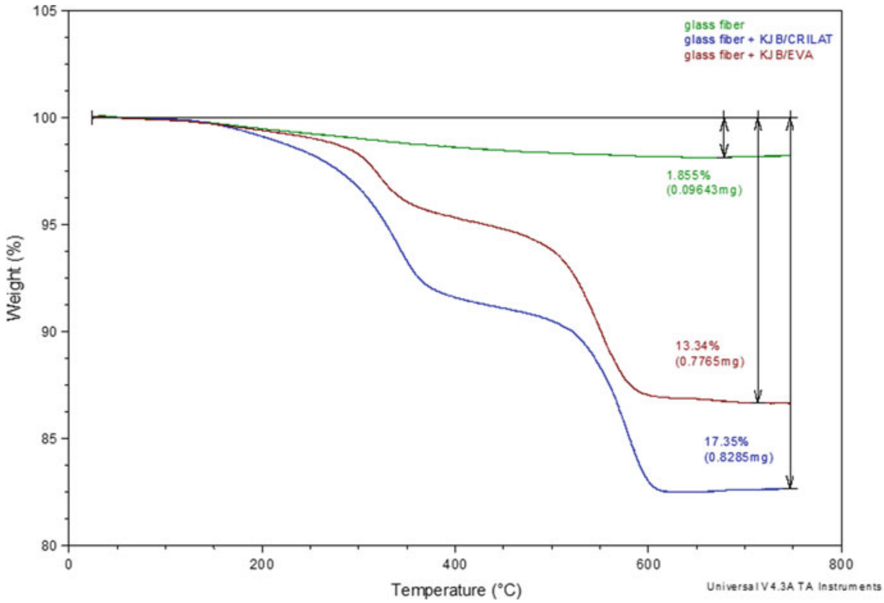


Fig. 2 TGA of the glass fibrer without KJB (green curve) and with KJB. Two different binders (EVA, red curve, and CRILAT, blue curve) have been tested

it corresponds to 11.5% by weight of the entire electrode. A similar argument can also be made for the KJB/CRILAT electrode. The initial weight of the sample is 4.774 mg. The contribution of the glass fiber is calculated to be 0.086 mg that has to be subtracted from the total weight loss of 0.8285 mg. The KJB/CRILAT electrode, therefore, weighs 0.743 mg and corresponds to 15.5% by weight of the entire electrode.

3.3 Electrochemical Characterization of the Electrodes

The Super P/EVA-based electrodes deposited on the glass fiber showed an initial specific capacity of about 1350 mA h/g at the first cycle and then undergo a continuous and gradual decrease up to about 900 mA h/g at the tenth cycle. The capacity loss decreases in subsequent cycles and the specific capacity evaluated at the 60th cycle was around 825 mA h/g (Fig. 3).

The KJB/CRILAT-based electrodes deposited on the glass fiber showed a higher first-cycle specific capacity. Also in this case a capacity reduction upon cycling is observed. After 10 cycles the specific capacity is reduced to about 1200 mA h/g (Fig. 4).

3.4 EIS Analysis

The EIS analysis was performed by using the model developed by Deng et al. [5] and Fig. 5 shows the equivalent circuit used to fit the results.

In this model, Re represents the resistance of the electrolyte. Rint//CPEint is the contact resistance at the interphase and its relative capacity in the body of the electrode. These elements simulate the electronic transfer between the carbon grains. Rct//CPEdl represents the resistance to charge transfer of the electroactive species and its capacity relative to the electrode/electrolyte interface. Finally, CPEdif represents the diffusive impedance referred to the lithium-ion diffusion process. Impedance analysis was performed on the Super P/EVA electrode. The cells assembled with this electrode show that the electrode interface changes drastically after the first charge/discharge cycles.

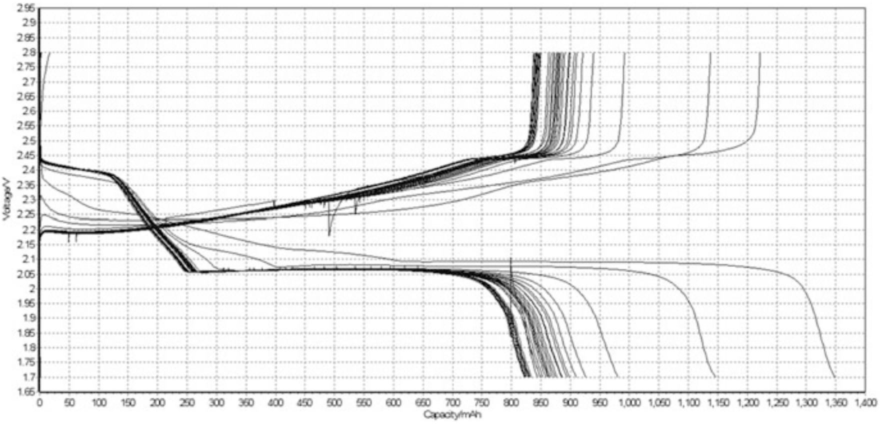


Fig. 3 Voltage profiles for the first 60 cycles of an electrode of Super P/EVA

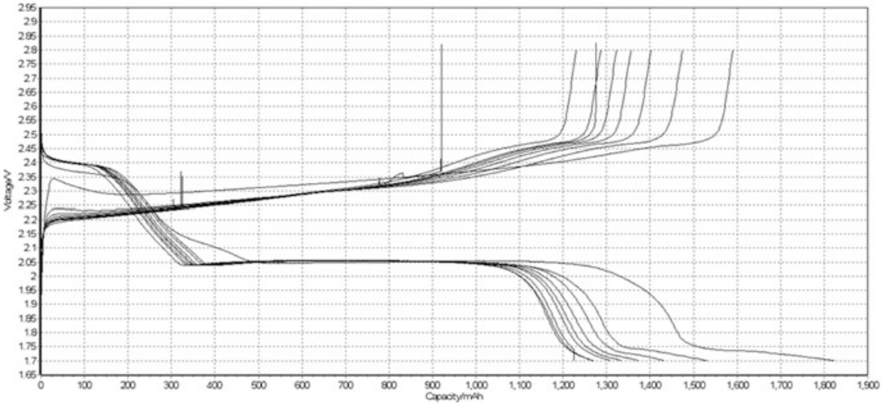
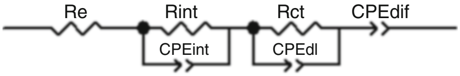


Fig. 4 Voltage profiles for the first 10 cycles of an electrode of KJB/Crilat

Fig. 5 Equivalent circuit for the Li-S cell



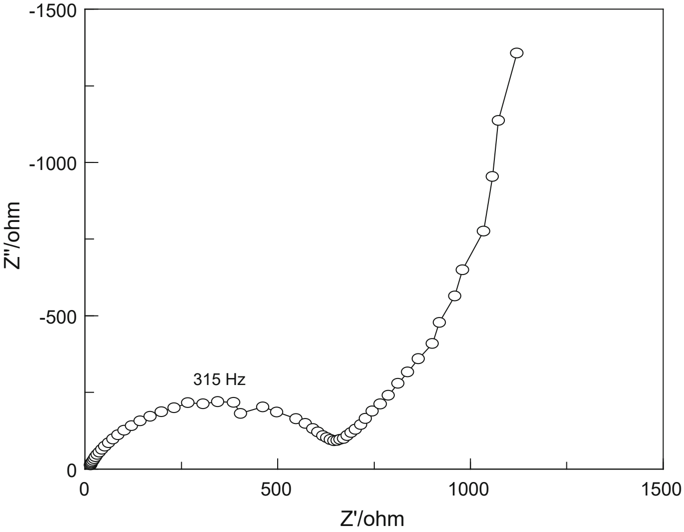


Fig. 6 Initial Nyquist diagram for cell with Super P/EVA electrode

Initially (Fig. 6) the Nyquist diagram shows a single semicircle with a maximum at a frequency of about 315 Hz and a diameter of about 760 Ω followed by a characteristic increase in the typical imaginary impedance of an electrode limited by a diffusion process.

In this situation in which the battery has not yet received the first discharge/charge, both the processes of electronic transfer between the grains of

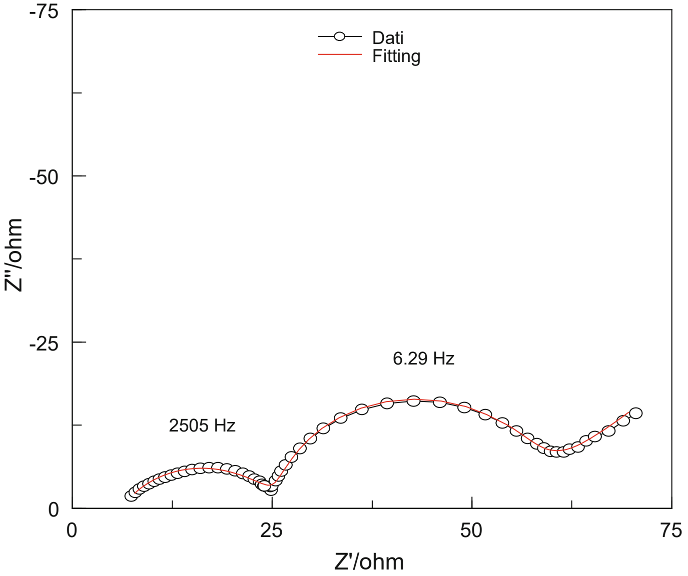


Fig. 7 Nyquist diagram for cell with Super P/EVA electrode after 10 cycles

which the carbon-based electrode is composed and the diffusion of the redox species to the electrode/solution phase, in this case Li_2S_4 presumably, are limited. After 10 cycles the inter-granular contact resistance, highlighted by the semicircle diameter at high frequencies, decreased at about 20 Ω. The resistance to charge transfer, highlighted by the second semicircle, also decreased (30 Ω, Fig. 7). The impedance indicates quite clearly that the charging and discharging process is limited by the charge transfer to the electrode/solution phase of the electro-active species. In any case, an improvement both in the process of charging and discharging (decrease in Rct) and in the process of electronic transfer between the grains of the carbon (decrease of Rint) is observed.

4 Conclusions

The cells assembled with the KJB- and Super P-based electrodes show excellent electrochemical performances in terms of specific capacity and cell resistance. In particular, the KJB-based electrodes, thanks to their characteristics of high specific capacity and stability, represent potential promising candidates for the construction of high-energy-density Li-S cells.

Acknowledgments Part of this work was carried out within the research program "Ricerca di Sistema Elettrico" inside the "Accordo di Programma MiSE - ENEA."

References

1. P.G. Bruce, B. Scrosati, J.M. Tarascon, Angew. Chem. Int. Ed. **47**, 2930–2946 (2008)
2. R. Van Noorden, Nature **507**, 26–28 (2014)
3. N. Moreno, A. Caballero, J. Morales, E. Rodriguez-Castellon, J. Power Sources **313**, 21–29 (2016)
4. M. Wei, P. Yuan, W. Chen, J. Hu, J. Mao, G. Shao, Electrochim. Acta **178**, 564–570 (2015)
5. Z. Deng, Z. Zhang, Y. Lai, J. Liu, J. Li, X. Liu, J. Electrochem. Soc. **160**, A553–A558 (2013)