Organic Cellulose-Based Binder for Lithium-Sulfur Batteries

K. Jasso[a]*, T. Kazda[a], P. Cudek[a]

[a] Department of Electrical and Electronic Technology, Brno University of Technology, Technicka 10, 616 00 Brno, Czech Republic
*kamil.jasso@vut.cz

Abstract
With the advancement of mobile technology, there has been an increase in the demand for batteries capable of meeting the requirements for high-energy power sources and low-cost. Although, lithium-ion batteries are constantly improving, they are struggling to meet these requirements as they are approaching to their technological and electrochemical limits. Due to their high theoretical energy density and potentially low cost, lithium-sulfur batteries are a promising successor to current lithium-ion batteries in many areas. Unfortunately, some shortcomings in lithium-sulfur battery technology must be addressed before it can be deployed in the commercial sector. Some of the shortcomings could be solved or at least supressed by binder. Due to environmental concerns, research is mostly focused on non-toxic binders, especially water-soluble binders used in food and cosmetics industry are of particular interest. The aim of this paper is to investigate the possibility of using the organic binder carboxymethyl cellulose in lithium-sulfur batteries.

Introduction
Lithium-sulfur batteries (Li-S batteries or LSBs) have a potential to overcome the limits of current Lithium-ion (Li-ion) technology and meet the demand for high energy density and low-cost energy sources. Li-S batteries are promising successor mainly due to the high theoretical energy density (2600 Wh kg^{-1}), high availability and low-cost, resulting from the use of sulfur as the cathode material. However, before they can be deployed in commercial production, several problems associated with the use of a combination of sulfur and lithium metal still need to be resolved. The most significant negative effects include low conductivity of sulfur and reaction products, lithium dendrite growth, sulfur volume changes, and the shuttle effect. The vast volume change during reversible conversion of sulfur species causes sulfur cathode cracking, pulverization, and structure collapse, which results in rapid capacity fading and short cycle life 0. Furthermore, the combination of weak electronic and ionic conductivity of the charge and discharge products with poor electrochemical reversibility of sulfur cause a relatively low rate capability of Li-S cell 0. To improve the weak electrical conductivity, conductive additives, most often carbon, are added to the positive electrode material, thus reducing the sulphur content in the positive electrode volume at the expense of the conductive element.

One possible way to prevent or at least suppress some of these drawbacks is to use special functional binders. Binders are an integral part of almost every battery electrode and greatly influence the resulting electrochemical parameters of the cell. Polymer binders play a critical role in maintaining the structural integrity and stability of the electrodes of lithium batteries. Binders serve two main purposes: (1) they establish a suitably close contact between active materials and conducting agent, (2) they ensure the electrode's mechanical integrity and strong adhesion to the current collector, and (3) they can possibly aid the chemical interactions 0. Their role is even more important in the case of lithium-sulfur batteries, which undergo large volume changes during cycling that cause mechanical stress in electrode material that can result in loss of contact between individual elements but also between the electrode material and current collector. Carefully chosen binder could potentially reduce or completely prevent these types of shortcomings. The structural integrity and mechanical qualities of the electrode are determined by the physical properties of the binder 0. Polymers with strong stickiness and elasticity are appropriate candidates for achieving these aims.

Carboxymethylcellulose (CMC) is cheap, nontoxic and biodegradable polymer. It is a anionic derivative of cellulose with carboxymethyl groups ($-CH_2-COOH$) commonly available with a degree of substitution (DS) in the range of 0.38-1.4. It is often used in the food, pharmaceutical and cosmetics industries as a viscosity modifier, stabilizer or thickener.

 ISBN: 978-80-574-0039-4

Experimental

Materials
The following materials were used to produce the positive electrode: Sulfur powder (Sigma-Aldrich, St. Louis, USA), Super P Carbon black (Timcal, Bodio, Switzerland) and CMC binder (CP Kelco, Atlanta, USA) in form of highly purified sodium carboxymethylcellulose. The electrolyte was prepared from 0,25M $LiNO_3$ and 0,7M LiTFSI lithium salts dissolved in a mix of DME and DOL (2:1) solvents (all Sigma-Aldrich, St. Louis, USA).

Electrode preparation
First, an electrode slurry was prepared from the materials using a classical method: dissolving the binder (10%wt.) in water with the help of a magnetic stirrer, followed by the addition of a conductive agent and an active material. Positive electrodes for LiS cells were prepared by applying the slurry to the aluminium current collector and allowing it to dry. One electrode sample before pressing was used for analysis under a scanning electron microscope (see Figure 1A), and the other was used in the assembly of the LiS cell, which was subjected to electrochemical analysis. Inspection of the electrode structure and electrochemical studies revealed that this method of manufacture was not suitable since the electrode components were not uniformly mixed. Therefore, a more precise preparation method was chosen and the amount of binder in electrode material was reduced to 7%wt. The electrode prepared in this way was again subjected to analyses, which showed a visible improvement in the structure (see Figure 1B) but also in the electrochemical properties of the electrode. Last, the electrodes were prepared by a fine-tuned method, with an even greater reduction in the amount of binder to 4% wt. (see Figure 1C).

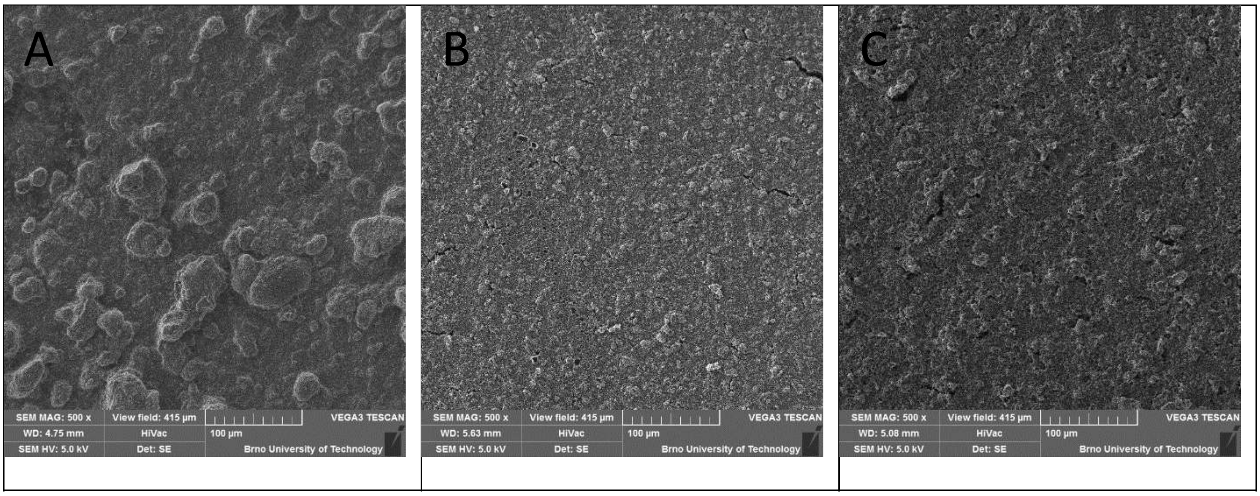

Fig. 7 Analysis of prepared electrodes under SEM: A) Classical preparation B) Modified preparation with less binder content C) Improved preparation with even less binder content

From the comparison of the structure of the prepared electrodes (Figure 1), it can be seen that a more porous electrode with a more uniform distribution of materials can be prepared with the aid of a modified more precise preparation method and a reduction in the binder content.

Electrochemical analysis
The remaining electrode samples were used in the assembly of LiS cells, which were subsequently subjected to electrochemical analyses. After initialization analyses, 50 cycles of galvanostatic cycling at variable loads (0.2C, 0.5C, 1C, 2C, 1C, 0.5C and again 0.2C) were performed (see Figure 2).

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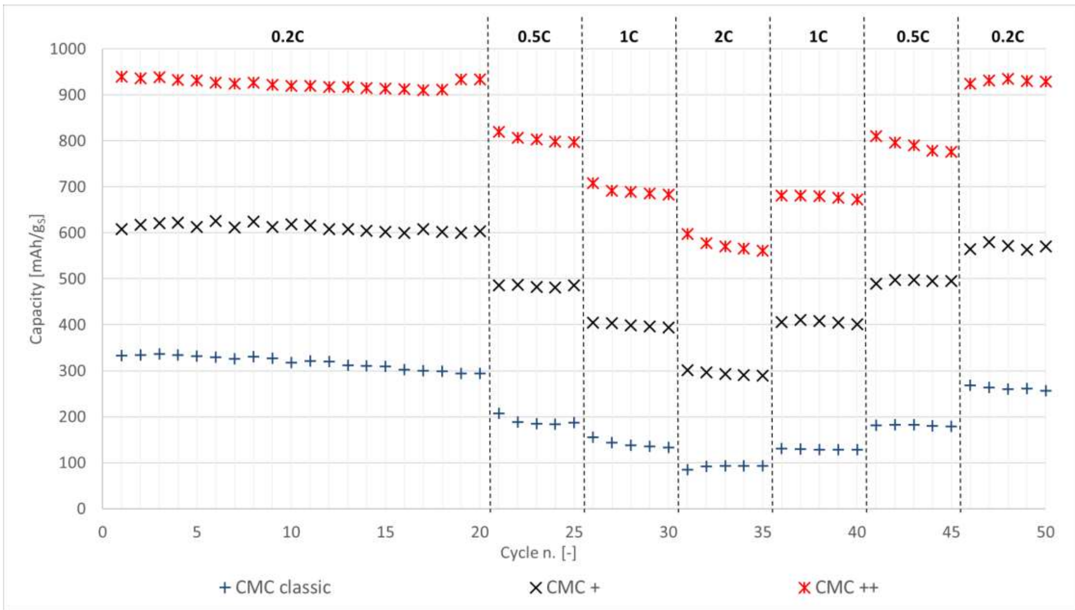

Fig. 8 Comparison of cell discharge capacities with respect to a positive electrode prepared by different preparation methods

From the galvanostatic cycling results, it is clear that the cell with the electrode prepared by the classical method of slurry preparation on a magnetic stirrer (CMC classic) is the worst off in terms of capacity values and stability, reaching the highest capacity equal to 336 mAh g^{-1} at 0.2C rate. The use of a more precise preparation method and a slight reduction in binder content resulted in better electrochemical properties of the LiS cell (CMC+). The LiS cell with the electrode prepared in this manner reached almost double the capacity at 0.2C rate at 626 mAh g^{-1}. After fine-tuning the electrode preparation method and reducing the binder content even further, a significant improvement in the electrochemical properties of the resulting LiS cell (CMC++) can be seen. The cell with such electrode showed the highest capacity values, at around 940 mAh g^{-1} at 0.2C rate, which is almost three times the capacity of the CMC classic. Furthermore, the capacity of this cell also shows the best recoverability to the original values at the end of cycling.

Conclusion

Since the classical slurry preparation method proved to be unsuitable for the CMC binder, the preparation method was modified during the experiment and the binder content was reduced. The measured results showed that the use of carboxymethyl cellulose as a binder for lithium-sulphur batteries is suitable, whereby it is possible to reduce the binder content and thus increase the energy density of the cell.

Acknowledgements

Authors gratefully acknowledge the financial support from the Ministry of Education, Youth and Sports of the Czech Republic under project No. LTT19001, BUT specific research programme (project No. FEKT-S-20-6206).

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 ISBN: 978-80-574-0039-4