Influence of different electrode compositions and binder materials on the performance of lithium–sulfur batteries

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ABSTRACT

The specific capacity and cycling stability of lithium sulfur batteries have been investigated with respect to the chemical composition and fabrication process of the sulfur electrode. Three different kinds of electrode compositions (containing Nafion, polyacrylonitrile/carboxymethylcellulose, and Teflon, respectively, as binder materials) have been tested. For the electrodes containing Nafion as the binder material, an additional Nafion coating has been deposited on top of the electrodes to enhance the sulfur retention and to suppress the polysulfide shuttle. Both SEM images before cycling and *post mortem* are presented in order to shed light on the influence of the composition of the electrode on its electrochemical performance. Good cycling performance can be attained based on relatively simple and therefore cost-effective electrode setups and production methods.

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1. Introduction

The performance values of state-of-the art lithium-ion batteries can only be increased within a limited range, despite the extensive research efforts currently undertaken. For new fields of applications such as electric vehicles, different battery concepts and new materials have to be considered. One particularly promising candidate is the lithium sulfur battery, where the sulfur offers a theoretical specific capacity of 1675 mAh/g and a theoretical energy density of ∼3518 Wh/kg, respectively (based on the weight of elemental sulfur and a discharge voltage of ∼2.1 V). However, the commercial application of the lithium–sulfur battery system is hampered by a couple of serious challenges, still preventing the practical exploitation of its impressive theoretical performance. Given that sulfur is an insulator, relatively high amounts of conductive additives are needed to ensure satisfactory utilization of the active material. Moreover, if the battery is fully discharged, the insoluble end products of the electrochemical reactions will precipitate on the positive electrode. As they are also insulating, this might lead to the formation of a passivating layer on the electrode and to a subsequent practical "loss"

of active material. Another challenge is the huge volume change which necessarily occurs in the electrode upon dissolution and precipitation of the sulfur active material and final reaction products, respectively. This will contribute to a fast aging of the electrodes and a quick fading of the practical specific charge of the battery. Another issue specific to the lithium–sulfur battery is the so-called polysulfide shuttle [1–3]. Upon discharge of the battery from the starting material S_8 to the insoluble final products Li_2S_2 and Li_2S, intermediate polysulfides S_x^{2-} are formed. They are well soluble in the standard liquid organic electrolytes, such as glyme ethers, 1,3-dioxolane or dimethoxyethane. Therefore, they can diffuse through the separator and directly react with the lithium negative electrode, leading to its passivation and a further "loss" of active material.

Various experimental strategies have been developed in order to tackle these issues. To name a few, polymer matrices have been used as well as meso- and microporous carbons [4,5], lithium-ion conductive ceramic materials [6,7], and different additives. Furthermore, lithium disulfide has been employed as starting active material and a lithium disulfide saturated gel electrolyte has been used [8,9]. While all of these experimental approaches have led to some improvement in the cycling behavior of the lithium–sulfur batteries, so far none of them has been able to solve all of the intrinsic problems involved. Moreover, some of them lead to a considerable increase in the complexity of the battery setup and therefore possibly to higher costs.


In this paper, we focus on industrially viable solutions. We describe the influence of several cost-effective electrode compositions and binder materials on the performance of lithium–sulfur batteries, while keeping a simple standard setup employing a lithium negative electrode, a polymeric separator, and a sulfur/binder/carbon composite positive electrode. This strategy is important in light of the fact that a new battery system will be able to compete with the well-established lithium-ion technology only if both the material and fabrication costs will be kept low. It will be demonstrated here that the cost-effective carbonaceous materials employed as well as the fabrication process significantly influence the performance and cycling stability of the sulfur electrodes in combination with the binder materials. A Nafion coating on top of the electrodes has been applied in an attempt to suppress the detrimental polysulfide shuttle, the beneficial results of this approach have already been reported [10]. *Post mortem* SEM images and EDX analyses are presented and compared to pristine electrodes in order to illustrate the changes occurring within the electrode upon cycling the battery.

Finally, we wish to explain why PVDF was not investigated in our study. PVDF is one of the most wide-spread binder materials currently used in the research (and in the fabrication of other but sulfur electrodes). However, keeping in mind an economically viable process, we deliberately forwent the application of PVDF in the present Li–S study for the following reasons: Firstly, NMP is generally needed as a solvent system when dealing with PVDF based cathode slurries. Consequently, drying the cathode sheets prepared this way requires vacuum conditions in combination with elevated temperatures. As sulfur would sublime under these conditions, low or even ambient temperature would have to be used for the drying step. This means that extremely long fabrication times (i.e., high fabrication cost) would have to be accepted in addition to an increased uncertainty in respect of the contamination of the cathode with NMP solvent rests. Moreover, NMP is a toxic material and, therefore, not preferable for this process. Therefore, our analysis showed that it is highly desirable to replace the PVDF with an alternative binder material at least for the Li–S battery system. This is why we focused on water-based systems as they offer, apart from the lower cost, both the advantage of easier drying procedures and a significant reduction of any contamination risk.

2. Experimental

Four different cathode tapes have been selected, prepared, and tested. They are labeled in the following according to the binder material employed as S_Nafion_1, S_Nafion_2, S_PAN_CMC, and S_Teflon. In order to facilitate comparison, the composition (in wt.%) of all electrodes was fixed to 60% sulfur, 30% conductive carbon additive, and 10% binder material.

The Nafion (DuPont) has been exchanged with lithium cations using a 0.1 M LiOH solution. For the preparation of samples S_Nafion_1, sulfur, soot (Printex XE-2), and lithium-Nafion dispersion have been mixed in an aqueous environment and dispersed by ultrasonic treatment. The dispersion has been sprayed on the aluminum current collector and laminated after the coating. The final drying process has been performed at 70 °C. Samples S_Nafion_2 have been prepared in an exactly analogous manner. However, after the final drying process the electrodes have been sprayed additionally with the lithium-Nafion dispersion. An airbrush pistol has been used to accomplish the spraying. The polyacrylonitrile-based sulfur composite electrodes (S_PAN_CMC) were prepared based on the method described in [11] by thoroughly mixing sulfur with polyacrylonitrile (PAN, Aldrich) and a carbonaceous material (Super P). The mixture was heated in a 300 ml steel autoclave to 280 °C for 12 h. The composite has been then mixed with graphite and
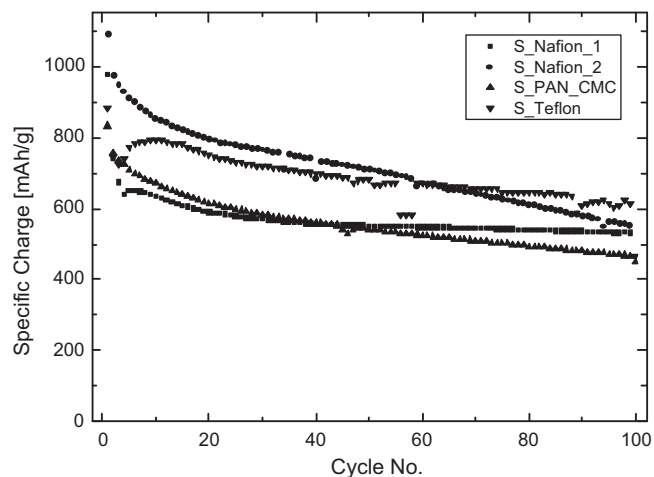

Fig. 1. Specific charge (with respect to sulfur) of electrodes employing Nafion as a binder material (S_Nafion_1 and S_Nafion_2), a polyacrylonitrile/carboxymethylcellulose composite (S_PAN_CMC), and Teflon (S_Teflon) (Rate: C/10, all curves are averages over several experiments).

carboxymethyl cellulose in water and dispersed by ultrasonic treatment. The obtained mixture has been sprayed on the aluminum current collector and laminated after the coating. The final drying process has been performed at 70 °C. Samples S_Teflon have been fabricated in the same way but with soot (Printex XE-2) serving as the conductive additive and Teflon as the binding material.

In this study, a 1 M solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of dimethoxyethane (DME): dioxolane (DOL) 2:1 has been used as the electrolyte. It has been shown that this solvent composition provides a good cycling behavior [12]. All solvents have been dried over sodium and benzophenone and distilled before usage, the LiTFSI has been dried under vacuum. A polypropylene based separator (Celgard 2400) has been used. Galvanostatic cycling was performed in coin-like cells. SEM images have been recorded on a Carl Zeiss Ultra 55 microscope, equipped with an Ametek EDX detector. For *post mortem* images, the electrodes have been removed from the cells in an argon filled glove box, washed with dry DME, and dried overnight.
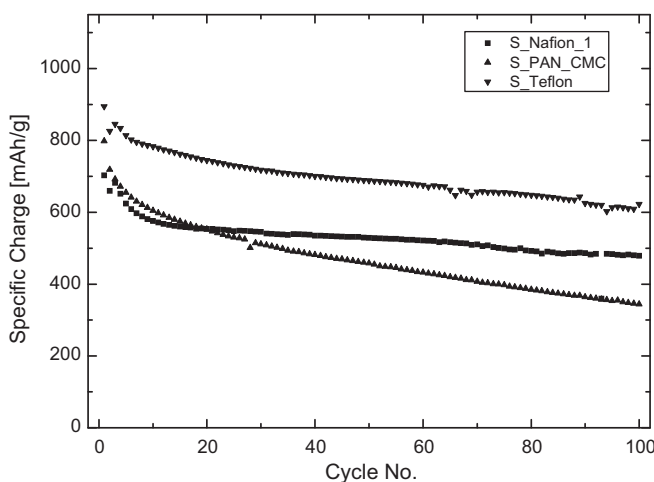
Fig. 2. Specific charge (with respect to sulfur) of electrodes employing Nafion as a binder material (S_Nafion_1), a polyacrylonitrile/carboxymethylcellulose composite (S_PAN_CMC), and Teflon (S_Teflon) (Rate:C/5, all curves are averages over several experiments).
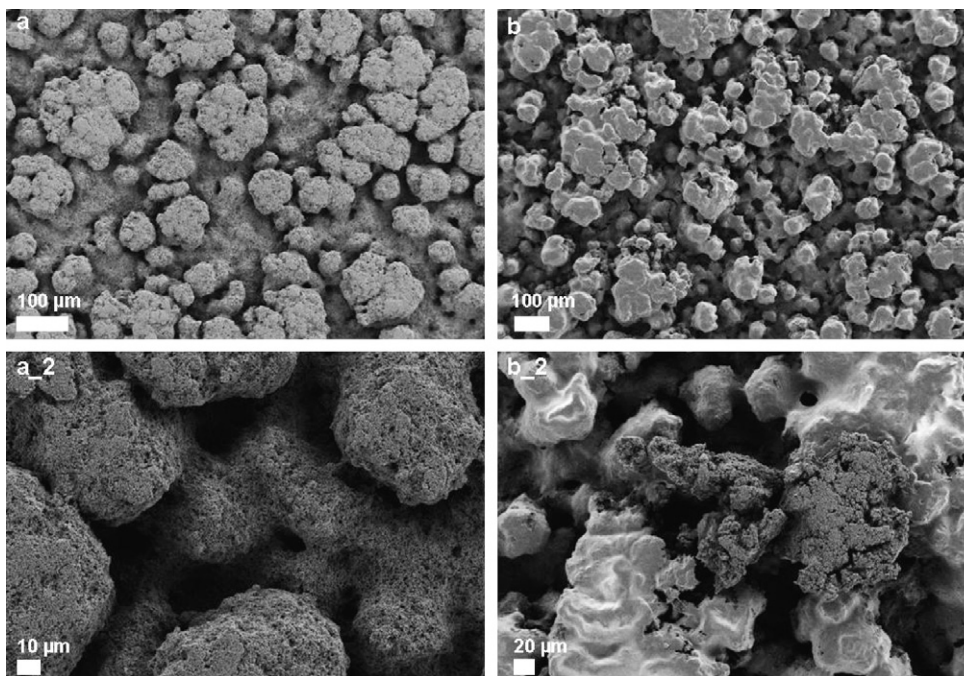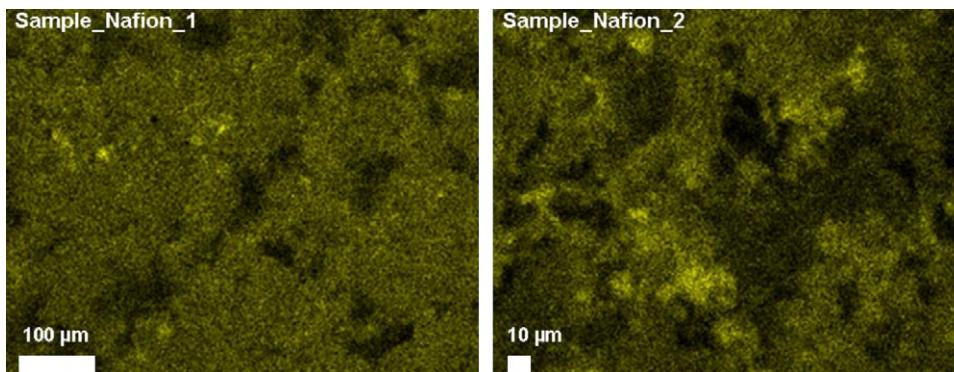
Fig. 3. SEM images of the electrodes before cycling (a) electrode with Nafion as binder material, (b) electrode with Nafion as binder material and sprayed with an additional Nafion layer after drying. (a_2) and (b_2) are enlarged views of (a) and (b), respectively.

3. Results and discussion

Representative electrochemical results for samples S_Nafion_1 and S_Nafion_2 are shown in Fig. 1 and Fig. 2, respectively. SEM images of the pristine electrodes are displayed in Fig. 3. The surfaces are smoothly covered with the carbonaceous conductive component and it can be seen from the EDX maps in Fig. 4 that the distribution of the sulfur active material is fairly homogeneous. The additional Nafion layer sprayed on top of the electrode (S_Nafion_2) is clearly visible in the SEM image. It results in a blurring of the SEM image due to charging effects in the non-conductive polymer layer in the electron beam of the SEM instrument. Both Nafion-based samples show good cycling behavior, with values for the specific charge with respect to sulfur of ~540 mAh/g after 100 deep cycles for the uncoated sample and ~575 mAh/g for the Nafion-coated electrode S_Nafion_2. It is interesting to note that sample S_Nafion_1 shows a very stable cycling behavior (as shown in Fig. 1), though with a lower value of the specific charge after 100 deep cycles as compared to the Nafion-coated electrode. However, the fading rate of the Nafion-coated electrode seems to be more pronounced.

The obvious question is why there is a big difference in the electrochemical performance between the S_Nafion_1 and S_Nafion_2 samples. The main difference between these two electrode types lies in the additional Nafion layer sprayed on top of the electrode sheet in the case of S_Nafion_2. At this point, we can only speculate about the main reason: One effect might be the cationic exchange properties of such a layer, hindering the polysulfides from quickly diffusing to the anode side and thereby effectively alleviating the challenge of the polysulfide shuttle. It is also possible that this effect is due to the additional polymer layer, which basically represents a zone of higher effective electrolyte resistance, leading to a similar result. Of course, a combination of both effects is conceivable. It can be seen from the *post mortem* SEM images discussed below that the Nafion coating is severely damaged upon cycling/disassembling, which might be one of the reasons why the electrochemical performance of both cell types converges after a given number of cycles.

Electrochemical impedance spectroscopy is generally considered a tool suitable to gain further insight into the changes happening within the cells upon cycling. This method has been successfully applied to lithium–sulfur test cells in order to gain a

Fig. 4. EDX maps showing the distribution of the sulfur active material in the electrodes using Nafion as binder material (S_Nafion_1) and with Nafion as binder material and sprayed with an additional Nafion layer after drying (S_Nafion_2).
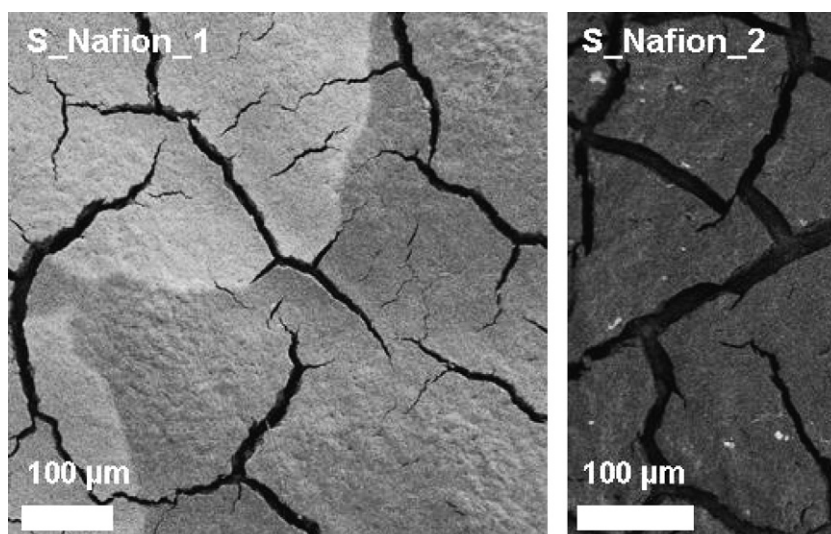
Fig. 5. *Post mortem* SEM images of the electrodes with Nafion as binder material (S_Nafion_1) and with Nafion as binder material, sprayed with an additional Nafion layer after drying (S_Nafion_2).

deeper understanding of the processes involved, as has been nicely shown before [13–15]. However, in this manuscript we do not provide any impedance spectra, as the method provides ambiguous results for a system with only minor variations in the relevant parameters, as understandable from the cycling curves shown in Figs. 1 and 2. It is because several complicated and non-uniform processes are happening at the same time on the electrode surface when cycling a Li–S cell, including electrolyte decomposition with continuous (inhomogeneous) surface layer(s) growth and Li_2S precipitation. All these processes significantly influence the shape of the measured impedance spectra, thereby masking the assignment of changes in the impedance spectra and making the possible conclusions on the influence of the binder material, which is of specific interest here, equivocal.

Nonetheless, the influence of the Nafion coating deserves a deeper discussion. The stable cycling of Nafion containing electrodes is in line with literature data which reported previously an improvement in the cycling stability of lithium–sulfur cells after introduction of a protective layer or coating [14,16], even on the lithium side through the addition of electrolyte additives such as lithium nitrate [17]. In this context, introduction of a Nafion layer coating was reported to show beneficial effects on the cycling stability of the cells [10]. It has been speculated that its cationic exchange properties improve the performance of sulfur containing cathodes by hindering the diffusion of the intermediately formed polysulfide species, thereby mitigating the polysulfide shuttle. Lithium-exchanged Nafion has also been found to be a promising electrode binder[18]. But the improvement observed in our experiments is somewhat less significant. The specific charge in the first discharge is high (close to ∼1000 mAh/g) for S_Nafion_1, but then it quickly falls before slightly recovering. This increase in capacity during the first cycles of a lithium–sulfur battery has been explained before through the formation of cracks and cavities in the electrode upon the dissolution of the sulfur active material [19]. Cracks and cavities lead to higher utilization of the insulating active material as it collapses into the cavities formed, thereby getting into contact with the conductive additive. The *post mortem* SEM images (Fig. 5) support this view, showing pronounced crack formation in the cycled electrodes. We caution that interpretation of the *post mortem* SEM images is complicated by the unavoidable mechanical damage of the electrode surfaces during disassembly of the cells (that is why we forego showing *post mortem* EDX maps).

In any case, the formation of cracks is plausible and is expected also within the bulk of the electrode.

Another problem of the lithium–sulfur battery becomes apparent when low cycling rates (C/10) are applied. The recorded specific charge of the charge step is considerably higher than for the discharge step. This leads to a low energy efficiency of the lithium–sulfur battery system and is a consequence of the polysulfide shuttle: the intermediate polysulfide species formed during the electrochemical reactions are soluble in the electrolyte and can therefore diffuse to the metallic lithium counter electrode where they are directly reduced. The reduced species can then diffuse back and be re-oxidized. This phenomenon was also observed in the case of the sample S_Nafion_2, showing that the polysulfide shuttle was not completely blocked by the additional Nafion coating. The differences in the coulombic efficiencies of the electrode tapes tested fall within the scatter of the individual experiments, so that no clear trend or improvement can be confirmed for the Nafion coating. However, the SEM images from the electrode S_Nafion_2 displayed in Fig. 3 show that the coating is not homogeneous and there are still considerable uncovered domains on the surface. This might
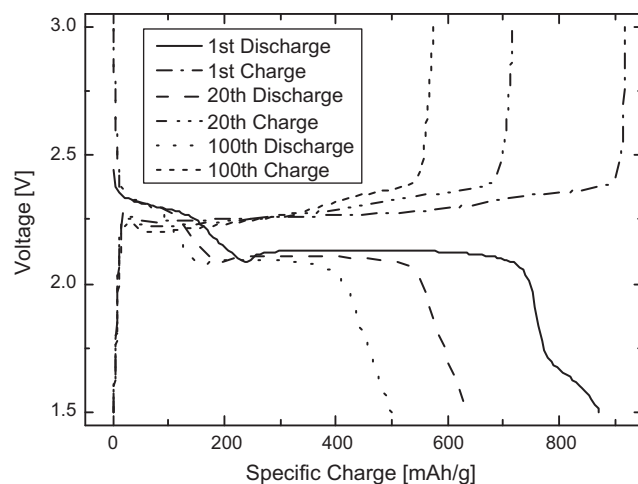

Fig. 6. Typical galvanostatic charge and discharge curves (rate: C/10) for lithium–sulfur test cells using a polyacrylonitrile/sulfur composite as active material and carboxymethyl cellulose as binder additive.
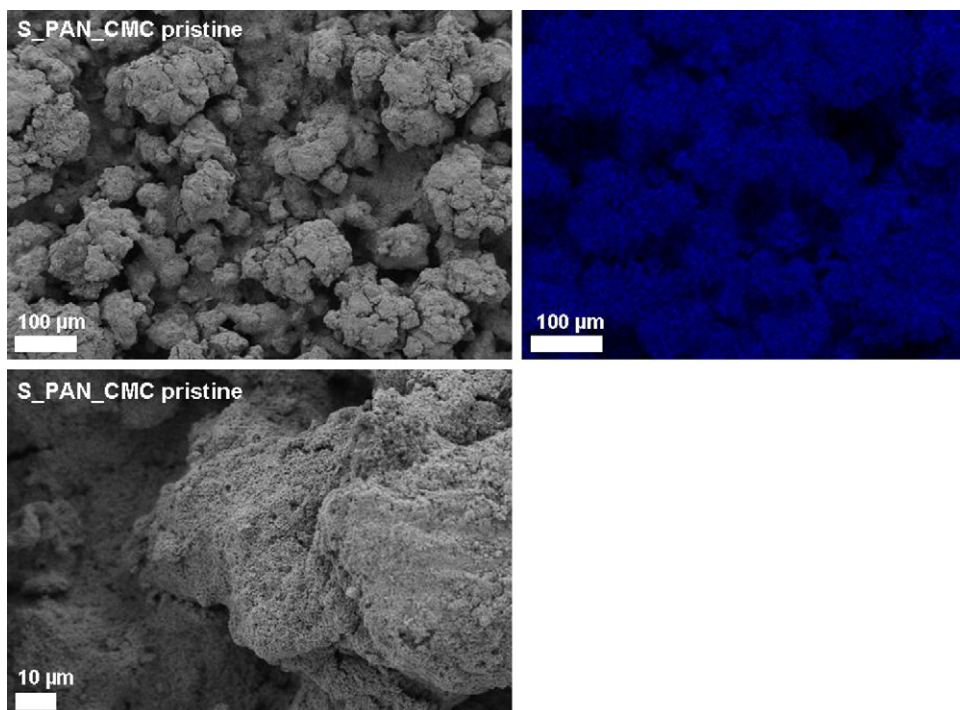
Fig. 7. SEM images of the electrode S_PAN_CMC before cycling and EDX map of sulfur (blue) of another electrode of the same composition.

explain the limited effect of the Nafion coating in our experiments. Clearly, the effect of the polysulfide shuttle is more pronounced the lower the cycling rate is, as in this case the back and forth diffusion of the reactive intermediates between the electrodes can prevail [1,2]. For this reason, we performed the experiments with the additional Nafion coating only for slow rates (C/10), but not for faster rates (C/5, Fig. 2).

The challenge of the polysulfide shuttle is also clearly visible in Fig. 6. The charge and discharge curves for the 1st, 20th, and 100th cycle of a lithium–sulfur cell employing a polyacrylonitrile/sulfur composite as active component and carboxymethyl cellulose as a binder additive are displayed. The recorded specific charge of the charge step is always considerably higher than for the discharge step. The characteristic features are the same as for the
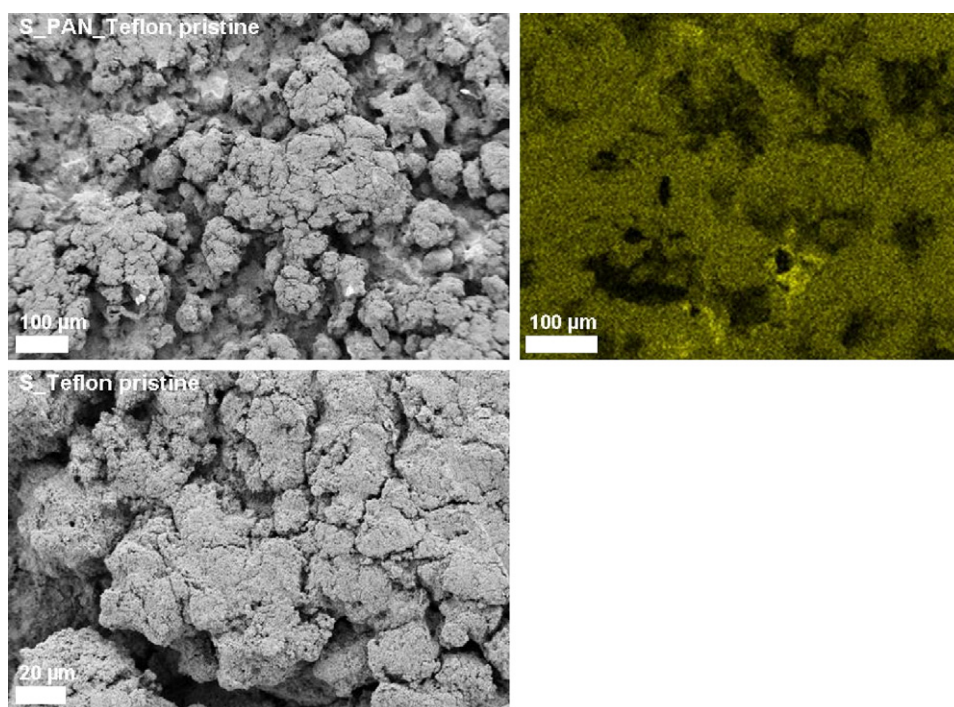
Fig. 8. SEM images of the electrode S_Teflon before cycling and EDX map of sulfur (yellow) of another electrode of the same composition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

samples containing Nafion as a binder material described above, with a higher potential plateau around 2.3 V and a lower potential plateau around 2 V. However, the attainable specific charge is somewhat lower than in the case of the electrodes employing Nafion as binder material and reaches only ~870 mAh/g in the first cycle, while dropping to ~500 mAh/g after 100 deep cycles. The same is true for a faster rate (C/5), with values dropping from ~830 mAh/g in the first cycle to ~440 mAh/g in the 100th cycle, as can be seen in Fig. 2. The coulombic efficiency is higher as compared to the lower rate. SEM images and EDX maps of pristine electrodes (Fig. 7) show that the sulfur active material is homogeneously distributed over the electrode's surface and smoothly covered by the carbonaceous conductive additive. We forego showing *post mortem* SEM images in this case, as their interpretation is seriously hampered by mechanical damage. It can only be speculated therefore at this point about the reasons of the inferior properties of the polyacrylonitrile/carboxymethyl cellulose mixture as a binder material. Possibly, it leads to both a worse adhesion of the slurry to the current collector during the fabrication of the electrodes and to a worse contact between the sulfur active material and the conductive additive during cycling. As a result, both the utilization of the active material and the cycling stability are impaired.

SEM images and EDX maps of pristine sulfur composite electrodes employing Teflon as a binder material are displayed in Fig. 8. They show a very promising cycling behavior (Fig. 1): a specific charge of ~960 mAh/g can be obtained in the first discharge. After 100 deep cycles, the attainable specific charge still amounts to values ~600 mAh/g. For faster rates (C/5) the values drop from ~900 mAh/g in the first cycle to ~600 mAh/g in the 100th cycle, as can be seen from Fig. 2. These performance values make Teflon the best of all binder materials considered in this study. We hypothesize that a good adhesion to the current collector and the creation of good electronic contact between the sulfur active material and the conductive additive are the main reasons. The specific chemical properties of Teflon, such as its high chemical stability and hydrophobicity, most probably also contribute to its good performance as a binder material.

4. Conclusions

In this work, the influence of different cost effective electrode compositions and binder materials on the performance of lithium–sulfur batteries was studied. We demonstrated that the binder material employed does influence the cycling behavior and stability of the electrode tapes. Moreover, there are strong hints that coating of the electrodes with an ion-conductive Nafion layer improves the properties of the electrodes. But the most important result is the demonstration that it is possible to achieve excellent specific charges and cycling stabilities even for very simple and economically viable electrode setups, which compare very well in performance with much more sophisticated and expensive approaches suggested in the literature.

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