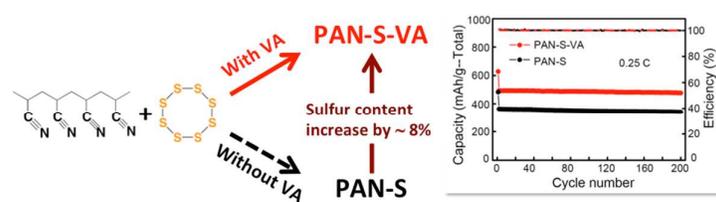**Journal of**
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Journal Name

ARTICLE

Vulcanization Accelerator Enabled Sulfurized Carbon Materials for High Capacity High Stability Lithium-Sulfur Batteries †

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Sulfurized carbon is a promising candidate for cathode materials in practical lithium-sulfur batteries due to its high and stable capacity retention, extremely low self-discharge, and excellent safety. The main disadvantage is the relatively low sulfur content in sulfurized carbon materials. Borrowing the idea from rubber crosslinking chemistry, here we report the use of vulcanization accelerator in carbon sulfurization. Vulcanization accelerators significantly improve the sulfur content by ~8 wt.%, which results in a remarkable increase in the discharge capacity of corresponding Li-S batteries by ~120 mAh g^{-1} while keeping the outstanding cycling stability and low self-discharge. The effectiveness of this approach and the wide variety of vulcanization accelerator chemistry will pave the way for sulfurized carbon materials towards practical applications in Li-S batteries.

Introduction

The main text of the article should go here with headings as appropriate. Lithium-sulfur (Li-S) batteries have been considered highly promising for next generation safer and cheaper batteries with higher energy density. Through a series of redox reactions between a lithium metal anode and a sulfur cathode, Li-S batteries assume a theoretical specific energy of 2600 Wh kg^{-1}, almost an order of magnitude higher than that of commercial lithium ion batteries.[1, 2] However, the Li–S battery technology is yet to be commercialized due to unresolved challenges such as short cycle life, low charging efficiency, and high self-discharge rate.[3, 4]

Sulfurized carbon materials, in which sulfur atoms or chains are covalently bonded to conductive polymer or carbon backbone, have been proposed as an alternative to C-S composites in conventional Li-S batteries.[5, 6] The C-S chemical bonding and the conductivity of carbon materials are expected to resolve the polysulfide shuttling problem and improve the slow charge transfer kinetics. The most important advantages of the batteries with sulfurized carbon cathode over conventional Li-S batteries are nearly 100% Coulombic efficiency (except for the first cycle), stable capacity retention, extremely low self-discharge rate, and excellent safety.[7] And even more attractively, they exhibit excellent cycling performances in inexpensive EC/DMC electrolytes, instead of the ester electrolytes[8, 9] such as DOL/DME preferred in conventional Li-S batteries.[10, 11] Prototype soft pack batteries with sulfurized carbon cathode have been reported with high energy density of 437 Wh kg^{-1},[11] which is much higher than the ~180 Wh kg^{-1} for typical LiCoO$_2$ batteries.

The main drawback of the sulfurized carbon material is its relatively low sulfur content. While the theoretical limit of S loading has been projected to be ~56 wt.% in sulfurized carbon[12], actual materials obtained via thermal sulfurization typically has a S loading of ~25-45 wt.%.[13-16] It has thus become a performance-limiting bottleneck, especially for the energy density of the battery. Here we report a novel approach to improve sulfur content in sulfurized carbon by using vulcanization accelerator (VA) additives. VAs are those compounds that are known to accelerate the crosslinking reaction of unsaturated polyolefin with sulfur in conventional rubber industry.[17] They are generally proposed to promote rubber sulfurization via formation of active accelerator species.[18, 19] We found that VA can also play a significant role in carbon sulfurization. Upon simple addition of VA to the sulfurization reactant mixture, the sulfur content of the resulting sulfurized carbon is increased by ~8 wt.%, and the corresponding Li-S battery exhibits a remarkable increase in discharge capacity by ~120 mAh g^{-1} while keeping its outstanding cycling stability and low self-discharge. Besides, the reaction temperature is also lowered upon the addition of VA, which is important in reducing the energy consumption in potential mass production.

Results and discussion

Polyacrylonitrile (PAN) as the model compound of carbon precursor and the widely used 2-mercaptobenzothiazoles (MBT) as the model VA were used in our proof-of-concept study[18,20] (see scheme S1 in SI for chemical structures). The effect of VA on the PAN sulfurization reaction was characterized with differential scanning calorimetry (DSC).

Reaction temperature with and without the VA additive was compared via heating at 10 °C /min under N_2. PAN and elemental sulfur mixture undergo dehydrogenation and sulfurization reactions at high temperature.[10, 21] Since the two reactions occur simultaneously and promote each other, and the DSC curve shows a single exothermic peak above 250°C (figure 1). The reaction temperature of the reagent with VAs (PAN-S-VA) was 20 °C lower than that without VA (PAN-S). Elemental analysis show that the atomic ratio of H to C is about 1:3.8 in both resulting products, which implies that VA has almost no effect on the dehydrogenation reaction. Importantly, the mass percentage of S in the product was increased by 8%, from 28% to 36%, upon addition of VA (elemental analysis results provided in SI). The data indicate that the VA additive enables higher degree of sulfurization in PAN. We speculate that the active radicals intermediates (see scheme S1d in SI) from the pyrolysis of MBT may promote S_8 ring opening via radical mechanisms, and thus enhance the sulfurization of PAN.[18, 19]
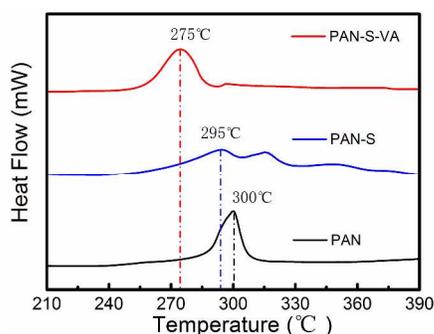

Figure 1. DSC curves of the different starting reactants, including pure PAN, mixture of PAN and sulfur (PAN-S), and mixture of PAN, sulfur, and VA (PAN-S-VA). Heating at 10 °C /min under N_2.

Although DSC curves clearly reflected the influence of VA on the sulfurization of PAN, almost no morphology difference is observed between the resulting products PAN-S and PAN-S-VA. Both materials show similar morphology of aggregated spherical structures with average diameter of about 300 nm (figure 2). Transmission electron microscopy (TEM) showed no excessive elemental sulfur on the surface; and EDX mapping data revealed a uniform distribution of sulfur in the material (Figure S1, SI).
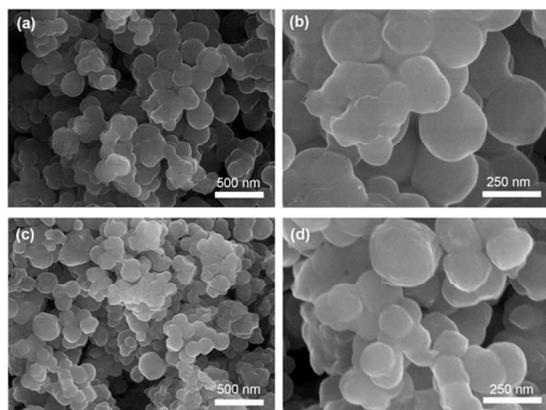

Figure 2. SEM micrographs of (a) and (b) PAN-S, (c) and (d) PAN-S-VA.

The difference in molecular structure between PAN-S and PAN-S-VA was revealed with X-ray photoelectron spectroscopy (XPS). The S_{2p} spectra in figure 3 show four sets of double peaks at about 161.3, 163.2, 166.6, and 168.6 eV for both compounds; however, the double peak at 163.2 eV (marked in red shade in figure. 3) is much more pronounced in PAN-S-VA than in PAN-S. Since this double peak is assigned to 2p electron of S atoms either directly bonded to carbon or in short-chain organosulfide,[22-24] the XPS data confirm that more carbon-sulfur bond or short-chain organosulfide-type sulfur species are present in the PAN-S-VA, which is consistent with the higher sulfur content result obtained from elemental analysis.
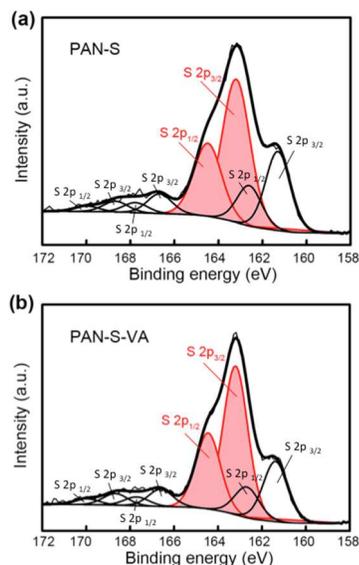

Figure 3. (a) S_{2p} XPS spectra of PAN-S and (b) PAN-S-VA
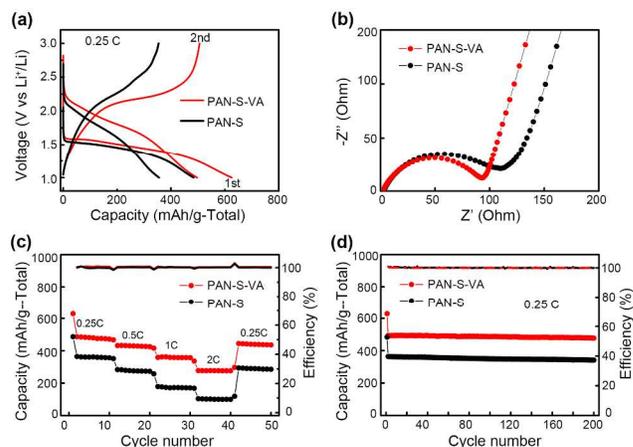

Figure 4. Electrochemical performance of PAN-S and PAN-S-VA batteries. Specific capacity is calculated against the total mass of the sulfurized carbon material. (a) Initial and second discharge/charge curves of PAN-S (black) and PAN-S-VA (red) batteries at a current density of 0.25 C (1 C=1672 mA g^{-1}); (b) EIS of PAN-S (black) and PAN-S-VA (red) batteries; (c) Rate performance of PAN-S (black) and PAN-S-VA (red) batteries at various current rates; (d) Discharge capacity and Coulombic efficiency cycling stability of PAN-S (black) and PAN-S-VA (red) batteries at a current density of 0.25 C.

Improved degree of sulfurization in PAN significantly affects the electrochemical properties. The PAN-S and PAN-S-VA

materials were used as the active cathode material in Li-S coin cells and their electrochemical performances are presented in figure 4. The discharge/charge profiles of both PAN-S and PAN-S-VA feature a single voltage plateau around 1.6 V with a significant voltage hysteresis (figure. 4a). It has been widely accepted that the single sloping voltage plateau in discharge curves suggests a solid-to-solid phase transition.[6,7] The specific capacity during the first discharge is much larger than the rest charging/discharging cycles. This phenomenon has been consistently observed in all sulfurized carbon materials and is ascribed to irreversible reactions possibly occurred at the sulfurized carbon/electrolyte interface.[11, 25, 26] Quantitatively speaking, the initial discharge capacity calculated based on the total electrode active mass for PAN-S and PAN-S-VA is 484 mAh g^{-1} and 628 mAh g^{-1}, respectively; and those in the second cycle are 364 mAh g^{-1} and 494 mAh g^{-1} respectively. The PAN-S-VA consistently shows higher specific capacity than the PAN-S control sample, indicating that the application of VA in sulfurization can significantly improve the performance.

The electrochemical impedance spectra (EIS) in figure 4b show that the charge-transfer resistance of the PAN-S-VA (93 Ω) is slightly smaller than that of the PAN-S cell (112 Ω), which agrees with the fact that the PAN-S-VA batteries showed a smaller polarization in the first discharge/charge cycle (Figure 4a). The different EIS may originate from differences in sulfur content or in the structure of the materials as reflected in the Raman spectra (Figure S3). The Raman results indicate that the PAN-S-VA may have more amorphous sections in its structure and thus facilitate lithium ion diffusion in the electrode, which improves the electrochemical kinetics and the rate performance of the battery. As shown in figure 4c, PAN-S-VA shows a reversible capacity of 450 mAh g^{-1} when cycling at 0.25 C after cycling at various rates, exhibiting little change compared with the first 10 cycles. Furthermore, as shown in Figure S2, the PAN-S-VA sample displays better rate performance than PAN-S, especially at high rates of 0.5C or 1C. It needs to be noticed that the Coulombic efficiency remains stable at 100% regardless of the discharge/charge rates.

The cycling profile of PAN-S-VA is shown in figure 4d. Not only is the second discharge capacity increased by ~120 mAh g^{-1} compared to PAN-S, and the Coulombic efficiency is nearly 100 % except for the first cycle, but also no obvious fading is observed in further 200 cycles and the capacity is stabilized at 477mAh g^{-1}. The decay rate is as low as 0.017 %, which is one of the best performances recorded to date. Moreover, almost no self-discharge occurred in the fully charged battery after one-month shelf time. These properties are generally attributed to the absence of soluble polysulfieds (Li$_2$S$_n$, $n<4$) in cycling.[7]

Sulfurized carbon is highly promising for practical Li-S batteries, considering the stable capacity retention, low self-discharge rate, high safety, and low manufacturing cost. The VA facilitated sulfurization process significantly improves the sulfur content and the discharge capacity in the Li-S battery without compromising other aspects of the electrochemical performance. Furthermore, the addition of VA effectively lowers the sulfurization temperature, which is important for reducing the cost and energy consumption in future mass production. While the benefit of this idea was demonstrated in this communication based on only one type of VA, the wide variety of available VA chemistry suggests a large space of optimization for further improvement of the properties of sulfurized carbon based Li-S batteries. Mechanistic investigations are currently underway and will be reported in future studies.

Conclusions

In summary, we demonstrate that vulcanization accelerators provide an effective approach to increase the sulfur content of sulfurized carbon; the resulting material displays significantly improved discharge capacity and more stable cycling performance. We expect the effectiveness of this approach and the wide variety of vulcanization accelerator chemistry will pave the way for sulfurized carbon materials towards practical applications in Li-S batteries.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: Descriptions of experimental methods, elemental analysis, SEM, TEM, Raman, and more discussion. See DOI: 10.1039/b000000x/

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