Solid-State Lithium–Sulfur Battery Enabled by Thio-LiSICON/Polymer Composite Electrolyte and Sulfurized Polyacrylonitrile Cathode

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1. Introduction

Increasingly demanding requirements of the automotive industry drive the vigorous pursuit of energy storage systems with higher energy density, higher safety standards, and lower costs.[1,2] Lithium–sulfur batteries (S–Li) have been considered promising as the conversion-type reaction of sulfur provides a theoretical specific energy density of 2660 Wh kg⁻¹ (calculated based on the theoretical capacity of S: 1671 mAh g⁻¹ and Li: 3862 mAh g⁻¹, and a cell voltage of 2.28 V), which is more than four times higher than the theoretical energy density of lithium ion batteries (606 Wh kg⁻¹, calculated based on the theoretical capacity of LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂: 279 mAh g⁻¹ and C₆: 372 mAh g⁻¹, and a cell voltage of 3.80 V).[3–5] However, its practical application has encountered formidable challenges, such as low sulfur active material utilization, the polysulfide shuttle effect, and on the anode side, safety concerns mostly represented by the high reactivity of Li metal, and uncontrolled Li electrodeposition process leading to high surface area Li (HSAL) deposits, etc. (Figure 1a).[6–9] Solid-state lithium–sulfur battery (SSLSB) is gaining increasing attention, mainly ascribe to its advantages in lithium metal implementation and conceivably high energy density, as well as the general potential of solid electrolytes in resolving safety concerns.[10,11] Furthermore, the polysulfide shuttle effect as a cross-talk reaction can be excluded in the solid-state configuration.[12–14]

In recent years, many solid electrolyte systems have been developed and demonstrated in SSLSBs, including solid...

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polymer electrolytes and inorganic solid electrolytes.[15] Among these, the inorganic solid electrolytes, especially the sulfide-based inorganic electrolytes have attracted major interests due to their high ionic conductivity, mechanical property, and good compatibility with sulfur cathodes.[16,17] However, the electrochemical performances and in particular, the practical energy densities of the ceramic electrolyte based SSLSBs are still far from expected theoretical values.[16,18] As illustrated in Figure 1b, the ceramic electrolyte based SSLSBs are commonly fabricated by pressing the solid electrolyte powder, sulfur, conducting carbon, and Li metal anode under high pressure to assemble a pellet-type battery cell.[10,19] This type of battery cell was generally accompanied by high interior stress as well as high interfacial resistances.[19] Grain boundaries, which inevitably exist in the particle stacking of solid electrolytes, compromise the ability of solid electrolytes in preventing HSAL growth.[20] At the interface of the solid electrolyte with Li metal anode, insufficient wetting and rigid contact result in void formation during cycling, which further promotes irregular Li deposition, leading to high local stress and eventually Li metal degradation.[21,22]

Besides the drawbacks of compressed inorganic solid electrolyte pellets in SSLSBs, the intrinsic limitations of the sulfur cathode are even more prominent in SSLSBs.[23] The poor electronic conductivity of sulfur as well as its discharge product (Li$_2$S) results in low reversibility and low active material utilization. Significant volume change takes place in the conversion between S and Li$_2$S during charge/discharge of a S–Li cell, which leads to the permanent separation between active materials, solid electrolytes, as well as conductive agents. This phenomenon was named as “chemomechanical” failure.[24] Unlike flowable liquid electrolytes,[19] which can effectively wet evolving cracks after volume expansion, in solid-state batteries, the “chemomechanical” failure may cause fast capacity fading and short life span of the cells. For improving the sulfur cathode performance in SSLSBs, various approaches have been investigated and adopted. One of the most commonly reported strategies is fabricating composite sulfur cathode by mixing the active materials with solid electrolytes.[26] This preparation method may improve the contact between the active materials and the solid electrolytes, although the improvements in cycling performance have been limited. Furthermore, a decrease in energy density per weight and an increase in cell fabrication costs can be expected.[27] Further approaches such as nanosizing the active materials,[28] modification of the porous structure of carbon conductive agents,[29,30] etc., have not been able to improve the sluggish electrochemical kinetics of the sulfur cathode in solid-state configuration.

Herein, we propose a novel construction of SSLSB, as presented in Figure 1c, a Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ (LGPS)/polyethylene oxide (PEO) composite electrolyte (LCE) was introduced to replace the conventional rigid inorganic solid electrolyte pellet, which was intended to increase the wettability of the electrolyte system and decrease the charge-transfer resistance. Sulfurized polyacrylonitrile (S/PAN) was utilized instead of a conventional S/C cathode due to its unique electrochemical characteristics.[31] Mechanistic and structural study revealed the radical-involved charge/discharge mechanism of S/PAN, which explained the outstanding performance of this novel SSLSB from a more fundamental perspective of the electrochemical characteristics of S/PAN.

2. Results and Discussion

2.1. Fabrication of LCE

The LCE fabrication procedure is presented in Figure 2a. Premixed LGPS powder and plasticized PEO polymer electrolyte at a mass ratio of 88:12 were hot-pressed to obtain flexible membranes. The X-ray powder diffraction (XRD) pattern of the LCE presented in Figure 2b reveals the main reflections of the crystal structure of LGPS powder.[12] Consequently, the crystal structure of LGPS is still intact after mixing with PEO.
The reflections of PEO in the XRD pattern of LCE can hardly be detected.

$^7$Li magic angle spinning (MAS) nuclear magnetic resonance spectroscopy (NMR) investigations were applied to reveal the local Li-ion environment in LCE. Two prominent signals at 0.6 and 0.9 ppm can be observed in the $^7$Li MAS NMR spectra in Figure 2c. These $^7$Li signals are representative of multiple Li environments in the main phase of the LGPS electrolyte. A minor contribution from additional phases of LGPS can be related as well. The low-intensity $^7$Li signals at $-1.3$ ppm can be correlated to the Li ions in the PEO domain of the LCE. Thus, the $^7$Li NMR spectra revealed the coexistence of Li ions in both the ceramic and the polymeric phases of the LCE.

As presented in the cross-section scanning electron microscope (SEM) image in Figure 2d, the thickness of the as-prepared LCE membrane was $\approx 100 \mu$m. Top-view SEM images and the result of energy-dispersive X-ray spectroscopy (EDS) mapping of LCE are presented in Figure 2e,f. The result of EDS mapping reveals the distribution of the F and P elements, which originate from the LiTFSI salt in PEO polymer electrolyte domain and the LGPS electrolyte domain in LCE, respectively.

The result provides direct-viewing of the high content of LGPS in LCE and their dense packing. In contrast to the majority of the composite electrolytes reported in the literature,[33–35] the ceramic powders were uniformly distributed throughout the polymer matrix. The PEO polymer electrolyte in this work was embedded in continuously tightly packed LGPS electrolyte particles, and the ceramic particles no longer just function as “filler” for suppressing the crystallinity of the polymer matrix. Instead, they could function as primary contributors to the Li ionic conductivity in LCE. For further probing the actual Li conducting mechanism of LCE, $^6$Li MAS NMR was applied. As shown in Figure S3 in the Supporting Information, the $^6$Li MAS NMR spectrum of LCE after cycling against $^6$Li metal electrodes includes the $^6$Li resonances of LGPS that show a pronounced broadening in comparison to LCE before cycling. While the $^6$Li signal of LiTFSI is clearly visible before cycling, it is on the other hand hardly visible after cycling. The results may indicate that the LGPS electrolyte contributes to the central Li-ion conducting in the LCE instead of the PEO polymer electrolyte.

The ionic conductivity of the solid electrolyte membranes was determined based on the impedance spectra of the
stainless-steel symmetric cells, the corresponding Arrhenius plots are presented in Figure 3a. The ionic conductivity of the LCE reached $4.2 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C, and the calculated activation energy was 35 kJ mol$^{-1}$ (0.36 eV) according to the Arrhenius equation. Even though the ionic conductivity of the LCE is lower than that of the pure LGPS electrolyte ($2.81 \times 10^{-3} \text{ S cm}^{-1}$ under 20 °C), it is still among the highest of the polymer/ceramic composite electrolytes that have been reported in the literature. Moreover, the LCE outperforms the ionic conductivities of PEO polymer electrolyte in the measured temperature range.

The lithium ion transference number of the LCE was determined by the Bruce & Vincent method according to Equation (1):\[ t_+ = \frac{I_{ss} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{ss} R_{ss})} \] (1)

Here, $\Delta V$ is the applied voltage (10 mV in this case), and $I_0$, $R_0$, and $I_{ss}$, $R_{ss}$ are the initial and steady-state currents and resistances, respectively. Figure 3b shows the chronoamperometry profile of the LCE at 60 °C. The lithium ion transference number was determined to be 0.87 according to Equation (1). The high lithium ion transference number may be ascribed to the high content and the dense packing of LGPS in the LCE, since the LCE differs from the polymer-based composite electrolytes that function as “solid solvents,” and commonly have lithium ion transference number less than 0.5. Furthermore, the densification of LCE could increase the contact between ceramic grains thus decrease the grain boundary resistance. For further elucidation of the influence of packing densities of the LCE on the lithium ion transference number, the LCEs were fabricated under different molding pressure and their corresponding chronoamperometry profiles were recorded (Figure S4, Supporting Information). We observed a dramatic decrease of the lithium ion transference number with the decline in molding pressure. Similar results have been reported by Sakuda et al. who observed an improved ionic conductivity of the sulfide electrolyte (80Li$_2$S:20P$_2$S$_5$) with increasing molding pressure, and the increased conductivity was ascribed to the decreased amount of grain boundaries along with the higher molding pressure. In this work, the higher molding pressure could not only improve the contact between LGPS grains in the LCE, but also reduce the interstitial spaces and interfaces between the polymer and ceramic electrolytes, resulting in improved and more continuous lithium ion transfer pathways.

### 2.2. Compatibility of LCE with Lithium Metal

The stability against lithium metal is vital for the implementation of solid electrolyte membranes in lithium metal batteries. For evaluating the performance of the solid electrolyte membrane against Li metal anode, symmetric Li–Li cells were fabricated by stacking two lithium metal foils and a solid electrolyte membrane in coin cell setup (Figure 4a). Figure 4b displays the impedance spectra of the LCE and LGPS electrolytes in Li–Li cells. The large semicircle presented in the Nyquist plot of the Li|LGPS|Li revealed a high interfacial resistance between the LGPS electrolyte pellet and the lithium metal electrode. A remarkable increase in resistance was observed after 12 days of aging, indicating the interfacial side reactions between the electrolyte and Li$^+$. The Nyquist plot of the Li|LCE|Li cell presented a lower semicircle compared to the LGPS-based cell, which is likely a result of the improved wetting property of the LCE membrane at the interface toward Li. Furthermore, a slight increase of impedance after 12 days resting period indicated lower reactivity of LCE and Li in comparison to the LGPS electrolyte.

Figure 4c presents the time-dependent voltage profiles during the Li electrodissolution/electrodeposition experiments in Li|LGPS|Li and Li|LCE|Li cells at 0.1 mA cm$^{-2}$. The initial overvoltage during charge reached a high value of 0.35 V for the Li|LGPS|Li cell, which correlated well with the discussed higher interfacial resistance of the cells with LGPS electrolyte. The overvoltage decreased slightly to 0.3 V after 40 cycles with a sudden drop at the 47th cycle, which indicated an internal short-circuit due to the severe form of HSAL. By contrast, the Li|LCE|Li cell was able to be cycled for 400 cycles with a low polarization voltage of 0.02 V. Overall, the improved wetting and higher cycling stability during electrodeposition/electrodissolution of the as-fabricated LCE membrane reveal high compatibility with Li metal electrodes compare to the LGPS electrolyte.

![Figure 3. a) Arrhenius plots of LCE, LGPS, and PEO+LiTFSI electrolytes, and b) chronoamperometry profile of the LCE (inset: Nyquist profiles of the cell impedance before and after polarization).](image-url)
2.3. Electrochemical Investigations of SSLSBs Fabricated with LCE and S/PAN Cathodes

The SSLSB full cells were assembled by sandwiching S/PAN cathodes, LCE electrolyte membranes, and Li metal anodes in coin cell setup. Figure 5a compares the cycling performance of the S/PAN|LCE|Li and S/C|LGPS|Li cells under the current density of 0.1 C. The S/C|LGPS|Li cell exhibited a low initial discharge capacity (176 mAh g\(^{-1}\)), and it continuously decayed to 77 mAh g\(^{-1}\) after 50 cycles. The inferior performance indicated that with a sulfur loading of 45% and coin cell setup, the SSLSB fabricated with S/C cathode and LGPS electrolyte can hardly be cycled. However, the S/PAN|LCE|Li SSLSB achieved a high initial capacity of 1772 mAh g\(^{-1}\), and capacity retention of 588 mAh g\(^{-1}\) could be accomplished after 50 cycles. Compared to the performances of SSLSBs reported in literature, the cycling performance in this work shows significant advancement, the SSLSBs in previous reports usually adopted low sulfur loading (<30%),\(^{[28,46,47]}\) and have limited cycle life (<20),\(^{[48,49]}\) while herein, the values are 44.7% sulfur loading in S/PAN, and the cell is able to achieve 100 cycles with a capacity retention of 374 mAh g\(^{-1}\) (Figure S5, Supporting Information). Further -more, when considering the cell-level energy density of the S/PAN|LCE|Li in this work, the specific gravimetric energy density (\(E_g\)) and the volumetric energy density (\(E_v\)) were calculated according to Equations (S1) and (S2) in the Supporting Information. The calculated \(E_g\) and \(E_v\) of the S/PAN|LCE|Li cell amount to 116 Wh kg\(^{-1}\) and 660 Wh L\(^{-1}\), respectively, which is higher than the most reported solid-state cells in the literature.\(^{[50]}\)

Figure 5b shows the charge/discharge curves of the S/C|LGPS|Li and S/PAN|LCE|Li cells in the first and second cycles. The voltage profile of the S/C|LGPS|Li is characterized by single voltage plateaus at \(\approx 2.35\) and 2.2 V for charge and discharge, respectively, which can be rationalized by the one-step transition between Li\(_2\)S and S during the charge/discharge process.\(^{[51]}\) This behavior is different from that of a liquid electrolyte based S/C–Li battery, in which the two discharge plateaus represent two reduction processes of polysulfides (Figure S6, Supporting Information).\(^{[52]}\) The charge/discharge profile of the S/PAN|LCE|Li cell shows differences for the first and second cycle, in accordance with the electrochemical characteristics of S/PAN in liquid electrolytes from the aspect of the large initial discharge capacity.\(^{[31,53]}\) The charge/discharge profiles of S/PAN|LCE|Li in different cycles are further presented in Figure 5c. After the first cycle, the voltage profiles of the following cycles were similar. They all showed single charge/discharge plateaus. Figure 5d displays the charge/discharge profiles of the S/PAN|LCE|Li cell at different C rates (the second cycle of 0.1 C is presented). Reversible capacities of 1183, 719, and 482 mAh g\(^{-1}\) could be achieved at 0.2, 0.5, and 1 C,
respectively, revealing a good rate performance of the SSLSB fabricated with S/PAN and LCE electrolytes, which indicate rapid kinetics of S/PAN cathode with Li-ions.\cite{54,55}

2.4. Mechanistic Insights into the Charge/Discharge Process of SSLSBs Fabricated with LCE and S/PAN

Ex situ $^7$Li MAS NMR measurements were applied to investigate the charge and discharge products of S/PAN, as summarized in Figure 6a,b. Two prominent $^7$Li resonances at 0.6 and 0.9 ppm are visible in all $^7$Li MAS NMR spectra. These are due to multiple Li environments in the LGPS electrolyte in LCE, since it was inevitable not to include the solid electrolytes while collecting the S/PAN samples after cycling. Similarly, the $^7$Li resonance at $\sim$1.3 ppm can be assigned to the LiTFSI from the PEO electrolyte. In the $^7$Li MAS NMR spectrum of the initially discharged S/PAN cathode, a broad $^7$Li signal was observed in the chemical shift region of 7.0–5 ppm, in addition to, a clear resonance at 2.4 ppm, which can be assigned to crystalline Li$_2$S. These results indicated the coexistence of distinct lithiation products of S/PAN. In the $^7$Li MAS NMR spectrum of the subsequently charged S/PAN cathode, the broad $^7$Li signal at the higher chemical shift region disappeared, while the signal of Li$_2$S is still visible. This might due to the insufficient conversion of the formed Li$_2$S during the prior discharge process and may also explain the following capacity decay in further cycles. On the spectrum of the second discharge of S/PAN, the $^7$Li signal at the higher chemical shift region again can be observed, which indicated good reversibility of the lithiation and delithiation process. The large $^7$Li resonance broadening may result from interactions with paramagnetic centers, which is an indication of the existence of unpaired electrons in S/PAN.\cite{56,57} To test this hypothesis, Figure 6c displays the ex situ electron paramagnetic resonance (EPR) spectra measured at different charge/discharge states of S/PAN in the initial cycle. The EPR spectra provide clear evidence of the existence of radical species along the charge and discharge process of S/PAN. Moreover, the structure and the quantity of the radical species experience transformations with the extent of lithiation and delithiation of S/PAN, which suggests a complex redox mechanism of S/PAN that involves different radical species.

The electrochemical characteristics of S/PAN are still under debate. Wang et al.\cite{58} ascribed the superior performance of S/PAN to direct conversion between the S and Li$_2$S embedded in PAN polymer chains, thus avoiding the polysulfides shuttle effect. Subsequently, researchers proposed that the conjugated PAN polymer backbones can form delocalized radicals, to activate the formed Li$_2$S to reconnect to PAN polymer backbones during the charging process.\cite{59,60} However more recently, instead of a general belief of the lithiation of S in S/PAN, extra Li storage mechanisms such as at C, N in S/PAN polymer structures were discovered.\cite{61,62} To the best of our knowledge, this is the first report concerning the S/PAN characterization in a solid-state battery configuration. Based on our analysis, there is no appearance of polysulfide species in the charged or
discharged S/PAN, while Li$_2$S does exist as discharge product of S/PAN. Furthermore, our results indicate clear evidence of extra Li storage in the S/PAN polymer structure except for S, which demonstrate the participation of PAN polymer structure itself during the charge and discharge process. It is worth noting that the S/PAN in this work was cycled in the solid-state configuration under different temperatures as previous reports, however, for proposing a conclusive reaction mechanism, the influence of electrolyte and temperature has to be further investigated, and the research is in progress in our laboratory for addressing these aspects.

Nevertheless, the exceptional performance, as well as the results of the mechanistic studies, demonstrates the feasibility of S/PAN as a promising sulfur cathode for SSLSB. First, the unique electrochemical characteristics of S/PAN suppress the direct conversion between S and Li$_2$S, thus alleviating the significant volume expansion and its associated stress/strain. Furthermore, in contrast to the vast formation of irreversible Li$_2$S during the cycling of a conventional S/C cathode in solid-state configuration,[23,52] the preservation of the radicals in the S/PAN structure can effectively provoke the conversion between the charge and discharge products to support fast redox kinetics and improve cyclability, which explains the high reversibility and the excellent performance of S/PAN also in a solid-state battery configuration.

3. Conclusions

We developed a high performance solid-state lithium–sulfur battery by incorporating the advantages of the LCE and S/PAN cathode, which delivered advanced performance with high initial discharge capacity 1772 mAh g$^{-1}$ and excellent rate performance: 1183 mAh g$^{-1}$ at 0.2 C and 719 mAh g$^{-1}$ at 0.5 C, respectively. The as-fabricated LCE processes high ionic conductivity ($0.42 \times 10^{-3}$ S cm$^{-1}$) and Li$^+$ ion transfer number (0.87), which was proved to achieve good interfacial wetting and stable lithium electrodeposition/electrodissolution cycling at comparatively low overvoltages. Mechanistic investigations revealed the involvement of radical species within the sulfur grafted conjugated polymer framework during the charge/discharge of S/PAN, supporting mitigation of large volume change in the cathode and maintaining fast redox kinetics. The results demonstrated the excellent performance of the SSLSB and rationalized our concept of design. This work may contribute to the future innovative design of solid-state lithium–sulfur batteries with superior performance.

4. Experimental Section

Fabrication of LCE: The composite electrolyte membranes were prepared by hot-pressing the premixed LGPS powder (MSE supplies,
99.99%) and binder material with weight ratio of 88:12 under selected pressure and temperature. The binder material was plasticized PEO, which includes PEO (nₜ = 400 000) (Sigma-Aldrich), LiTFSI (Solvionic, 99.9%), and Pyr₅TFSI (Solvionic, 99.9%) in a molar ratio of 10:1:2. The Pyr₅TFSI was added as a plasticizer for the PEO electrolyte to achieve a more amorphous state, which was found to be beneficial for increasing the adhesion between the ceramic powders in order to form a paste for hot-pressing. The hot-pressed membranes were then punched to afford solid electrolyte disks for cell fabrication.

Fabrication of S/PAN Cathodes: Details on the synthesis and characterization of S/PAN are provided in the Supporting Information. The S/PAN cathodes were prepared by doctor blading the S/PAN slurry (S/PAN, Super C65, and PEO binder materials in a mass ratio of 45:35:10 in ACN, and the S/C cathodes were fabricated by mixing the sulfur powder, Super C65, and PEO binder in a mass ratio of 45:35:10 in ACN, and the slurry was coated in the same procedure as for S/PAN cathodes. All the cathodes were dried at 50 °C under vacuum before using for cell assembling.

Materials Characterization: SEM images were obtained on a Carl Zeiss AURIGA CrossBeam workstation (Carl Zeiss SMT AG, Germany) equipped with a field emission gun (Schottky) at an acceleration voltage of 3 kV. The EDS mapping spectra were obtained at the same workstation with an acceleration voltage of 15 kV. XRD measurements were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range from 10° to 80°. The ex situ 7Li MAS NMR spectra were recorded on a 500 MHz Bruker AVANCE NEO spectrometer equipped with an 11.70 T widebore magnet using a 2.5 mm Bruker MAS probe (DVT design) at 25 kHz MAS. The 7Li MAS NMR spectra (ν_Li = 194.47 MHz) were acquired by the use of a Hahn Echo experiment with one rotor period echo delays. The 7Li chemical shift was referenced to an aqueous solution of 1 M LiCl and set to 0 ppm. Spectral analysis and fitting of the NMR data were achieved by using the dmfft program.[63] The continuous-wave (CW) solid-state EPR spectra were measured on a Bruker EMXnano X-band EPR spectrometer. For the acquisition, a power of 3.16 mW and 80 repetitions were applied. The modulation frequency was set to 100 kHz and modulation amplitude of 0.4 G was used. Furthermore, for determining the amount of radical species, the mass of the scratched S/PAN materials was measured and the marker positioned at 3480 C was used as an internal reference.

Electrochemical Measurements: The SSLSBs were assembled by stacking the lithium metal anode, LCE, and S/PAN cathode in 2032-coin cell setup in an argon-filled glovebox.[64] The galvanostatic cycling was performed on a MACCOR Series 4000 battery tester at 60 °C. The voltage window was 1–2.5 V. The Li/Li symmetrical cells were assembled in coin cell setup as well, and the electrodesposition/electrodeposition experiments were conducted at 60 °C for 1 h at a current density of 0.1 mA cm⁻². The EIS spectra were measured by using a Novocontrol Alpha Analyzer in the frequency range of 1 MHz to 1 Hz and an AC amplitude of 10 mV. For determination of the overall ionic conductivity of the solid electrolyte membranes, EIS measurements were conducted for the solid electrolytes enabled stainless steel symmetric cells in the temperature range of 0–80 °C. The lithium ion transfer number of the solid electrolytes was determined by the Bruce & Vincent method.[39] The chronoamperometric and impedance measurements for the Li/Li symmetrical cells were performed on a potentiostat (Metrohm Autolab PGStat302 N using the Nova 1.6 Electrochemistrysoftware), and the Li/Li symmetrical cells were rested for 10 h before the impedance measurements.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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polymer/ceramic composite electrolytes, solid-state lithium–sulfur batteries, sulfurized polyacrylonitrile cathodes

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