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Improving the performance of Li–S Batteries by reinforced PPy wrapping over acetylene black-coated sulfur

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A strategy of reinforced PPy wrapping over acetylene black-coated sulfur composite (PPy-AB/S) was designed for synthesizing cathode materials of Li-S batteries with improved performance. It was found that the resulting PPy-AB/S cathodes were able to maintain 630 mAh g⁻¹ even after 200 charge–discharge cycles at a rate of 0.5 C.

Due to the ever increasing energy demands and environmental crisis, it is necessary to develop advanced energy storage systems that can keep long-term high-rate discharge for the popularization of electric vehicles (EVs) and hybrid electric vehicles (HEVs).\(^1\) Among those energy storage systems, the lithium-ion battery has the distinct advantages, including high energy density, light weight, wide operating temperature, and no memory effect, and this is applicable for use as the main or sub electrical power supplies of EVs and HEVs.\(^3\)–\(^5\) Though the state-of-the-art lithium-ion battery has an improved discharge property that can keep its high energy density under large current density, the widespread use is still limited by its low theoretical specific energy densities (e.g. \(\sim 400\) Wh/kg for LiCoO\(_2\)/graphite system).\(^6\)–\(^12\) Therefore, the current research interests focus on the exploration of novel lithium battery systems. Lithium-sulfur (Li–S) batteries have received special attentions because of their high theoretical specific capacity (1675 mAh g⁻¹) and high specific energy (2600 Wh kg⁻¹) at a moderate voltage of 2.2 V vs. Li/Li⁺.\(^1,\)\(^13\) In addition, the cathode material elemental sulfur also has other advantages, including its natural abundance, low cost (about $150 per ton), and low environmental impact.\(^14\)

Despite these promises, the commercial applications of Li-S batteries are still hindered due to the existent several challenges. For example, the inherent low electrical conductivity of sulfur (5×10⁻¹⁰ S cm⁻¹), resulting in limited active material utilization efficiency and rate capability. In addition, shuttling of high-order polysulfides between cathode and anode as well as the high solubility of polysulfides intermediates in the electrolyte, leading to limited cycle stability. Additionally, sulfur undergoes severe volumetric expansion/shrinkage during charge and discharge (~80%), which gradually decreases the mechanical integrity and stability of the electrode over cycles.\(^1\)\(^,\)\(^15\)\(^,\)\(^16\) Therefore, addressing these issues by improving the conductivity of the sulfur cathode and trapping soluble polysulfides within a mechanically stable cathode structure are critical to develop a viable Li-S system.

Over the past decades, various approaches have been made on the fabrication of rationally designed nanostructures and demonstrated a significant improved cyclability and capacity by employment of carbon materials\(^8\)\(^,\)\(^17\)–\(^20\) (such as graphene, carbon nanotubes, carbon nanofibers, carbon sphere), polymer additives\(^21\)–\(^23\) (such as PEDOT: PSS, PANI, PVP) or oxides additive\(^24\)–\(^26\) (such as TiO\(_2\)). It has been reported that the high specific capacities exceeding 1000 mA h g⁻¹ in terms of sulfur have been achieved under low discharge rates (~0.1C). Nevertheless, there still existed shutting effect, especially at high rates, which results in a stable problem under high rates. Most recently, of notable successes, Cui et al. developed Li-S batteries with very high specific capacities of around 700 mA h g⁻¹ at a rate of 1C and excellent cycle stability.\(^23\) In our previous work, we synthesized a cathode made with G-S-CNFs multilayered coaxial nanocomposites, which can deliver an initial capacity of 745 mA h g⁻¹ and maintain ~273 mA h g⁻¹ even after 1500 charge–discharge cycles at a high rate of 1C.\(^27\) However, the high cost and the elaborate synthetic process involving in varied carbon materials, such as mesoporous carbon, carbon nanotubes, and graphene, are considered to be the drawbacks of the approach.

Acetylene black (AB) is well known as an excellent conductive additive used in plastics, rubber, and batteries, due to its good conductivity, liquid absorbing ability, compressibility and elasticity. To the best of our knowledge, no other conductive additives except AB are used in commercial cells.\(^28\) Although the cost may play the main role from the viewpoint of the manufacturers, the inherent advantage of AB nanoparticles over other types of nanoparticles, such as carbon fibers, and large graphites is that they can form extended network structures to provide both conductivity and super mechanical properties at low loadings.\(^29\) Considering its application in the Li-S batteries, AB could be incorporated with sulfur by ball-milling or thermal treatment to form sulfur–AB composites as the electrical conductor in the electrode. It was reported that such sulfur-AB
composites exhibit poor electrochemical properties. Recently, Su Y.S. et al, developed an in situ sulfur deposition route for synthesizing sulfur–carbon composites as the cathode materials for Li-S batteries, involving the precipitation of elemental sulfur at the interspaces between carbon nanoparticles in aqueous solution at room temperature. However, the resulting electrode had low capacity retention, and its electrochemical properties under high charge-discharge rates were not investigated yet.

Here we report an approach to assemble PPy-AB/sulfur (PPy-AB/S) coaxial structured nanocomposite, in which PPy wraps AB coated sulfur particles. They presented markedly improved cycle stability and capacity and could be used as a cathode for Li-S batteries. In our approach (Fig. 1), nanoscale AB particles were first coated uniformly onto the surface of microscale sulfur particles in an aqueous solution, subsequently, a layer of stacked PPy nanospheres was used to closely wrap around the whole structure in order to enhance the degree of wrapping over sulfur. In this well designed structure, both PPy and AB not only serve as good conducting fillers to improve the overall conductivity of the composite, but also trap the polysulfide intermediates. More importantly, PPy has a high absorption ability to restrain the dissolution of polysulfides in the electrolyte. It was found that the electrodes made with such composite were able to deliver a high specific capacity of 1189 mAh g\(^{-1}\) at 0.2C and still maintain 640 mAh g\(^{-1}\) at 2C, demonstrating their high-rate capability due to the highly conductive network formed by PPy and AB. Meanwhile, significantly improved stability and capacity at high charge-discharge rate were achieved. PPy-AB/S electrode can deliver a high capacitance of 992 mAh g\(^{-1}\) at the 5\(^{th}\) cycle, and maintain 630 mAh g\(^{-1}\) after 200 charge-discharge cycles at 0.5C, while the coulombic efficiency remained nearly 100%. These improved rate capability and cycle stability could be attributed to the unique architecture of the composite, that is to say, the synergistic contribution of PPy and AB could enable the electrodes to possess improved electrical conductivity and better ability to trap and absorb the soluble polysulfide intermediates.

![Schematic illustration of the assembled PPy-AB/S composites for improving cathode performance.](image)

The microstructures of the acetylene black, AB/S composite, and PPy-AB/S composite are shown in Fig. 2. From Fig. 2a, AB has the varying particle sizes between 50 and 100 nm. It also demonstrates spherical morphology without agglomeration, which is beneficial to achieve good electronic conductivity between active materials and/or current collector in the batteries. Fig. 2b presents that the nanoscale AB particles uniformly distributed on the surfaces of the spherical microscale sulfur particles. From the enlarged photo of Fig. 2b (Fig. 2h, inserted), it can be seen that the sulfur particles actually are not fully covered by AB. In order to reinforce the wrapping degree over sulfur, PPy stacked by PPy nanospheres was used to fill the gaps among AB. As can be seen from Fig. 2c and its enlarged photo (Fig. 2c, inserted), the diameter of the spherical composite was remarkably increased, indicating that a uniform PPy layer was formed over the spherical composite, which will effectively enhance the conductivity of the composite material. As a result, the obtained uniform structure provides not only excellent electron pathways for the insulating sulfur but also many adsorbent points for the soluble polysulfides to avoid their loss into the electrolyte. The energy-dispersive spectroscopy (EDS) of the PPy-AB/S composites (Fig. 2d, inserted) clearly shows the existence of sulfur. The actual content of sulfur in the composites were determined by thermo gravimetric analysis (TGA) conducted under nitrogen environment (Fig. 2d) to be 45%, which is similar to that as determined from the precursors.

![Fig. 2 SEM images of (a) pristine acetylene black; (b) sulfur with AB coating, inserted with the enlarged photo; (c) sulfur with AB and PPy wrapping, inserted with the enlarged photo; (d) TGA results of the PPy-AB/S composite, inserted image is the EDS result.](image)

![Fig. 3 Comparison of specific capacity and coulombic efficiency as a function of cycle numbers for electrodes assembled with and without PPy wrapping.](image)

A series of electrochemical tests were carried out to study the effects of the PPy-AB/S composites on the cyclic performance of the electrode. The cathodes for Li-S battery testing were prepared by slurry coating of PPy-AB/S and PVDF binder on Al foil. All the test batteries were assembled as coin cells (type 2032) with a small piece of lithium foil used as the counter electrodes. Fig. 3 compares the cyclabilities of the AB/S composite electrodes with and without PPy coating at 0.5C (where 1C corresponds to a current density of 1675 mA g\(^{-1}\)) within 1.5 ~ 3.0V (vs Li/Li\(^+\)). Both of these two electrodes have similar sulfur content of ~40.5 wt%. Obviously, the PPy-AB/S composite electrode exhibited more stable cycling performance and higher discharge capacity than the AB/S composite electrode over 200 cycles. Based on the discharge results, the PPy-AB/S composite cathode was able to deliver an initial discharge capacity of 847 mAh
g$^{-1}$ (calculation based on the weight of S), and which gradually increased until the 5th cycle (992 mAh g$^{-1}$). This behavior could be associated with the activation of the PPy-AB/S electrode, that is, it takes some time for the electrolyte to flood the internal surfaces of the PPy-AB/S electrode. Thereafter, the deeply buried sulfur and disulfide bonds can contact with the electrolyte and become electrochemically active. Subsequently, the capacities almost stabilized and demonstrated little fading upon extended cycling. In summary, the electrode can exhibit a reversible and comparable capacity of 630 mAh g$^{-1}$ after 200 cycles, corresponding to a capacity retention of 63.5% (of its highest capacity of 992 mAh g$^{-1}$). At the same time, the electrode exhibited well-overlapped and flat plateaus as shown in Fig. 4, suggesting its good stability and reversibility. Furthermore, the electrode displayed a high coulombic efficiency at around 100%. On the basis of such superior cyclic stability, it is reasonable to conclude that the synergistic effects of PPy and AB can effectively improve the cycle stability of sulfur probably through confining and absorbing the polysulfide intermediates, and provide better conductivity and mechanical support to accommodate the volume changes during charge and discharge. For the control sample without PPy wrapping, the AB/S electrode had a higher initial discharge capacity of about 1094 mAh g$^{-1}$ than that of the PPy-AB/S, indicating that the electrolyte can flood the surface of sulfur quickly through those unwrapped pores. With continued cycling, the AB/S electrode was able to stabilize at 366 mAh g$^{-1}$ after 200 cycles, corresponding to a capacity retention of 33.5%. All the results show that the cycling performance and discharge capacity can be significantly enhanced by the reinforced PPy wrapping on AB/S.

We further compared the discharge/charge voltage profiles of the PPy-AB/S and AB/S electrodes at various current densities from 0.2 C to 2 C between 3.0 and 1.5 V. All of the discharge/charge curves demonstrated similar plateaus, as shown in Fig. 5. In detail, two plateaus at 2.35 and 2.05 V were clearly observed during the discharge process, which correspond to the formation of long-chain lithium polysulfides (Li$_2$S$_x$, 4≤x≤8) and short-chain lithium polysulfides (such as Li$_2$S$_2$ and Li$_2$S), respectively.

The rate capability of the PPy-AB/S composite electrode at various current densities from 0.2 C to 2 C was also investigated and was presented in Fig. 6. As the current increases, the capacity of the PPy-AB/S composites electrode decreased slowly from the reversible 1130 mAh g$^{-1}$ at 0.2 C to 928, 688 and 633 mAh g$^{-1}$ at 0.5 C, 1 C and 2 C, respectively. Compared with the PPy-AB/S composite electrode, the AB/S composite electrode exhibited a lower capacity. Importantly, a reversible capacity of 642 mAh g$^{-1}$ was obtained when the current was switched back to 1 C, which is close to the initial capacity (688 mAh g$^{-1}$), indicating a highly reversible and efficient electrode enabled by the reinforced PPy wrapping.

**Conclusions**

In summary, we developed a method of reinforced PPy wrapping over the AB/S composites for high-performance Li-S batteries. In this well-designed structure, sulfur was not only coated by AB but also reinforced by PPy. Owning to the unique core-shell architecture, PPy-AB/S was able to deliver high specific capacity, high retention ratio at increased charging/discharging rates with outstanding stability. This work proposed a general strategy for improving performance of
sulfur cathodes in terms of having high capacity and cycle stability during cycling from the viewpoint of the reinforced wrapping. In addition, we expect that this strategy will cover general interests and influence many other fields.

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Notes and references