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Binder-free cathodes based on sulfur-carbon nanofibers composites for lithium-sulfur batteries

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Binder-free S-FCNFs composite films with sulfur coated uniformly on the surface of FCNFs were used as cathodes for lithium-sulfur batteries. Such cathodes have both high sulfur content (78 wt%) and large areal mass loading (8 mg cm^{-2}), and they can deliver a high areal specific capacity of 1.87 mAh cm^{-2} (234 mAh $g^{-1}_{electrode}$) after 100 cycles at 0.1C.

Rechargeable lithium sulfur batteries are based on the redox couple of S_8+16Li=8Li_2S and have output voltage ~ 2.2V.[1-4] According to this couple, sulfur has a high theoretical gravimetric capacity of ~1675 mAh g^{-1} and a high theoretical energy density of ~2600 Wh/kg, which are both much substantially higher than commercial cathode materials (for example, ~150 mAh/g for layered oxides and ~170 mAh g^{-1} for $LiFePO_4$).[5-8] Combined with other advantages of sulfur (low toxicity and naturally abundant), lithium sulfur battery is a promising technology for the next generation energy storage and has attractive applications, especially for electric and hybrid vehicles. Despite these numerous advantages, there are still several barriers for the communization of lithium sulfur batteries. The first one is the low electrical conductivity of sulfur ($5x10^{-3}$ S cm^{-1}), the second one is the huge volume expansion during discharge due to the differences in volume densities of Li_2S (1.67 g cm^{-3}) and S (2.03 g cm^{-3}), the third one is the dissolution and diffusion of lithium polysulfide intermediates that are formed during the charge/discharge process. These problems will cause loss of active sulfur, short cycle life, limited specific capacity, and low coulombic efficiency of Li-S batteries.[9-19]

In order to address these barriers, many efforts have been made. According to current papers, a widely pursed approach to solve these problems is to trap polysulfides by using physical barriers and/or polymer absorbers.[1,2,12,15,19-27]As a result, high specific capacities of more than 800 mAh g^{-1} have been reported by many groups.[12,18,19,26-28] However, the commercialized application of the Li-S system hasn't been realized yet, largely because most of the as-prepared electrodes have low areal sulfur loading (typically less than 1 mg cm^{-2}). In addition, to the best of our knowledge, the highest percentage of sulfur in the cathode is still less than 75wt.%.[11,12,15,18,19,27,29]As a result, the areal specific capacities of electrodes fabricated by previous works were mostly under 1.0 mAh cm^{-2}, which greatly decrease the usable capacity of a battery system.[11,15,27,30]

During our recent work on coaxial graphene wrapping of sulfur coated functionalized carbon nanofibers (S-FCNFs) for high performance lithium sulfur batteries,[21] we found that S-FCNFs composites themselves could form binder-free films and showed excellent performance as the cathodes even at both high sulfur content and large areal mass loading (78 wt%, 8 mg cm^{-2}). As a result, lithium sulfur batteries assembled using such cathodes had improved areal specific capacities. They were able to deliver a reversible areal specific capacity of 4.49 mAh cm^{-2} (561 mAh $g^{-1}_{electrode}$) at 0.1C and maintained 1.87 mAh cm^{-2} (234 mAh $g^{-1}_{electrode}$) even after 100 charge-discharge cycles.

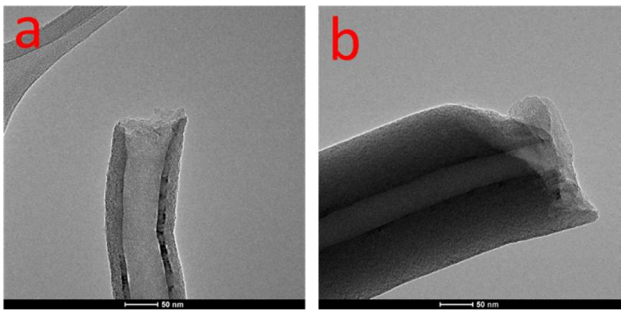

Figure 1. Typical TEM image of (a) FCNFs and (b) S-FCNFs with uniform sulfur coating.

Figure 1 shows typical transmission electron microscopy (TEM) images for FCNFs without (a) and with (b) sulfur coating. As can be seen from these two images a continuously and uniform tubular layer of sulfur was coated on the surface of FCNFs and formed nanomicrosphere structure. The increases in diameter of FCNFs after sulfur coating indicate that the sulfur layer had thicknesses around 45.5 nm. On the basis of thermogravimetric analysis (TGA, Figure 2), about 78wt % S was loaded into S-FCNFs.

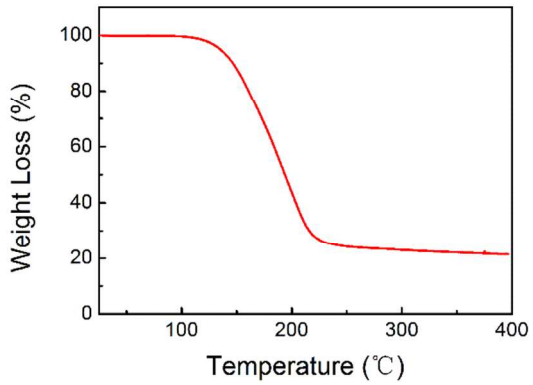

Figure 2. TGA curve of S-FCNFs nanocomposite recorded in N_2 with a heating rate of 10 °C min^{-1}

The cathode for Li-S batteries testing was prepared by pressing a piece of a freestanding film (with typical areal mass loading of 8.0 mg/cm^2) onto a piece of nickel mesh. Unlike the conventional sulfur electrode preparation approach that involves substantial amount of carbon additive and binder, the approach used in this work is binder-free and could reduce the total weight of an electrode. The test batteries were assembled as coin cells (type 2032), with lithium foil used as the negative electrodes. The charge/discharge tests were measured with 0.1C (where 1C corresponds to a current density of 1675 mA g^{-1}) and voltage window of 1.5-3.0V. Typical voltage profiles were shown in Figure 3 and are in good agreement with those reported previously. As can be seen, two plateaus at 2.35V and 2.05V were clearly observed during the discharge process, which correspond to the formation of long-chain lithium polysulfides (Li_2S_x, $4 \le x \le 8$) and short-chain lithium polysulfides (such as Li_2S_2 and Li_2S), respectively. On the basis of the discharge results, a high areal specific discharge capacity of 4.49 mAh cm^{-2} (561 mAh $g^{-1}_{electrode}$) was obtained during the initial discharging process.

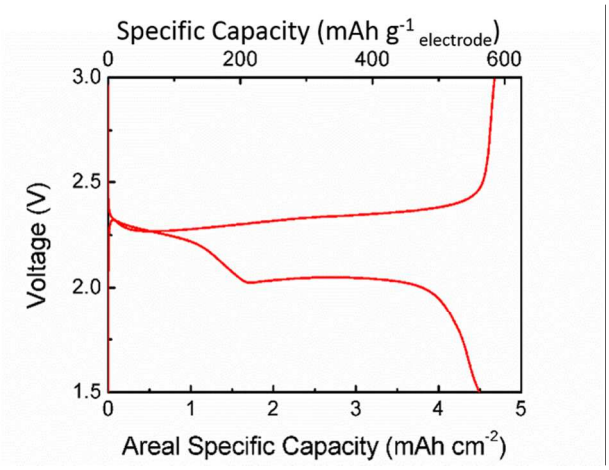

Figure 3. Charge–discharge profile of S-FCNFs electrode at a current density of 0.1 C (168 mA g^{-1})

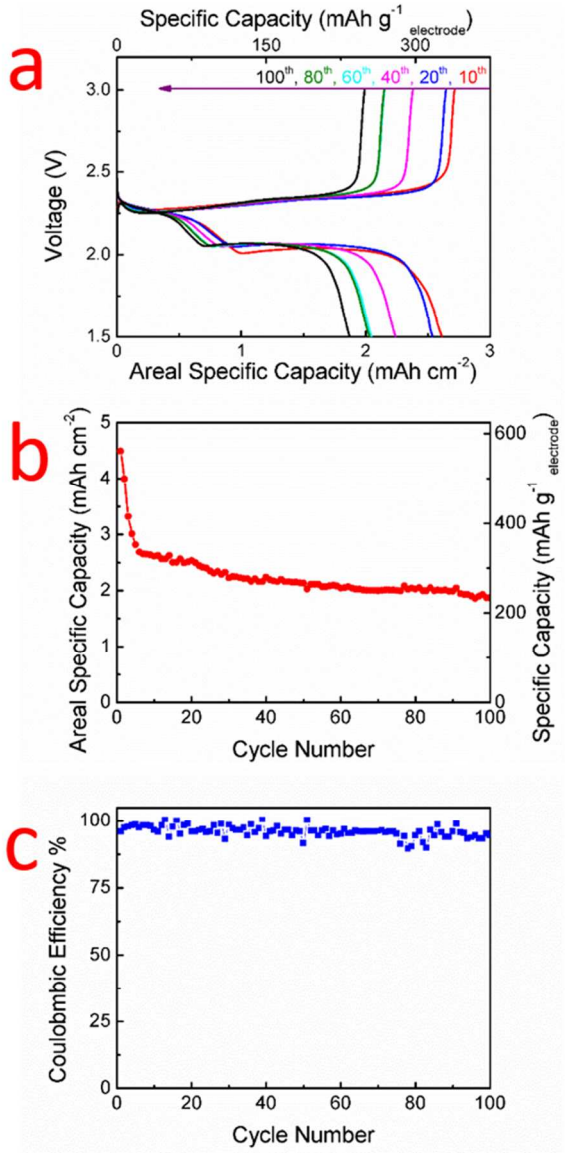

Figure 4 a) Charge-discharge profiles at different cycle numbers as labeled; b) specific capacity and c) coulombic efficiency as a function of cycle numbers for S-FCNFs electrode at a current rate of 0.1 C (168 mA g^{-1})

The electrode exhibited well-overlapped and flat plateaus with continued cycling (Figure 4a), suggesting good stability and reversibility. Figure 4b compares the capacity of the electrode as a function of cycle numbers. At a rate of 0.1C, an initial areal specific discharge capacity of 4.49 mAh cm^{-2} (561 mAh $g^{-1}_{electrode}$) was observed. The discharge capacities had large dropping in the following few cycles due to loss of active sulfur. However, the capacity was quickly stabilized and exhibited a reversible areal specific capacity of 1.87 mA h cm^{-2} (234 mAh $g^{-1}_{electrode}$) after 100 cycles, which could be attributed to the absorption of polysulfides intermediates by the FCNFs. Furthermore, at the same time, as can be seen from the figure 4c, the coulombic efficiency remained at around 98% for all the S-FCNFs cathodes during cycling, showing another promising property of the S-FCNFs cathodes.

Conclusions

In summary, we have successfully synthesized a novel binder-free cathode by effectively coating FCNFs with sulfur. In this S-FCNFs structure, the highly conductively FCNFs act as electrical conductor and accommodating the volume expansion of sulfur during discharge and can absorb polysulfides intermediates in the cathode, which significantly improved cyclic stability of Li-S batteries. As a result, a reversible and satisfied specific capacity of 1.87 mAh cm^{-2} (234 mAh $g^{-1}_{electrode}$) was obtained after 100 cycles at 0.1C, showing promising performance for lithium-sulfur batteries.

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Notes and references

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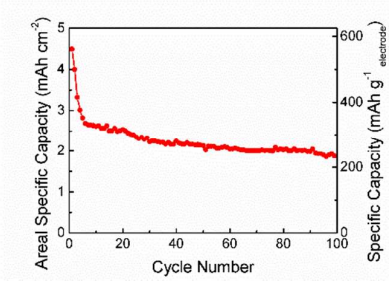

Binder-free cathodes based on sulfur-carbon nanofiber composites was prepared though a liquid process and showed good performance for lithium-sulfur batteries