

# Freestanding CNF/Sulfur-copolymer Cathodes for Li-S Batteries: Effect of Host Porosity on Battery Performance

Lithium-sulfur batteries have been considered as the next generation energy storage devices due to their high energy density of  $\sim 2600$  Wh/kg. However, the challenge of developing Li-S with long-term cycling stability still exists due to shuttling of intermediate polysulfides. Recently, a class of sulfur-rich copolymers has shown several advantages compared to their sulfur counterpart owing to the (a) presence of C-S bond, which can chemically bind lithium polysulfides and suppress shuttle effect, and (b) enhanced  $\text{Li}^+$  transport and electronic conductivity due to conjugated structure. However, the use of such active material is in its nascent stage and the role (if any) of the conductive host material porosity in enhancing the polysulfide suppressing functionality of such chemically-bound active material is unclear.

In our work, we use freestanding, binder and current collector-free electrospun nanofibers as a platform to understand the role of host porosity in sulfur-rich copolymer-based Li-S batteries. The sulfur rich copolymer (SDIB) was synthesized using 1,3-diisopropenylbenzene (DIB) and sulfur (S) in a weight ratio of 20:80 (SDIB20) at  $185^\circ\text{C}$ . To study the effect of porosity of CNFs on the cycling and capacity of polymerized sulfur based Li-S cells, two different porous samples were designed using PAN: Nafion weight ratio as 4:6 (mi-CNF) and 3:7 (me-CNF) followed by carbonization. The BET results showed that mi-CNF exhibited slightly higher micropore volume ( $0.315\text{ cm}^3/\text{g}$  vs.  $0.271\text{ cm}^3/\text{g}$ ) and substantially lower mesopore volume ( $0.192\text{ cm}^3/\text{g}$  vs.  $0.502\text{ cm}^3/\text{g}$ ) and size ( $<4.5\text{ nm}$  vs.  $<7\text{ nm}$ ) than me-CNF. A heat-press assisted ultra-rapid melt diffusion technique (2 minutes) developed in our group was used to incorporate SDIB20 into mi-CNFs and me-CNFs. The as-prepared free-standing SDIB/CNF cathodes with final sulfur loading of  $1.1\text{--}1.3\text{ mg}/\text{cm}^2$  (45–50 wt%) were used in Li-S cells. When mi-CNF was used as a host material, the capacity was stabilized to  $577\text{ mAh}/\text{g}$  within 50 cycles and remained stable up to 600 cycles with a small capacity decay rate of 0.046% per cycle along with coulombic efficiency  $>98\%$  (Figure 1a). On the other hand, SDIB/me-CNF cathodes delivered a stable capacity of  $\sim 600\text{ mAh}/\text{g}$  with negligible decay. However, the stability only lasted for 145 cycles (figure 1a inset). Additionally, the control/reference cell with sulfur as the active material (mi-CNF as host) showed a rapid decay in capacity in less than 100 cycles (Figure 1a) suggesting a clear advantage of sulfur-rich copolymers as active material (over pure loose sulfur) due to the presence of C-S bond leading to chemically bound insoluble polysulfides. We hypothesize that porosity of the cathode host still plays a significant role as loose soluble  $\text{-S}_n\text{-}$  chains start to gradually emerge from S-S bond breakage in C-S- $\text{S}_n\text{-S-C}$  over the course of cycling. This slow polysulfide formation rate in SDIB/mi-CNF results in effective polysulfide adsorption by micropores in SDIB/mi-CNF cathodes leading to substantial enhancement of cycling stability. We believe that as the pore size and volume increase in me-CNFs, the electrolyte accessibility enhances, which results in relatively higher capacity. However, this also potentially

leads to easier escape of polysulfides and early capacity fade in SDIB/me-CNFs based Li-S cells. We calculated the effective capacity of our SDIB/me-CNF cathode and compared it to other works on sulfur rich copolymers in powdered nanostructure (Fig. 1b) at C/2 (presented in red) and C/5 rates (presented in black). To calculate the effective capacity, the discharge capacity of sulfur after 100 cycles is adjusted based on the total weight of the electrode (i.e., current collector, binder, sulfur and conductive material). The effective capacity analysis clearly manifests the advantages of using current-collector and binder-free electrospun CNFs as a host matrix for SDIB.

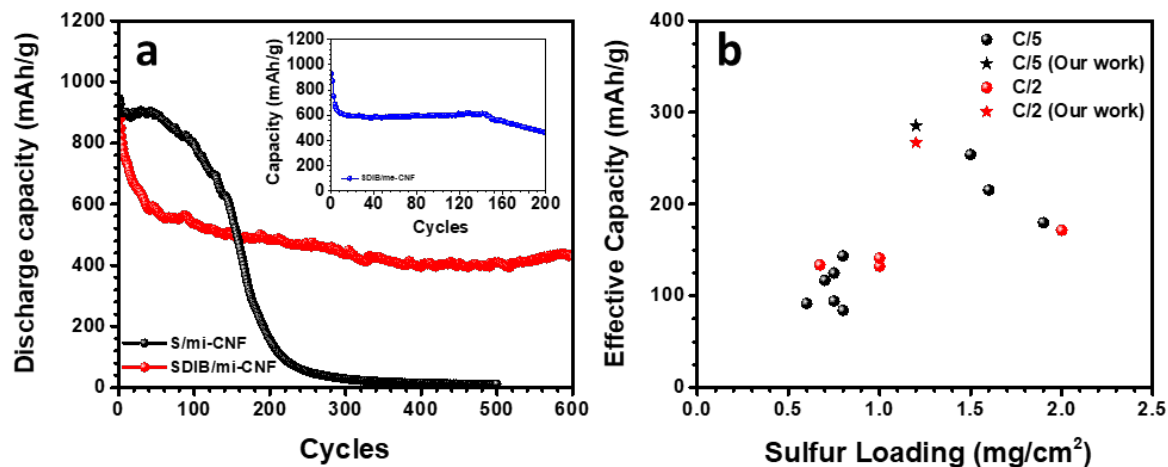


Figure 1. (a) Cycling stability comparison between the SDIB/mi-CNF and S/mi-CNF batteries and SDIB/me-CNF (inset) at C/2 rate (b) Effective discharge capacity after 100 cycles accounting for total electrode weight in the cathodes reported in literature compared to our work at C/2 and C/5