

Li₂S Encapsulated by Nitrogen-Doped Carbon for Lithium Sulfur Batteries

Lin Chen ^{a,b}, Yuzi Liu ^c, Maziar Ashuri ^{a,b}, Caihong Liu ^{a,b} and Leon L. Shaw ^{a,b,*}

^a Wanger Institute for Sustainable Energy Research

^b Department of Mechanical, Materials and Aerospace Engineering
Illinois Institute of Technology, Illinois, USA

^c Center for Nanoscale Materials
Argonne National Laboratory, Illinois, USA

Supplementary Information

1. On the First Charge Voltage Profile

There is difference in the first charge voltage profile between the uncoated and carbon coated cells although the first activation charge is a transient process. As shown in Figure S1, both types of cells exhibit an initial potential hump at the early stage of the activation charging curve. This potential hump has been attributed to the energy barrier for nucleation of polysulfides.^{R1} Furthermore, the height of the potential hump is found to be associated with the thermodynamic barrier for nucleation as well as the kinetic factors, particularly the charge transfer overpotential associated with the formation of polysulfides.^{R1} The long flat plateau (Figure S1(b)) after the initial potential hump is related to conversion of Li₂S to lower-order polysulfides, then to higher-order polysulfides, and finally to elemental sulfur.^{R1} We note that the carbon-coated cell has a lower potential barrier for nucleation than most of the uncoated cells (as shown in Figure S1(a)), indicating the benefit of the nitrogen-doped carbon coating in reducing the charge transfer overpotential. In contrast, the uncoated cells not only have higher potential barriers in most cases, but also exhibit several different behaviors after the initial potential hump. These different behaviors include a long flat plateau (Figure S1(b)) and a long process with a gradual increase in the voltage (Figure S1(a)).

We ascribe the different charge behaviors of the uncoated cells to the statistically random processes of ball milling of Li₂S with ~4.5 vol% CB and subsequent mixing of CB with the ball milled Li₂S during cathode fabrication. As schematically shown in Figure 1b (see the article), most of the 4.5vol% CB will be embedded inside Li₂S particles during ball milling, but some may expose to the surface of Li₂S particles. We hypothesize that when many of the CB particles

added during cathode fabrication are in contact with those CB embedded in Li_2S particles but with exposure to the surface, the nucleation of polysulfides will be easy and the charge transfer overpotential will be low. In other words, under this situation the overpotential required for nucleation is lower for the uncoated cells than that for the carbon coated cells (see below for additional explanation of this phenomenon). As a result, the activation voltage profiles of Figure S1(b) appear. However, if many of the CB particles added during cathode fabrication are in contact with the surface of Li_2S particles directly, then the energy barrier for nucleation of polysulfides will be high and the charge transfer overpotential will be large. As a result, the activation curve of Figure S1(a) appears. Because of the random nature of the mixing and ball milling processes, the uncoated cells sometime display the first charge behavior of Figure S1(b), while in most cases the uncoated cells exhibit the first charge behavior of Figure S1(a).

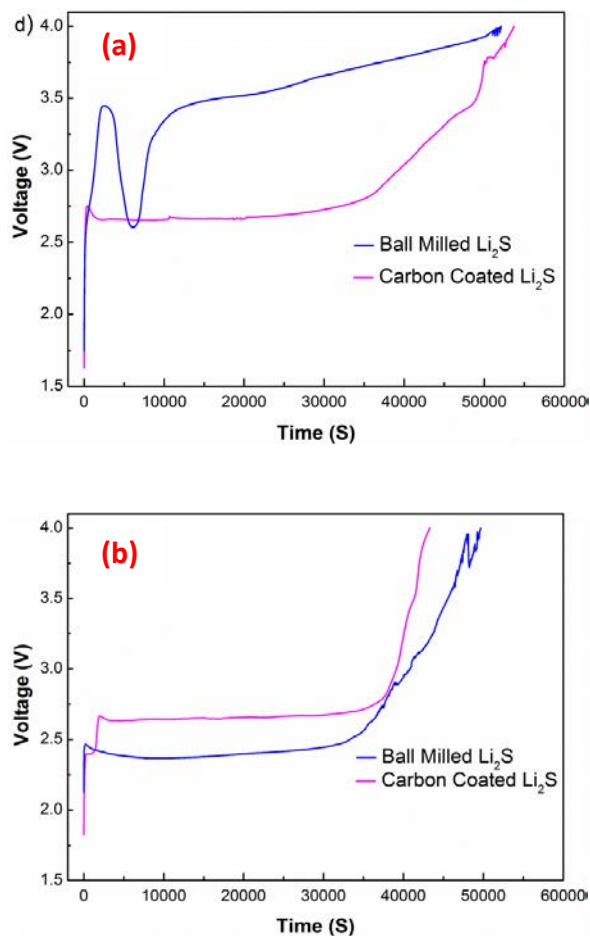


Figure S1. Voltage profiles of the first galvanostatic charge of ball milled Li_2S and carbon coated Li_2S cells as indicated with a C/20 rate. (a) and (b) show that ball milled Li_2S cells display two significantly different voltage profiles, whereas carbon coated Li_2S cells exhibit much consistent voltage profiles.

It is important to stress that the ball-milling embedded CB with exposure to the surface of Li_2S particles is more effective in reducing the charge transfer overpotential and making nucleation of polysulfides easier than the CB added during cathode fabrication because the contact between Li_2S and the embedded CB is intimate (due to compression during high-energy ball milling). In contrast, the contact between the CB added during cathode fabrication and the surface of Li_2S particles is relatively loose and may have a PVDF thin film between CB and Li_2S . This makes the CB added during cathode fabrication less effective in reducing the charge transfer overpotential associated with the formation of polysulfides. In addition, the gradually increased voltage profile of the uncoated cell in Figure S1(a) after the initial potential drop suggests the presence of significant energy barriers for repeated nucleation of polysulfides and/or high charge transfer overpotential associated with the formation of polysulfides. This phenomenon is different from the carbon coated cells shown in Figure S1 and the observations reported in an earlier study.^{R1} Additional studies are needed in the future to understand this unusual phenomenon.

The carbon coated cells, in sharp contrast, display much more consistent behavior, i.e., a lower initial potential hump followed by a long flat plateau, as shown in Figure S1(a) and (b). This more consistent behavior is due to the presence of a nitrogen-doped carbon coating on the surface of *all* Li_2S particles, as schematically shown in Figure 1d. Clearly, this coating not only increases the utilization of Li_2S in the cathode (Figure 8), but also makes nucleation of polysulfides easier for all Li_2S particles and reduces the associated charge transfer overpotential substantially (Figure S1).

Finally, it is worthy of emphasizing that the carbon coated cells always display higher specific capacities than the uncoated cells regardless of their first charge potential profiles. This is true even for the case of Figure S1(b) where the uncoated cell displays a lower energy barrier for the nucleation process than the carbon coated counterpart. In spite of its lower energy barrier for the nucleation process, the uncoated cell has a lower specific capacity because Figure S1 does not tell us what percentage of Li_2S has participated in redox reactions during charge/discharge cycles. It only tells us what cell voltage is needed to activate the cell. Indeed, for this particular uncoated cell shown in Figure S1(b), the first charge specific capacity is 897.8 mAh/g (the activation process), and the first discharge specific capacity is 632.4 mAh/g. This first discharge specific capacity is similar to the data of the uncoated cell we have presented in

Figure 9 and also similar to the uncoated cell shown in Figure S1(a) which has the first discharge specific capacity of 640.1 mAh/g.

2. Discussion of the Effect of the Carbon Coating on Capacity Retention

Although Figure 9 shows that the two cells have a very similar capacity fading rate, it may not mean that the carbon coating has no effect on dissolution of polysulfides *at all*, as explained below. In a previous study,^{R2} it has been shown that the capacity fading can be reduced by adding soluble polysulfides to the electrolyte. Further, the higher concentration of the soluble polysulfides in the electrolyte, the lower capacity fading rate will be,^{R2} suggesting that a high concentration of the soluble polysulfides in the electrolyte can slow down the dissolution of soluble polysulfides into the electrolyte during charge/discharge cycles.

If there is significant dissolution of polysulfides in the first charge process for the uncoated cells, then the concentration of polysulfides in the electrolyte will be higher for the uncoated cells than that for the carbon coated cells. As a result, there will be a smaller driving force for polysulfide dissolution in the uncoated cells because of its higher concentration of polysulfides in the electrolyte. Since the carbon coated cells have a higher driving force for polysulfide dissolution (because of its lower polysulfide concentration in the electrolyte after the first charge process), it would display a faster capacity fading rate than the uncoated cells. However, we did not observe this trend, suggesting that the carbon coating has some effect on impeding polysulfide dissolution.

References:

R1: Y. Yang, G. Zheng, S. Misra, J. Nelson, M. F. Toney and Y. Cui, *J. Am. Chem. Soc.*, 2012, **134**, 15387.

R2: S. Chen, F. Dai, M. L. Gordin, and D. Wang, *RSC Adv.*, 2013, **3**, 3540.