Free-Standing Carbon Nanofoam Papers Vapor-Infiltrated with Sulfur as Lithium-Sulfur Battery Cathodes

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Abstract: Sulfur-based battery systems offer the potential to achieve high practical energy densities without the need for expensive and exotic material components. However, low electronic conductivity and tendencies toward redox shuttling of soluble polysulfide species in alkali-metal-sulfur systems inhibit the practical capacity of these batteries, which often falls short of achieving the 1675 mAh g^{-1} theoretical specific capacity of sulfur. In addition to the gravimetric aspect of these electrodes, areal and volumetric capacities must be considered for practical applications of such systems. To address these issues, we investigate the use of a highly scalable porous carbon nanofoam paper (CNFP) scaffold that has highly tunable pore size distributions, developed at the U.S. Naval Research Laboratory. A facile vapor deposition technique used to deposit sulfur on these CNFPs ensures that the electrode is binder-free. These sulfur-loaded CNFPs were examined via electrochemical cycling in a Lithium-Sulfur system, and the results of this study have indicated that an equilibrium between the pore size and sulfur mass loading yields the optimal performance of these materials with regards to the mass, areal, and volumetric capacities. Additionally, the CNFP scaffold has been demonstrated to be robust enough that it can function in pouch cell geometries without the need for an aluminum current collector, effectively reducing the amount of materials required for fabrication and overall mass of the cell.

Introduction

Although the past couple decades have seen a dramatic increase in the number of small consumer products powered by Li-ion batteries, many larger items, most notably electric vehicles, remain out-of-budget for the average consumer largely due to the high cost of the material components of the battery systems used to power them. There are three main factors hindering the widespread proliferation of these battery systems: availability of critical materials, expense of those materials, and limitations to the theoretical capacity of certain Li-based systems. Common Li-ion cathodes are composed of materials such as lithium iron phosphate (LFP) or mixed metal oxides that include metals like nickel, manganese, and cobalt (NMC). Though NMC has a higher energy density than LFP, expensive, rare, and geographically localized components like cobalt make forward-thinking consumers wary of placing too much stock in this type of cathode. And while its relative abundance and low cost make LFP seem an attractive substitute, the theoretical capacity of these electrodes is almost half that of NMC electrodes.

An alternative to the intercalation-based energy storage employed by Li-ion batteries is the conversion-based Lithium-Sulfur (Li-S) battery. The simple, widely available, non-toxic, and inexpensive materials used in this system can achieve a theoretical 1675 mAh g^{-1}, approximately an order of magnitude higher than that of LFP. [1] However, “polysulfide shuttling,” where soluble polysulfide species dissolve into the electrolyte, effectively diminishes the coulombic efficiency of the cell, thus reducing cycle life and preventing the system from reaching its full capacity. [1] [2] To mitigate this shuttling effect, many studies focus on the material properties of the sulfur host, which is critical to effective performance of the sulfur electrode. Due to their high surface area, low mass, and moderately high conductivity, carbon aerogels or nanofoams serve as effective hosts for the active sulfur material, and it has been shown that sulfur infiltration of these materials followed by formation of a composite electrode with a polymer binder form capable Li-S electrodes. [3] [4]

Here, we demonstrate the unique capabilities of the highly versatile carbon nanofoam paper (CNFP) developed at the U.S. Naval Research Laboratory, which contains a porous carbon aerogel network supported by a robust scaffold of carbon fiber paper, thus enabling the CNFP to act as a free-standing electrode without binders or additives. The pore sizes of the nanofoam are tunable, making CNFPs highly adaptive to system optimization, and they have been proven an effective sulfur host in Li-S battery systems. In this work, we demonstrate that these papers have the potential to be used on a practical level, such that higher voltages and larger format cells are possible with CNFPs.

Experimental details

CNFP fabrication

The CNFPs used in this study were synthesized via a resorcinol-formaldehyde (RF) sol–gel process as previously described [5] [6] that allows for control of the pore size distribution, making these papers highly tunable for different applications. In short, resorcinol and formaldehyde were mixed in a 1:2 part ratio in water with Na_2CO_3 to create the sol precursor. Commercial carbon fiber paper (Lydall, 90 µm thick, 0.2g cm^{-3} density) was soaked in the sol precursor under vacuum, then the paper was aged and heated to ~90°C. The sheets were extracted, dried, and pyrolyzed under argon at 1000°C for 2h at a 1°C/min ramp rate.

The carbon fiber paper scaffold of the CNFPs makes this material robust and easy to work with. Coin cell electrodes can be cut from the CNFPs, or the full sheet can be used for pouch cell geometries. Figure 1a demonstrates both types of CNFP electrode shapes.

Sulfur infiltration

Once the desired electrode geometry was determined and prepared, the CNFP was infiltrated with sulfur using a vapor technique [7] [8]. The electrodes were put into a Teflon infiltration chamber on a 316 stainless steel mesh above a well containing sulfur powder. The chamber was sealed and placed in an oven at 175°C for 2h, then allowed to cool for approx. 30 minutes. The electrodes were massed before and after infiltration to determine sulfur loading.

EDS analysis on a cross section of a sulfur infiltrated CNFP (S@CNFP) electrode shows that the sulfur is deposited evenly throughout the depth of the sample, and that the sulfur preferentially deposits within the carbon nanofoam pores instead of on the larger carbon fiber features.

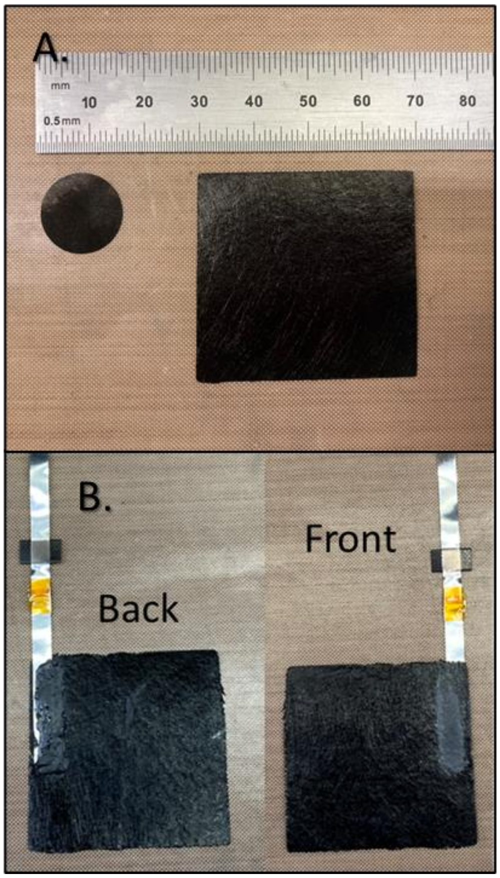

Figure 1. CNFP electrodes in different shapes. (A) The stiff carbon fiber framework allows the CNFP to be cut into different shapes and used for any number of cell geometries. (B) For use in the pouch cell, an aluminum tab can be glued directly to the CNFP without the need for a metal current collector.

Electrochemical testing

Standard 2032 coin cells were fabricated using Hohsen coin cell parts and an automated Hohsen 2032 coin cell crimper for characterization of the S@CNFP electrodes versus a Li metal (MTI) electrode with an Entek Gold separator and 1M LiTFSI and 0.2M $LiNO_3$ in DOL/DME (50/50) electrolyte.

The coin cell assembly does not allow for demonstration of the current-collector-free capabilities of CNFP; however, pouch cells were also fabricated to exhibit the ability of the CNFP host material to act as cathode and current collector simultaneously. Aluminum pouch cell tabs were adhered to a small portion of the CNFP electrode using conductive carbon glue (Fig. 1b). Pouch cells were fabricated using Li metal (MTI) on a copper current collector, an Entek Gold separator, and the S@CNFP electrode with tab. During assembly, the pouch cell was flooded with ~500 µL of electrolyte.

Electrochemical cycling was performed on a ParSTAT multichannel potentiostat PMC1000 under constant current conditions at 0.1C from 1.8 V to 2.6 V for the single pouch cell and 6.0 V to 7.8 V for the coin cells in series.

Results

Ongoing studies will determine the optimal CNPF pore structure for the Li-S system, but preliminary results show that when cycled at a rate of 0.1C, this material can enable stable cycling capacities over 300 mAh g^{-1} with regards to the full electrode. While these data indicate that there is much room for improvement with the system, this cathodic capacity is already greater than the theoretical capacity of NMC (~275 mAh g^{-1}). Additionally, although NMC has the advantage in terms of specific energy because its average discharge voltage is much higher than that of a Li-S cell, one facile method to increase the voltage of a cell and thus improve the Wh kg^{-1} of a system is to place two or more cells in series.

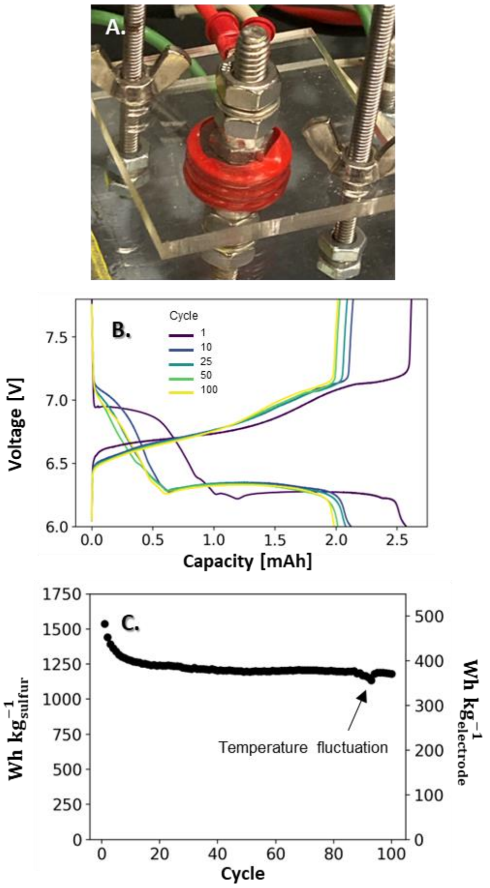

Figure 2. Three S@CNFP coin cells in series. (A) Coin cells can be placed in series to produce a high voltage Li-S system. Here, three coin cells are stacked to generate a system capable of >7.0 V. (B) Voltage profiles at various cycles and (C) cycling capacity are also shown.

Increasing the voltage of the Li-S system was achieved by putting three S@CNFP coin cells in series (shown in Figure 2a), raising the maximum voltage of the system from 2.6 V to >7.0 V. Figure 2 not only shows the cycling stability of the system, where after the first initial capacity loss the capacity remains stable from cycle 10 through cycle 100 (voltage profiles in Fig. 2b), it also shows the remarkable specific energy of the system, which can achieve ~1250 Wh kg^{-1} with respect to sulfur, or almost 400 Wh kg^{-1} when the whole electrode is taken into account (Fig. 2c). This is a much higher gravimetric energy density than the current benchmark for commercial Li-ion technologies, which achieve approximately 240 Wh kg^{-1} with NMC electrodes.

In addition to cell voltage, total capacity of the cell is an important metric to improve. While a modular approach of placing multiple cells in parallel would serve to increase the overall capacity, perhaps a more efficient means of producing a higher capacity

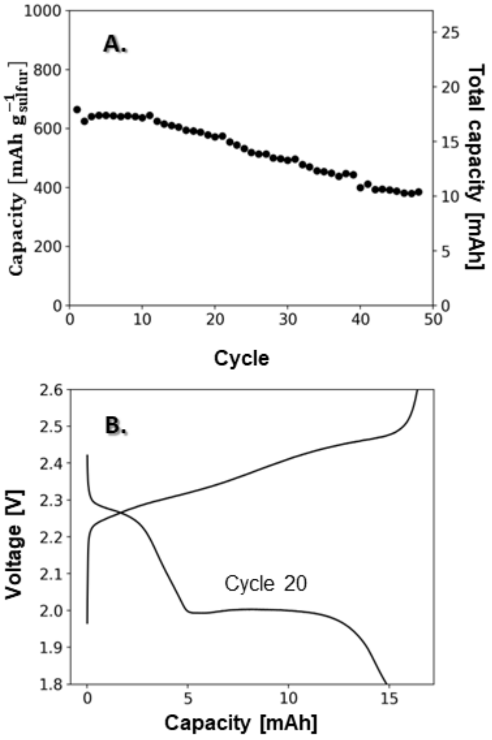

Figure 3. Electrochemical data for a pouch cell fabricated from a full sheet of S@CNFP. No metallic cathodic current collector was used in this cell. (A) Cycling data for ~50 cycles and (B) a representative voltage profile taken from cycle 20 detail the performance of the pouch cell.

Li-S system is simply to increase the size of the S@CNFP electrode. These cathodes were prepared for pouch cells by infiltrating the full CNFP sheet (~16 cm^2) in the same Teflon chamber as the coin cell electrodes. Even though the electrodes are ~10x the area of the coin cell electrodes, this process was simple and effective when scaling up to the larger electrode.

Figure 3a displays the cycling performance of the pouch cell fabricated from the S@CNFP electrode. Though the initial capacity of the pouch cell scaled well with the increase in electrode size (from ~2 mAh for a 1.77 cm^2 coin cell electrode to ~18 mAh for the 16 cm^2 pouch cell electrode), it declined over 50 cycles to approximately half of its initial value. Despite this diminution in performance, the similarity of the charge-discharge profile of this cell (Figure 3b) to a typical Li-S cell establishes the ability of the S@CNFP to function sans current collector. This feature, as well as the lack of binders and conductive additives, are just a few of the more beneficial aspects of the CNFP material, which has been demonstrated to be a capable sulfur host material for Li-S batteries. The material efficiency of CNFPs serves to improve overall gravimetric energy density and reduce the material needs and costs of the cell.

Conclusions

The simplicity of the Li-S system makes it attractive for future batteries, and here we show how sulfur-infiltrated CNFPs can provide high energy systems efficiently and with materials that incur a much lower cost than other Li-based systems. The high voltage system comprised of three coin cells in series serves as a proof-of-concept that the S@CNFP material can provide realistic gravimetric energy densities needed to power large commercial devices. Additionally, the fabrication of a larger capacity pouch cell without a metallic current collector shows the capability to scale both the CNFP material and the integrated Li-S@CNFP system such that it would be a viable, lightweight, and inexpensive option for commercial batteries.

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