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EERE 355: Federal Assistance Reporting Checklist (FARC)

Statically and Dynamically Stable Lithium-sulfur Batteries

Final Scientific-Technical Report (RD&D Projects)

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Section I. Executive Summary:

The commercialization of lithium-sulfur (Li-S) batteries is hampered by several intrinsic materials challenges: low electronic and ionic conductivity of the active material, severe polysulfide migration from the cathode to the anode, and instability of the Li-metal anode. The poor conductivity limits the electrochemical utilization of the active material and often necessitates a high content of electrochemically inactive, conductive carbon or functional polymers in the cathode region, which lowers the practical energy density. The polysulfide migration causes static and dynamic instabilities with high capacity fade, poisoning of the Li-metal surface, and poor cycling efficiency, hindering the practical viability of Li-S batteries. Recently, it is becoming obvious that the development of practically viable high-energy-density Li-S batteries is determined largely by attaining the necessary cell-design parameters. The essential extrinsic parameters include a sulfur loading of at least 5 mg cm^{-2}, a sulfur content of over 65 wt.%, and a low electrolyte/sulfur (E/S) ratio of less than 11 μL mg^{-1}. To overcome the above challenges, our group has demonstrated in this project that innovations in polysulfide-filter-coated separators and advanced electrode substrates greatly enhance the electrochemical utilization and efficiency with reasonably high sulfur loadings and low E/S ratios in the cells. This is because Li-S batteries involve conversion reactions unlike the insertion-reaction electrodes in commercial Li-ion batteries, so cell components/designs directly borrowed from Li-ion batteries may need new architectures or chemical/physical characteristics to be adapted to sulfur cathodes. Our cell-component design provides the fabricated Li-S cells with enhanced electrochemical performance: high utilization of the active material, extended cycle life, and good storage properties. More importantly, these custom cell configurations allow the cells to employ the easily prepared sulfur cathodes with a high sulfur loading (up to 60 mg cm^{-2}) and a high sulfur content (80 wt.%) with a low E/S ratio of as low as 4.0 μL mg^{-1}. Our progress illustrates that the approaches presented and developed in this project offer practically viable solutions for the Li-S technology development.

Section II. Accomplishments Vs. Milestones:

Tables 1 – 3 summarize the objectives/milestones in this project and the corresponding accomplishments. We have accomplished all of the milestones. In several cases, we have achieved much more progress, such as reducing the self-discharge effect of sulfur cathodes (Year 2), improving the amount of sulfur in cathodes (Years 2,3), and reducing the E/S ratio (Years 2,3).

Table 1. Milestones and accomplishments obtained in Year 1

Objectives for Year 1		
MM/YY	Objectives (Milestones)	Accomplishments
Dec. / 2015	Establish materials chemistry database for the coating materials	We established a materials chemistry database, investigating the physical and chemical characteristics of 12 coating materials with four different morphologies.
Mar. / 2016	Establish fabrication database for the PS-filter-coated separator	We developed the corresponding fabrication methods for preparing lightweight, flexible PS-filter-coated separators, including binder-supporting, carbon-nanotube (CNT)-supporting, and layer-by-layer (LBL) methods.
Jun. / 2016	Assess capacity fade and self-discharge	The LBL-CNF-coated separators enable the cells to attain a low capacity fade during cycling (0.11% per cycle for 500 cycles) and low self-discharge effect during resting (0.3% per day after 120 day).
Sep. / 2016	Improve the energy density (target areal capacity of above 4 mAh cm^{-2})	The cells fabricated with the LBL-CNF-coated separators enable the statically and dynamically stable Li-S batteries to have a high areal capacity of 4.3 mA h cm^{-2}, which is higher that the target value.

Table 2. Milestones and accomplishments obtained in Year 2

Objectives for Year 2		
Month / Year	Objectives (Milestones)	Accomplishments
Dec. / 2016	Improve the dynamic electrochemical performances (*i.e.*, high electrochemical utilization of 80 – 90 % and long cycle life of 500 cycles) by inserting PS-filter-coated separators	The LBL-CNF-coated separators demonstrate enhanced dynamic performances, exhibiting high electrochemical utilization of sulfur at 80 % and a high areal capacity of above 4.3 mA h cm^{-2}. The corresponding cells also attain long-term cycle stability for over 500 cycles with a low capacity-fade rate.
Mar. / 2017	Improve the static electrochemical performances (*i.e.*, low self-discharge rate of < 0.5% per day and reversible cycle stability) by inserting PS-filter-coated separators	The LBL-CNF-coated separators show excellent static performances, achieving a low self-discharge rate of only 0.14% per day and a long shelf-life of one year. The cell rested for 365 days keep a high capacity with a low capacity-fade rate of 0.10% per cycle for 100 cycles. The static performances are better than the target values.
Jun. / 2017	Increase the sulfur loading of the cells to 5 mg cm^{-2} with sulfur content of 70 wt.%	We have advanced the cathode configuration and demonstrated a carbon-cotton cathode featuring a high sulfur loading (30 mg cm^{-2}) and content (80 wt. %) at a low E/S ratio of 6.8 µL mg^{-1}. The developed cathode achieves higher sulfur loading than the milestones.
Sep. / 2017	Fabricate cells with high sulfur content/loading and good electrochemical stability	The carbon-cotton cathode containing a high amount of sulfur delivers a high charge-storage capacity of 1,173 mAh g^{-1} with a high capacity retention of 70% after 100 cycles and a low self-discharge rate of just 0.12% per day after storing for 60 days. The effective areal capacity and energy density are 36 mAh cm^{-2} and 72 mW cm^{-2}, respectively. The developed high-loading sulfur cathode achieves better electrochemical stability during cycling and resting.

Table 3. Milestones and accomplishments obtained in Year 3

Objectives for Year 3		
Month / Year	Objectives (Milestones)	Accomplishments
Dec. / 2017	Introduce anode stabilization techniques for the Li-S cells using Li-metal anode	We applied a kimwipe (KW) paper on the Li-metal anode to realize a dendrite-free surface. The KW-stabilization layer physically creates a uniform redeposition layer so that the smooth Li-anode surface demonstrates an improved electrochemical stability.
Mar. / 2018	Introduce Li_2S cathodes in Li-S cells	We demonstrated a shell-shaped carbon architecture for developing pure Li_2S cathodes with superior cell-design parameters (*i.e.*, the highest amount of sulfur and the lowest electrolyte volume) and excellent electrochemical characteristics (*i.e.*, a high capacity retention of 90% and long cycle life of over 200 cycles). We presented the Li_2S cathodes that have the highest cell-assembly specifications and the best cycle stability.
Jun. / 2018	Fabricate 4+ mg cm^{-2} sulfur cathodes in coin cell prototypes and pouch cells	An optimized graphene-coated-carbon-cotton cathode displays a high sulfur loading and content of 57.6 mg cm^{-2} and 75 wt%, respectively. At a remarkably low E/S ratio of 4.2 µL mg^{-1}, the cell exhibits a high areal capacity and energy density of 31 mAh cm^{-2} and 66 mWh cm^{-2}, respectively. We reported a sulfur cathode with the highest sulfur loading ever.
Sep. / 2018	Couple the proposed technology with additional costs and environmental impact assessment	In order to realize practically viable Li-S cells, we developed Li-S pouch cells with a high sulfur content and loading (*i.e.*, 65 wt.% and 6 mg cm^{-2} sulfur in a size of 47.8 mm x 81.5 mm) and optimized the cells with low-cost materials and fabrication methods.

Section III. Summary of project activities:

Project activity I: Materials chemistry database (Y1Q1 – Y1Q2)

The electrochemical stability of the Li-S cells could be improved by fabricating the cells with PS-filter-coated separators and/or the porous cathode substrates. Thus, it was instructive to initiate this project with an understanding of the materials characteristics and by designing the corresponding fabrication parameters. Therefore, we investigated the physical and chemical characteristics of the materials for creating a material chemistry database in Year 1. We selected four major carbon materials categorized by their different morphologies: (i) spherical carbons, (ii) carbon nanofibers (CNFs), (iii) graphene, and (iv) carbon nanotubes (CNTs). The materials chemistry database allowed for the establishment of the PS-filter-coated separators in Years 1 – 3 and the cathode substrate in Years 2 – 3 with light weight and high mechanical strength.

12 carbon materials were analyzed and categorized into four main groups by their unique morphologies: spherical, fibrous, tubular, and flaky carbon materials. The first group includes spherical carbons with nonporous and porous structures (micro-/meso-/macro-porous structures). The second group includes carbon materials with different morphologies: carbon nanofibers (CNFs), carbon nanotubes (CNTs), and graphene (G). **Table 4** summarizes their materials chemistry, porosity, and the coating-method study for preparing the PS-filter-coated separators. The most interesting results are that we have developed three modified coating methods for preparing smooth and robust carbon coatings onto a polypropylene membrane (Celgard 2500): (i) tape-casting method coupled with binders, (ii) vacuum-filtration process coupled with carbon nanotube (CNT), and (iii) layer-by-layer (LBL) coating configuration. These approaches provide the coatings with strong adhesion in between the carbon materials and with the polypropylene membranes.

Table 4. Material chemistry database

(Coating material): coating methods	Carbon sample	Surface area [m^2 g^{-1}]	Pore volume [cm^3 g^{-1}]	Pore size [nm]	Microporosity	
					Surface area [m^2 g^{-1}]	Pore volume [cm^3 g^{-1}]
(i-a): T&B, V*	Acetylene Black	82	0.29	14	0	0
(i-a): T&B, V*	Super P Carbon	89	0.44	19	0	0
(i-a): T&B, V*	Carbon Black (Lampblack)	30	0.22	29	0	0
(i-b): T&B, V*	Carbon Black (Vulcan)	298	1.03	14	85	0.04
(i-b): T&B, V*	Activated Carbon	732	0.53	3	585	0.31
(i-b): T&B, V*	Activated Charcoal	1,002	0.70	3	754	0.40
(i-b): T&B, V*	Microporous Carbon	1,321	3.62	10	753	0.41
(i-b): T&B, V*	Ketjen Black	950	2.92	12	58	0.02
(ii): LBL-V	CNF	26	0.09	14	0	0
(iii): LBL-V	CNT	40	0.20	36	0	0
(iv): T, B, V	R-GO	272	0.57	2	0	0
(iv): T, B, V	EO-GO	251	0.43	7	36	0.017
Coating materials: (i) spherical carbons: (i-a) nonporous carbon and (i-b) porous carbon, (ii) carbon nanofibers (CNF), (iii) carbon nanotubes (CNT), and (iv) graphene: reduced graphene oxide (R-GO) and edge-oxidized graphene oxide (EO-GO) Coating methods: (T) tape-casting, (B) binder-supporting, (V*) vacuum-filtration process with carbon nanotube (CNT) as the framework, and (LBL-V) layer-by-layer vacuum-filtration process						

Project activity II: Statically and dynamically stable lithium-sulfur batteries (Y1Q3 – Y2Q2)

According to the scientific insights obtained in Project activity I, we developed LBL coated separators with nonporous CNFs as the coating materials. Three LBL nonporous CNF-coated separators prepared by the newly-developed vacuum filtration are termed as CNF#1 (0.1 mg cm^{-2} CNF coating), CNF#2 (0.2 mg cm^{-2} CNF coating), and CNF#3 (0.4 mg cm^{-2} CNF coating). The nonporous CNFs had a low surface area of 26 m^2 g^{-1} and no micropore absorption behavior. The Celgard membrane that is used as the substrate in our case and as the conventional separator in the Li-S literature weighs 1.0 mg cm^{-2} and has a thickness of 25 μm. The cells fabricated with the thin-film CNF#3-coated separators displayed a high peak capacity of 1,329 mA h g^{-1} (areal capacity: 4.3 mA h cm^{-2}) at C/10 rate and a high reversible capacity of 529 mA h g^{-1} after 500 cycles (**Figure 1a**). The enhanced electrochemical utilization and stability were based on the use of pure sulfur directly as the active material. The pure sulfur cathodes used in the tested cells were fixed with a high sulfur loading of 3.4 mg cm^{-2} and a high sulfur content of 70 wt. %.

Moreover, the LBL-CNF-coated separators provided the Li-S cells with an extended cell shelf-life of one year, which is the longest cell-storage period reported for Li-S cells in the literature (**Figure 1b**). In this extended low self-discharge demonstration, the cells fabricated with the LBL-CNF-coated separators retained 50% of the initial capacity after storing for 1 year and exhibited a low self-discharge rate of only 0.14% per day, much lower than the target value of less than 0.50% per day. In addition, the stored cells still displayed good cyclability. The cell rested for 365 days kept a high capacity with a low capacity-fade rate of 0.10% per cycle for 100 cycles (**Figure 1c**). Thus, in addition to showing the excellent dynamic electrochemical performance, the LBL-CNF-coated separators enable the cells attain excellent static electrochemical performances with: (1) the longest shelf-life, (2) the lowest self-discharge rate, and (3) good cyclability after resting (storing) for 1 year.

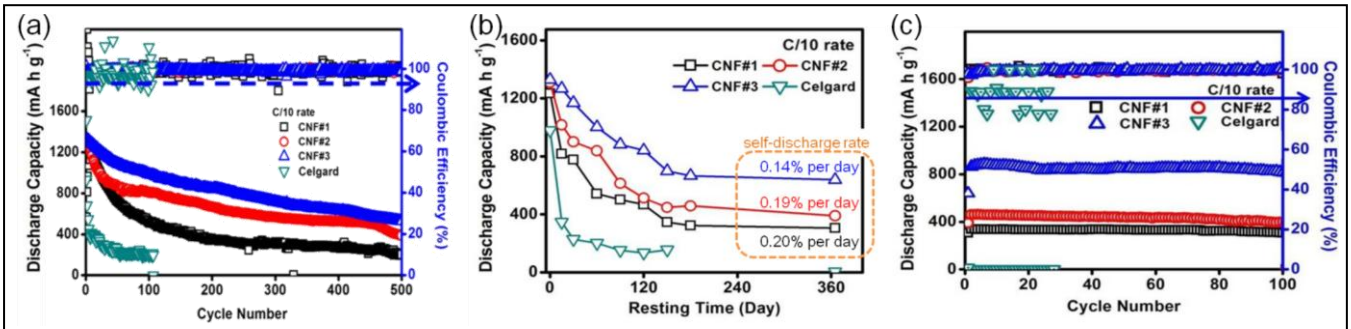

Figure 1. (a) Dynamic electrochemical analysis of the cells fabricated with the LBL-CNF-coated separators at C/10 rate. Static electrochemical analysis of the cells fabricated with the LBL-CNF-coated separators after resting for 365 days (black, red, and blue lines) and with the polypropylene membrane after resting for 150 days (green line): (b) static electrochemical stability with the self-discharge rates, and (c) post-resting cyclability.

Project activity III: Impact from applying practically necessary parameters in the cells (Y2Q3 – Y2Q4)

It is becoming increasingly clear that the Li-S battery chemistry and the electrochemical performances are distinctly different between low-loading sulfur cathodes (< 2.0 mg cm^{-2}) and practically-relevant high-loading cathodes (> 4.0 mg cm^{-2}). Moreover, the E/S ratio, another key issue that has been lacking in the literature investigation for years, has recently been pointed out to have a strong influence toward the electrochemical utilization and stability of Li-S cells, and even the basic cyclability of the cells. An even low E/S ratio of less than 11 μL mg^{-1} should be applied in the investigation of Li-S battery chemistry. Accordingly, we also focused on improving the dynamic and

static electrochemical characteristics of high-loading sulfur cathodes under a low E/S ratio by integrating our findings in the above accomplishments (Project activities I and II) with advanced cathode architectures. We have realized Li-S cells featuring a sulfur loading of as high as 30 – 60 mg cm^{-2}, a sulfur content of up to 80 wt. %, and a low E/S ratio of only 6.8 µL mg^{-1}.

The advanced cathode design that was fabricated with a cotton-carbon electrode employed polysulfide as the catholyte. Our cotton-carbon cathodes with a high sulfur loading (30 mg cm^{-2}) and content (80 wt. %) represent the highest sulfur loading/content among the literature reports and are able to smoothly cycle and stably rest at a very low E/S ratio of only 6.8 µL mg^{-1}, which is much lower than the values used in the literature. The cells show good cyclability with a capacity retention of 70% after 100 cycles, and improved cell-storage stability with a low self-discharge rate of just 0.12% per day after storing for 60 days (**Figures 2a** and **2b**). Such a well-designed cathode configuration further allowed an ultrahigh sulfur loading of 60 mg cm^{-2}, while the cells retained high electrochemical reversibility and efficiency with a high areal capacity and energy density of, respectively, 56 mA h cm^{-2} and 118 mW h cm^{-2} (**Figure 2c**). The cell performance metrics are higher than the values obtained with the current commercial Li-ion batteries (4 mA h cm^{-2} and ~ 10 mW h cm^{-2}) based on $LiCoO_2$ cathode.

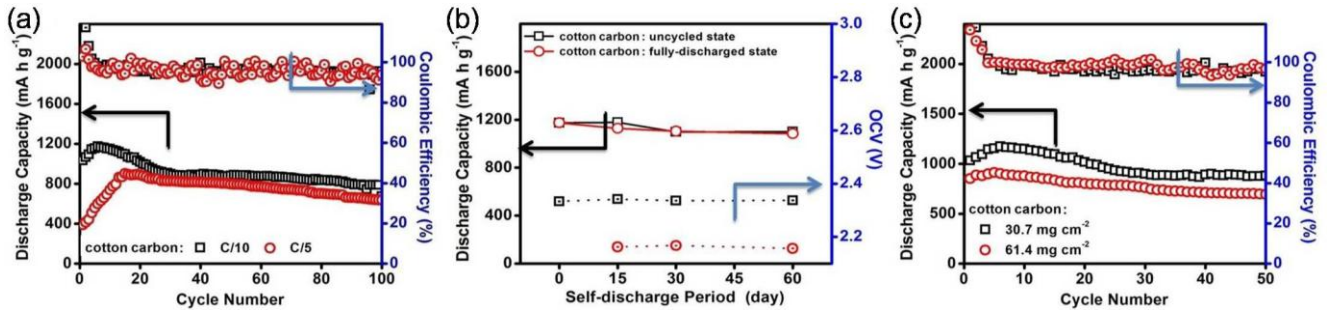

Figure 2. (a) Electrochemical analysis of the Li-S batteries fabricated with the cotton-carbon cathodes with a sulfur loading of 30 mg cm^{-2}, a sulfur content of 80 wt.%, and an E/S ratio of 6.8 µL mg^{-1}: (a) cycling performance at C/10 and C/5 rates and (b) self-discharge analysis after resting for two months with freshly-made cells and fully-discharged cells. (c) Cycling performance of the cotton-carbon cathode with a higher sulfur loading of 60 mg cm^{-2} at C/10 rate.

Project activity IV: Applying practically necessary parameters in the Li_2S cathodes (Y3Q2)

Li_2S is considered a highly attractive cathode material for establishing high-energy-density rechargeable batteries, especially due to its high charge-storage capacity (1,165 mAh g^{-1}) and compatibility with Li-metal-free anodes. Besides these materials metrics, assembled in a less-dense discharged state, Li_2S also alleviates issues with volume change and pulverization of the cathode architecture in the Li-S battery chemistry. Attracted by these advantages, we have demonstrated in this project a shell-shaped carbon architecture for developing pure Li_2S cathodes with superior cell-design parameters and electrochemical characteristics.

The key concept of the Li_2S core – carbon shell electrode aimed to encapsulate the insulating Li_2S and its redox products within the conductive shell to facilitate good electron/ion accessibility and limit the irreversible loss of the active material. In order to realize the best cell-design specification, the core-shell Li_2S cathode was initially carefully evaluated in relation to the critical cell-design parameters, such as the loading and content of Li_2S in the cathode and the electrolyte amount in the cells. Accordingly, our cells presented the highest Li_2S loading of 8 mg cm^{-2} (a value that is 5 times higher than the average value in the literature) with 100% Li_2S content (63 wt.%, including all cathode components), as shown in **Figure 3a**, and the lowest electrolyte/Li_2S (E/L) ratio of 9 (a value that is 5 times lower than the average value in the literature, **Figure 3b**). Even with such strict cell-design parameters, **Figure 3c** demonstrates that our

core-shell Li_2S cathodes achieved a high peak charge-storage capacity of 601 mA h g^{-1} and kept a high reversible capacity of 540 mA h g^{-1} after 200 cycles at a C/14 rate. Such enhanced battery performance demonstrates (i) superior electrochemical Li_2S utilization, (ii) high capacity retention of 90%, and (iii) enhanced rate performance from C/14 – C/3.5 rates.

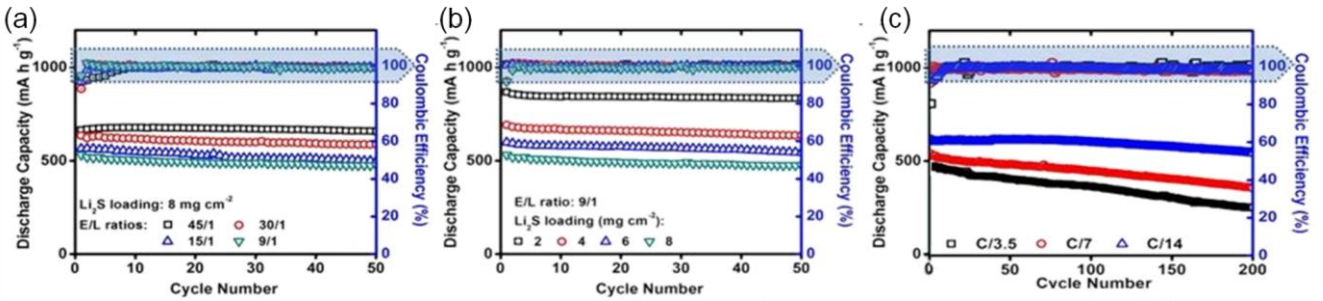

Figure 3. Cyclability (a) with various E/L ratios from 45 to 9 µL mg^{-1} at a fixed Li_2S loading of 8 mg cm^{-2} and (b) with various Li_2S loadings from 2 to 8 mg cm^{-2} at a fixed E/L ratio of 9µL mg^{-1}. E/L ratio and Li_2S loading of, respectively, 45 µL mg^{-1} and 2 mg cm^{-2} are the average values reported in published Li_2S papers. (c) Performances of the cells with a Li_2S loading of 8 mg cm^{-2} and an E/L ratio of 9 µL mg^{-1} at various cycling rates.

Project activity V: Li-metal anodes with high electrochemical stability (Y3Q1)

Besides optimizing the sulfur cathodes, the development of Li-S batteries with long cycle life also requires an advanced Li-metal anode. In order to enhance the stability of the reacted Li-metal electrode during long-term cycling, we have applied a Kimwipe (KW) paper on the surface of Li-metal anode as a stabilization layer (KW-stabilization layer). The KW-stabilization layer aims to create a uniform, smooth Li redeposition with no Li dendrites. Moreover, the fresh cellulose fibers of the KW paper have abundant polar functional groups like –OH and C-O-C, which can adhere to Li ions, improve the wettability with the electrolyte, and impede the inhomogeneous aggregation of Li ions around the protrusions of the deposited Li. To demonstrate these physical and chemical functions, cells with and without the KW-stabilization layer were prepared for the comparative research.

Figures 4a and **4b** show the Li deposition tests of the Li-Copper (Cu) cells, respectively, with and without the KW-stabilization layer. We controlled the Li to be plated on the Cu-foil substrate at a current density of 3 mA cm^{-2} for 3 hours in both cases. The control cell without the KW-stabilization layer exhibited non-uniform and rough Li deposits with huge cracks, in which we could clearly observe the growth of Li dendrites (**Figure 4a**). In contrast, at the same plating condition, **Figure 4b** demonstrates that a KW-stabilization layer allowed the cycled Li-metal anode to possess a dendrite-free, smooth Li deposition layer. The KW-protected Li-metal anode exhibited a well-preserved integrity after cycling. The dendrite-free morphology and smooth surface observed in the KW-protected cell provide evidence of homogeneous Li-ion distribution and stabilized Li-metal electrodes. **Figures 4c** and **4d** show the electrochemical testing of the Li-Li symmetric cells, respectively, with and without the KW-stabilization layer. Without the KW-stabilization layer, the control cell showed a typical high and increasing voltage polarization (~ 700 mV) with unstable voltage fluctuations in the voltage versus cycling time profile during 400-hour cycling (**Figure 4c**). In contrast, the symmetric cell with the KW-stabilization layer showed excellent cycling stability for 400 hours with a low polarization (~ 200 mV) at the same current density of 2 mA cm^{-2} (**Figure 4d**). The high reversibility of the KW-protected cell suggests that the KW paper provides a polar lithiophilic interface for the Li-metal anode, which effectively eliminates inhomogeneous Li-ion distribution on the surface, resulting in a dendrite-free morphology of the deposited Li.

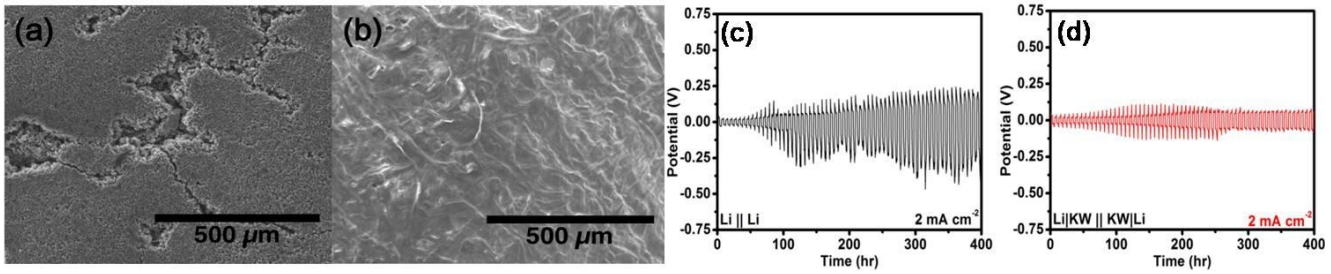

Figure 4. Scanning electron microscope (SEM) images of Li deposits using Li-Cu cells (a) with and (b) without the KW-stabilization layer at 3 mA cm^{-2} for 3 hours. Overpotential of Li-Li symmetric cells (c) with and (d) without the KW-stabilization layer at 2 mA cm^{-2} for 400 hours.

Project activity VI: Impact assessment – high-loading, lean-electrolyte cathode with long life (Y3)

It is recognized by the research community that the necessary parameters to develop high-energy-density Li-S batteries include a sulfur loading of at least 5 mg cm^{-2}, a sulfur content of over 65 wt.%, and a low E/S ratio of less than 11 μL mg^{-1}. Different from this practical conditions, commonly used conditions in the literature, including a low amount of sulfur and a high electrolyte volume, cause low effective capacity values and lower the energy density.

In this project, we integrated the advantages obtained in Project activities I – IV and demonstrated a high-loading, lean-electrolyte sulfur cathode by assembling two nonporous carbon-paper sheets as a cathode substrate, into which Li_2S_6 polysulfide catholyte was added. Two cathodes were fabricated with this design: one with 13 mg cm^{-2} and 75 wt.% sulfur with an E/S ratio of 4.0 μL mg^{-1} and the other with 17 mg cm^{-2} and 80 wt.% sulfur with an E/S ratio of 3.9 μL mg^{-1}, based on the total mass of the cathode including the carbon paper. So far, this is the only high-loading, lean-electrolyte sulfur cathode that simultaneously achieves the highest amount of sulfur and the lowest E/S ratio. Operating under such strict cell-design conditions, the cells with 13 and 17 mg cm^{-2} showed high charge-storage capacities of, respectively, 717 and 593 mA h g^{-1} at a C/10 rate with high capacity-retention rates of 71% and 85% after 200 cycles (**Figure 5**). Such cycling performance satisfies the benchmarks set for making practically viable Li-S batteries (*i.e.*, 80% capacity retention after 200 cycles). With the extensive work we carried out in this project with a high sulfur loading and lean electrolyte in coin cells, we also applied the knowledge to fabricate pouch-type Li-S cells.

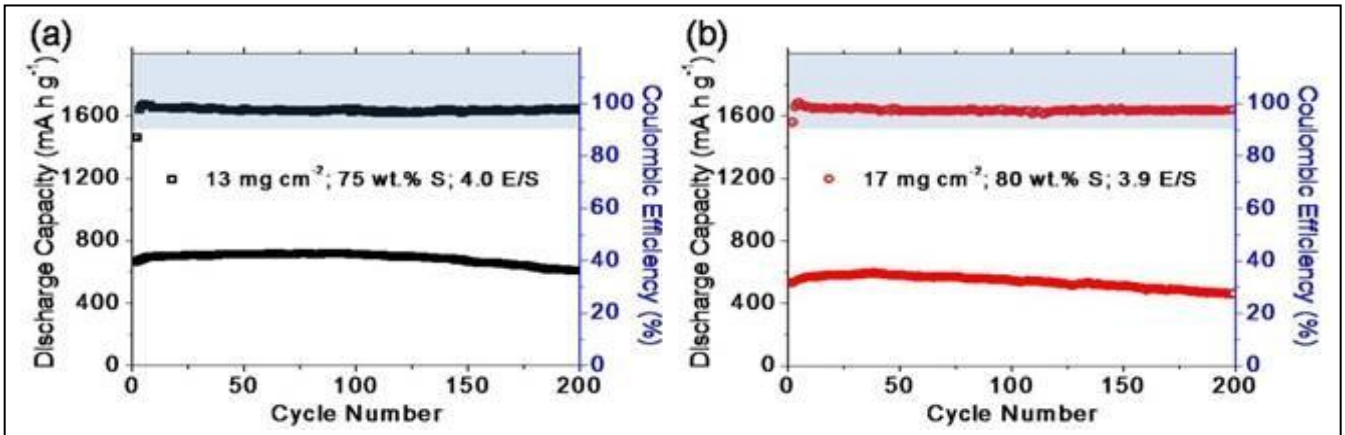

Figure 5. (a) Cyclability of the cells fabricated with the carbon-paper cathodes with a sulfur loading, sulfur content, and E/S ratio of, respectively, (a) 13 mg cm^{-2}, 75 wt.%, and 4.0 μL mg^{-1} and (b) 17 mg cm^{-2}, 80 wt.%, and 3.9 μL mg^{-1}.

Project activity VI: Impact assessment –from coin-type Li-S cells to pouch-type Li-S cells (Y3)

For practical applications, it is necessary to rethink and develop the Li-S technology by transitioning from coin-type cells with small size electrodes to pouch-type cells with electrode sizes similar or close to that of practical battery electrodes. In order to develop and assess the design of pouch-type Li-S cells with a high sulfur loading, we focused on cathode engineering (**Figure 6a**). In addition, we also considered the cost and environmental issues involved with high-loading cathode configurations in pouch cells. Thus, a simple sulfur-based active-material composite was used. The active-material composite with pristine sulfur (S), KetJen Black (KJB), and carbon nanotube (CNT) was prepared through a melt-diffusion process at 155 ^{o}C. The synthesized active-material composite (S/KJB/CNT) was mixed with additional conductive carbon and polymer binders. The resultant active-material slurry was then coated onto an aluminum foil and dried in a vacuum oven at 50 ^{o}C. All materials, including active sulfur and other inactive materials, and the heat-treatment methods are similar to those commonly used with Li-S cathodes. Thus, we made the cathode preparation as simple as possible. A simplified cathode-preparation method allowed us to prepare a high volume of cathodes with high repeatability and stability, limiting the cost issues encountered in cathode optimization. The prepared cathode was cut in a size of 47.8 mm x 81.5 mm and had a sulfur content of 65 wt.% and a sulfur loading of 6 mg cm^{-2}. In the cell-assembly process, a lithium foil was cut into the same size as large as the size of the cathode. A sheet of separator was then placed between the two electrodes and the assembled cell was sealed in a plastic film pouch with the E/S ratio fixed at 5 μL mg^{-1}.

Figure 6b shows the electrochemical performance of the pouch-type Li-S cells. The assembled cells were rested for 2 h and then cycled in the voltage window of 1.65 – 2.60 V at a C/20 rate. After the first cycle, the discharge-charge curves exhibit the typical two-step redox reaction of the Li-S chemistry. The discharge capacity at the first cycle reaches 995 mA h g^{-1}, corresponding to 60% electrochemical utilization. Considering the larger areal size of the cell (38.9 cm^2), the cell still shows outstanding performance. As a reference, the areal size of the regular coin cell is only 1.13 cm^2. After 18 cycles, the discharge capacity remains at 661 mA h g^{-1} with a high capacity retention of 66% (**Figure 6c**). Thus, we demonstrated promising pouch cell performance by using simple sulfur-based active-material composites, which might offer a facile path forward to fabricate pouch-type Li-S cells with good consistency.

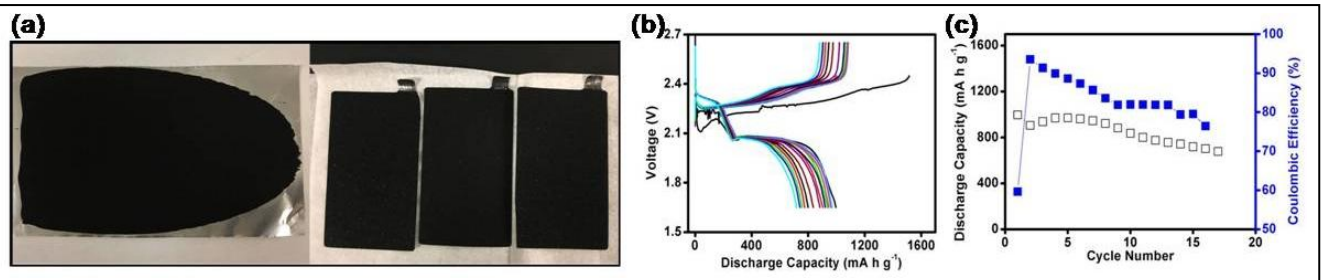

Figure 6. (a) Sulfur cathodes fabricated for pouch-type Li-S cells. Electrochemical performance of the pouch-type Li-S cells: (b) voltage profiles and (c) cycling performance.

Project conclusion

In this project, we have developed PS-filter-coated separators, advanced cathode substrates, and stabilized Li-metal anodes. These focused studies demonstrate optimized cell components that are suitable for Li-S battery chemistry. Thus, these well-designed cell components enable our Li-S cells attain the lowest self-discharge and the longest shelf-life (*i.e.*, the LBL-CNF-coated separator), the

highest sulfur loading with the lowest electrolyte volume (*i.e.*, the Li_2S core – carbon shell electrode, carbon-cotton cathodes, and graphene-coated-carbon-cotton cathodes), and promising electrochemical stability with the most practical cell-assembly conditions (*i.e.*, the carbon-paper cathodes). Our research progress enabled the demonstration of electrochemically stable Li-S cells with the high charge-storage capacities of up to 1,300 mA h g^{-1}, a long cycle life of 500 cycles, a low self-discharge rate of < 0.14% per day, and a long shelf-life of over one year. Also, we demonstrated electrochemically stable Li-S cells with the use of high-loading, lean electrolyte sulfur cathodes (*i.e.*, sulfur loading of up to 60 mg cm^{-2}, sulfur content of up to 80 wt.%, and E/S ratio of as low as 4.0 μL mg^{-1}). With the extensive work we carried out in this project with high sulfur loading and lean electrolyte in the coin cells, we also applied the knowledge to fabricate pouch-type Li-S cells, which proves the practical feasibility of our research.

Section IV. Project Output:

A. Publications:

1. L. Luo, S.-H. Chung, and A. Manthiram, "Trifunctional Multi-walled Carbon Nanotubes/Polyethylene Glycol (MWCNT/PEG)-coated Separator through a Layer-by-layer Coating Strategy for High-energy Li-S Batteries," Journal of Materials Chemistry A **4**, 16805-16811 (2016).
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B. Patent Applications:

1. A. Manthiram and S.-H. Chung, "Core-shell Cathodes for Lithium-Sulfur Batteries," Filed on June 13, 2016, Serial Number: 62/349,465 (pending).