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Enhancement of cycle performance of Li-S batteries by redistribution of sulfur†

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A practically available strategy is employed to improve the cycle life of lithium-sulfur batteries. The simple process of activation cycling at the polysulfide dissolution region leads to the partial dissolution of polysulfides and the redistribution of sulfur on the electrode. After 50 cycles, the activation-cycled sulfur cathode exhibits a capacity that is roughly double that of a cathode without activation cycling.

Sulfur is one of the most promising candidates for next-generation battery cathode materials because of its high theoretical specific capacity (i.e., 1672 mAh g^{-1}). Furthermore, sulfur is very cheap and abundant on Earth. Although the lithium-sulfur (Li-S) battery has many advantages, its commercialization with liquid electrolytes has been hampered by the following issues. Firstly, the loading level of the sulfur cathode and the sulfur utilization are rather limited because of the extremely low electrical conductivity of sulfur (i.e., 5×10^{-30} S cm^{-1} at room temperature).[1] Secondly, a series of polysulfide species produced during the charge and discharge processes are easily dissolved in organic electrolytes. Dissolved polysulfide species spontaneously diffuse out from the cathode, resulting in active material loss; they also react with the lithium metal anode, which leads to self-discharge.[2,3] Thirdly, an electrically insulating and insoluble Li$_2$S compound precipitates and agglomerates on the cathode surface during prolonged cycling, which leads to the continuous increase of cell impedance; this produces an electrochemically inaccessible region, which results in the fading of the battery's capacity.[4]

One of the most effective and popular methods of overcoming the problems mentioned above is based on the infiltration of sulfur into carbonaceous materials with high specific surface areas and large pore volumes (e.g., highly ordered meso- and/or micro-porous carbon).[5,6] The high surface area not only increases the electronic contact area between carbon and sulfur, but also provides more reactive sites. Furthermore, the pores in carbonaceous materials can physically trap dissolved polysulfides and accommodate the volume change during cycling, which is beneficial for maintaining electronically conductive networks. However, the preparation of porous carbon materials involves complex and expensive processes. In addition, further heat treatment is required to allow for the infiltration of sulfur into porous carbon materials, which is a time- and energy-consuming process. Therefore, there exists a considerable impetus for developing a commercially available method to prevent rapid capacity fading.

Herein, we introduce a powerful and economical method through a very simple electrochemical control to improve the cycle life performance. Several discharge and charge cycles at high-potential regions (i.e., above 2.2 V vs. Li$^+$/Li) before cycling result in the dissolution of a certain amount of polysulfide into the electrolyte, as well as the redistribution of sulfur on the cathode. Ultimately, these processes significantly enhance the cycle retention of the Li-S battery.

Li-S batteries exhibit two main discharge or charge potential plateaus. During the discharge reaction, sulfur is reduced to a long-chain polysulfide Li$_2$S$_X$ (4 ≤ X ≤ 8) at the high-potential plateau region. As the discharge continues, the long-chain polysulfide is reduced to a short-chain polysulfide, and finally to lithium sulfide at the low-potential plateau region.[7] The sulfur utilization can be calculated from the specific capacity of the first plateau. The active material utilization of the electrode is related to the injected current density in various battery systems, and it is more pronounced in Li-S battery systems owing to the low electrical conductivity of sulfur. Fig. S1 (ESI†) shows the specific capacity at the first plateau region for different current densities. The capacities at the current densities of 0.05 C-rate and 0.02 C-rate are about 20% and 25% higher, respectively, than that at the current
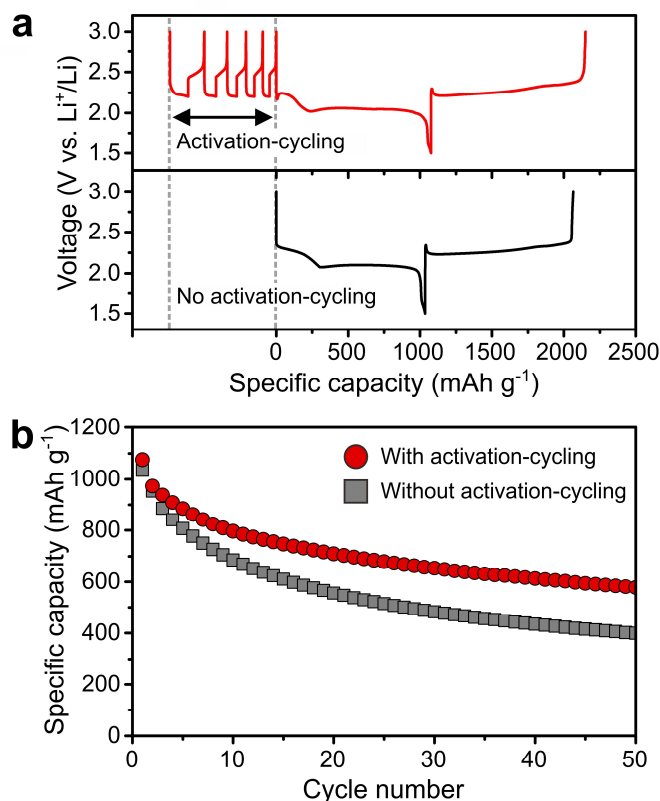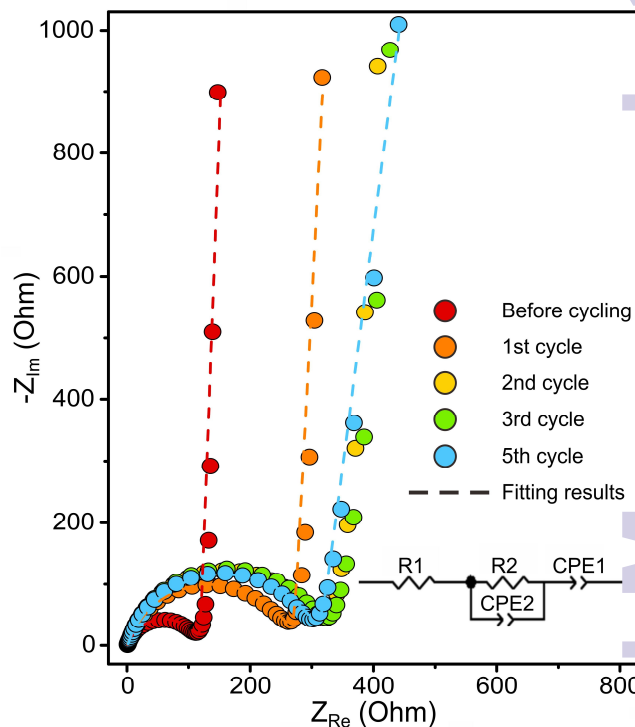
Fig. 1. (a) Voltage profiles at the first cycle of the sulfur cathode with activation cycling (top) and without activation cycling (bottom). (b) Cycle performances of the sulfur cathode with activation cycling and without activation cycling.

Fig. 2 Nyquist plots of a lithium-sulfur cell during 5 activation-cycles. Inset shows the equivalent circuit applied for fitting.

density of 0.1 C-rate. Faradaic reactions and disproportionation reactions simultaneously occur at the first plateau.[8] The low current density provides enough time for both reaction processes, and finally leads to high sulfur utilization. Therefore, we attempt to increase the sulfur ratio that participated in the electrochemical reaction by cycling at a low C-rate at the high plateau region before normal cycling; this technique is referred to as "activation cycling" in this study.

The specific conditions for activation cycling consisted of charging and discharging at a potential window from 3.0 to 2.2 V (vs. Li$^+$/Li) by 0.05 C-rate. Fig. 1a (top) shows the initial voltage profile with 5 cycles of activation cycling; for comparison, Fig. 1a (bottom) shows the initial voltage profile without activation cycling. Interestingly, the cycle retention for the electrode with activation cycling is significantly enhanced compared to the electrode without activation cycling at 0.1 C-rate (Fig. 1b).

The irreversible capacity loss is observed in the first activation cycle (Fig. S2 in ESI†) because the generated polysulfide diffuses out from the electrode during discharge, a certain portion of which cannot return to sulfur during charge. The concentration of sulfur in the electrolyte after activation cycling can be easily estimated (Fig. S2 in ESI†), and can reach as high as 0.23 M. In order to quantify the enhanced cycle stability for an activation-cycled cell, we prepared a 0.25 M polysulfide-dissolved electrolyte and tested the cell performance. The electrochemical properties with the polysulfide-dissolved electrolyte are very similar to those of

the activation-cycled cell (Fig. S3 in ESI†), which implies that the improved cycle life performance of the activation-cycled cell is closely related to the amount of dissolved polysulfide.

In fact, many research groups have reported that a certain concentration of polysulfide-dissolved electrolyte could significantly improve the cycle life performance. More specifically, the dissolved polysulfide provides a mass buffering effect, which reduces the active material dissolution during cycling.[9,10] However, in our case, the polysulfide concentration is very low, and provides a limited mass buffering effect, so it is therefore difficult to maintain that the dissolution of polysulfides is only the reason for improved cycle stability in the activation-cycled cell.

We also consider the effect of reduced charge transfer resistance by polysulfides as an additional factor. It has been reported that a small amount of polysulfide dissolved in electrolyte could act as a redox mediator, and thus effectively reduce the charge transfer resistance.[11] This phenomenon can also be supported by our experiment (see Fig. S4 in ESI†). We made a Li$_2$S cathode by discharging a S cathode. After the first discharge cycle, the cathode was washed with the solvent 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) at a 1:1

Table 1. Resistance and capacitance values obtained from fitting results of EIS.

ACT-CYC	R1 (Ω)	R2 (Ω)	CPE2-T (F)	CPE2-P	CPE1-T (F)	CPE1-P
0	0.77	118	2.21×10^{-5}	0.80	1.75×10^{-3}	0.98
1	0.90	270	1.27×10^{-5}	0.81	1.70×10^{-3}	0.97
5	1.26	312	0.99×10^{-5}	0.81	1.51×10^{-3}	0.92
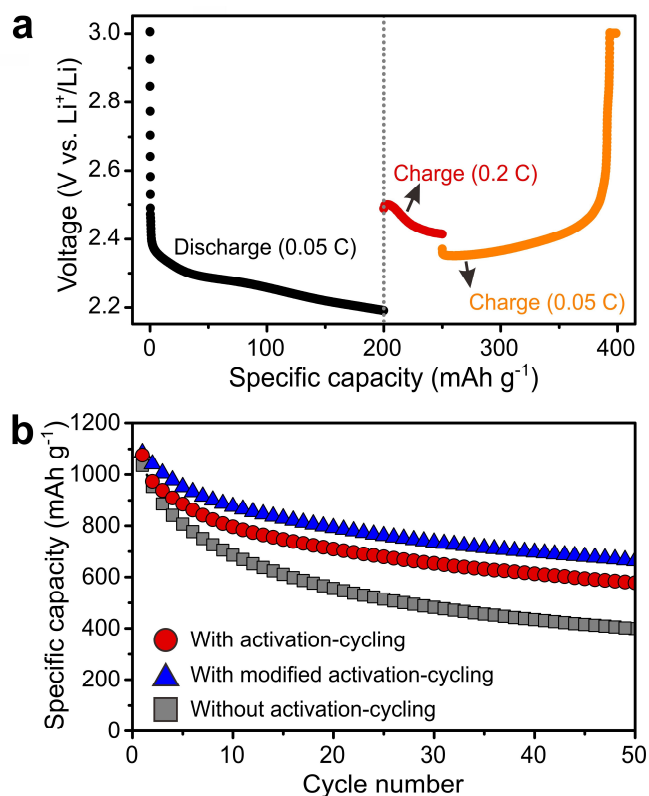
Fig. 3. (a) Voltage profiles of modified activation cycling. (b) Cycle performances of sulfur cathode with modified activation cycling (0.1 C-rate).

Fig. 4. Scanning photoelectron microscopy (SPEM) mapping of (a) an as-prepared sulfur electrode, (b) a sulfur electrode after activation cycling, and (c) a sulfur electrode after modified activation cycling. The scale bars in (a-c) are 50 μm. (d) Schematic illustration of partially dissolved polysulfide and sulfur redistribution under activation cycling and modified activation cycling.

volume ratio; we then reassembled the cell with fresh electrolytes in an Ar-filled glove box. A huge overpotential was observed at the first charge, though the overpotential disappeared during following cycles. This suggests that the polysulfide dissolved in the electrolyte after the first cycle significantly decreases the charge transfer resistance.

Aside from the positive effects of polysulfide on the electrochemical properties that we mentioned above, there must be other factors that contribute to the enhancement of the cycle life of the activation-cycled cell. That is because a certain amount of polysulfide will be dissolved into the electrolyte after the first discharge for normal sulfur cells as well, and the cycle retention properties of an activation-cycled are even better than those of a cell with a 0.25 M polysulfide-dissolved electrolyte (inset, Fig. S3 in ESI†). Therefore, in order to elucidate the enhanced cycle property of activation-cycled cell, we conducted electrochemical impedance spectroscopy (EIS), and proposed a simplified equivalent circuit based on the shape of the Nyquist plots (inset of Fig. 2). The experimental points are well described by the equivalent circuit. R1 corresponds to the resistance of the electrolyte. The semicircle is represented by a parallel circuit consisting of a resistance (R2) and a constant phase element (CPE2). The straight line in the low-frequency region is modeled by CPE1. The constant phase element (CPE) replaces the capacitor in order to compensate for the non-ideal behavior of the electrode. CPE1-T is two orders of magnitude larger than CPE2-T, which implies that CPE1 results from a large carbon surface (Table 1). Moreover, it is observed that the resistance (R2) significantly
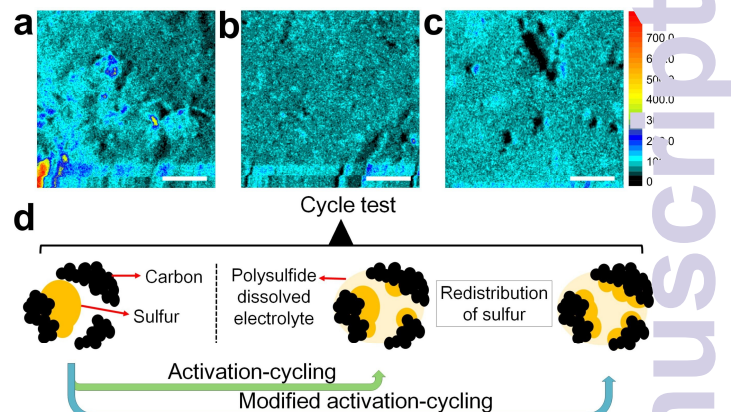
increased after the activation cycles, which is attributed to the increased interphase contact resistance.[12] The insulating sulfur on surface of carbon particle could increase the interphase contact resistance, indicating that much more carbon surface is covered by sulfur after activation cycles.

The capacitance can be expressed by Equation 1 as follows:

$$C = \varepsilon_r \varepsilon_0 A / d \qquad (1)$$

where C is the capacitance (F), A is the area of overlap between the two plates (m^2), ε_r is the relative static permittivity (sometimes called the dielectric constant) of the material between the plates (for a vacuum, ε_r = 1), ε_0 is the electric constant (ε_0 = 8.854 × 10^{-12} F m^{-1}), and d is the separation between the plates (m). For a single battery cell, the parameters are almost constant during activation cycling except for the area A. Therefore, the capacitance is in direct proportion to the electrochemically active surface area (ECSA) of carbon. The capacitance (CPE1-T) is reduced by 14% after 5 activation cycles. This means that the ECSA of carbon decreases as a result of being covered with sulfur. Ultimately, the rearrangement of sulfur in the cathode is induced through repetitive dissolution and precipitation processes.

We modified the activation cycle conditions to further improve the dispersion of sulfur (see Fig. 3a). More specifically, polysulfides were oxidized to sulfur at the high-potential charging plateau region. The nucleation of sulfur occurs at the initial charging region, which is followed by nucleation growth. In order to make more nuclei, the charging C-rate at the nucleation region during activation cycles was increased. The large overpotential at the beginning of charging process is related to the activation energy of nucleation at 0.2 C rate. However, the overpotential becomes rather smaller compared to that in reference electrode after activation cycling (Fig. S6). The capacitance of modified activation cycle is further reduced by 21% from EIS result (Fig. S5). After more effective dispersion of sulfur, the cycle life performance of the modified activation-cycled cell is much improved (Fig. 3b). The specific capacity of the modified activation-cycled cell after 50 cycles is about twice as large as that of the cell without activation cycling. Furthermore, the capacity decay rate of the modified

activation-cycled cell is only 0.7% per cycle for 50 cycles; on the other hand, the capacity of the cell without activation cycling decays at a rate of 1.4% per cycle.

In order to further understand the enhanced cycle properties of activation-cycled cells, scanning photoelectron microscopy (SPEM) analysis was performed. SPEM is a powerful tool for mapping a specific element at identical chemical state. Fig. 4a, 4b, and 4c show SPEM images of S^0 (binding energy, 163.9 eV) before activation cycling, after activation cycling, and modified activation cycling, respectively. The images are taken from an area of 200 × 200 μm with a 1 × 1 μm resolution. Before activation cycling, there were several agglomerated sulfur clusters present (Fig. 4a). However, after activation cycling, no agglomerated sulfur regions were observed (Fig. 4b). In addition, the sulfur was dispersed more homogeneously after modified activation cycling (Fig. 4c). Sulfur experiences serious phase transitions (solid-liquid-solid) during cycling. Therefore, it will induce significant stress and damage the cathode during full discharge, which can be more pronounced at the sulfur-agglomerated regions. We effectively dispersed sulfur through activation cycling, which reduced the damage from volume change during subsequent cycling, and ultimately enhanced the cycle life.

In summary, we have demonstrated a simple electrochemical method for improving the cycle life of a Li-S battery. Through precisely controlling the charging and discharging at the polysulfide dissolution region, the redistribution of sulfur at the electrode structure and the partial dissolution of polysulfide was observed (see Fig. 4d). We expect that this simple strategy can be applied to other Li-S battery systems in order to effectively limit capacity fading.

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