

Superior stable sulfur cathodes of Li–S batteries enabled by molecular layer deposition†

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For the first time, we report the employment of an ultrathin alucone film enabled by the molecular layer deposition technique to dramatically stabilize the sulfur cathodes for Li–S batteries. The alucone coated C/S cathode displayed over two-times higher discharge capacity than the pristine one after 100 cycles, demonstrating a greatly prolonged cycle life.

Li–sulfur batteries have been intensively studied in recent years owing to their high theoretical capacity and energy density, and are being considered as the most promising power candidates for electric vehicles and hybrid electrical vehicles.¹ However, the reality of commercial Li–S batteries is hindered by their poor cycle life.² One critical issue currently in Li–S batteries is the well-known “shuttle effect”, which is caused by the dissolution of polysulfide. The polysulfide species migrate to the anode and chemically react with Li metal, resulting in Li metal corrosion as well as irreversible sulfur loss.³ Furthermore, the insulating nature of sulfur and its large volume expansion during the lithiation process hinder the commercialization of Li–S batteries.⁴

Surface coating with carbon or metal oxides has been proven to be a promising approach towards mitigating the “shuttle effect” in Li–S batteries.⁵ In previous studies, surface coatings were generally conducted on sulfur composites by solution-based methods. Unfortunately, it is hard to reach good control over the uniformity and thickness of the coating layer, which are essential to achieve the optimal performance of the sulfur composite in Li–S batteries.⁵ Ideally, the surface coating on sulfur cathodes should be mechanically robust to accommodate the large volume expansion, as well as be thin enough to effectively prevent the dissolution of polysulfide without blocking ion and electron transport.⁶ Atomic layer deposition (ALD)

is an ideal technique to synthesize ultrathin and conformal coatings due to the self-limiting nature.⁷ Al₂O₃ coating *via* ALD has been studied for sulfur cathodes.⁸ The ultrathin, conformal metal oxide coating layer prevents the migration of polysulfides to improve the stability of Li–S cells.⁸

Molecular layer deposition (MLD), an analogy of ALD, also provides precise control over film thickness and allows for conformal film growth over nanostructure substrates.⁹ However, ALD processes are limited to metal oxides or metal films, whereas MLD can be employed to produce pure polymeric thin films or inorganic–organic hybrid thin films.¹⁰ The combination of ALD and MLD to produce inorganic–organic hybrid thin films holds many advantages such as lower growth temperatures, tunable thermal stability, and improved mechanical properties.¹¹

Furthermore, the toughness and flexibility of polymeric metal thin films by MLD are strengthened with the introduction of C–C and C–O bonds in this system.^{9a,b,12} Lee *et al.*¹³ reported a flexible MLD coating employed on a Si anode to accommodate its huge volume expansion, and significantly improved the cycling stability of the Si anode.

Herein, for the first time, we demonstrate that an MLD alucone coating directly on sulfur electrodes can dramatically improve the cycling stability and capability of Li–S cells. Furthermore, the alucone coated sulfur cathode delivers a discharge capacity of 710 mA h g^{−1}, which is over two times higher than the bare sulfur cathode after 100 cycles. The improvement in the electrochemical performance could be attributed to the mitigation of “shuttle effect” by alucone coating.

The alucone film was directly deposited on as-prepared sulfur-carbon electrodes (C/S electrodes) using trimethyl aluminium (TMA) and ethylene glycol (EG) as precursors at 100 °C. MLD of alucone from TMA and EG has been well studied, and can be performed at low temperatures.^{9a,11a} Direct coating on the electrode at this low temperature retains the electron-conductive network,^{7a} and avoids the evaporation of sulfur (ESI[†]). Fig. 1 illustrates the surface reactions between TMA and EG occurring in one typical MLD cycle, and the alucone

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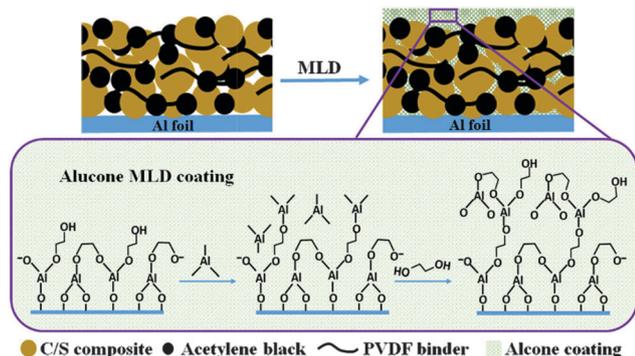


Fig. 1 Schematic of alucone MLD thin film formation as a coating layer applied on a C/S cathode. The self-limiting reaction is conducted by using two precursors to produce a layer-by-layer inorganic-organic hybrid composite.

thin film is coated on the sulfur cathode by repeating the MLD cycles. The influence of alucone coating thickness is investigated in detail with 2, 5, 10 and 20 MLD cycles on sulfur electrodes (ESI[†]).

Electrochemical characterization was carried out to evaluate the effect of the alucone coating on the performance of sulfur cathodes. Fig. 2a shows the cycling performance of sulfur cathodes with/without alucone coating measured at a current density of 160 mA g^{-1} . All of the alucone coated sulfur cathodes show significant improvement in both cycling capability and columbic efficiency (CE). Interestingly, the 5-cycle alucone coated sulfur cathode delivers a specific discharge capacity of 710 mA h g^{-1} after 100 cycles, which is over two times greater than that of the bare C/S cathode (310 mA h g^{-1} of 100 cycle). Furthermore, alucone coated C/S cathodes retain a stable CE over 90%, as opposed to only 70–80% of the bare C/S cathode. The impressive cycling stability of the alucone coated sulfur cathode shows that the strengthened coating layer effectively protects polysulfides from migration, resulting in prolonged durability of Li-S batteries. The 10-cycle alucone coated sulfur cathode also demonstrates improved cycling stability and maintains a capacity over 80% from the 25th to 100th cycle. However, the 10-cycle alucone coated cathode delivers a lower initial specific discharge capacity of 1155 mA h g^{-1} , which could be due to the limited sulfur utilization as a result of the thick alucone coating.¹³ The 2-cycle alucone coated sulfur cathode delivers progressive degradation with cycling, indicating that 2-cycle alucone coating is too thin to protect the C/S cathode effectively.

To reveal the detailed electrochemical processes occurring within each system, discharge-charge profiles of sulfur cathodes are shown in Fig. 2b. The bare and 5-cycle alucone coated cathodes demonstrate a typical Li-S redox process, which exhibit two potential plateaus at 2.3 V and 2.1 V during the discharge process, and one potential plateau at about 2.4 V during the charge process. The bare C/S cathode shows an obvious overcharge effect due to the serious “shuttle effect”, accounting for the low CE in cycling performance.¹⁴ The 5-cycle alucone coated cathode exhibits a nearly closed circle in its

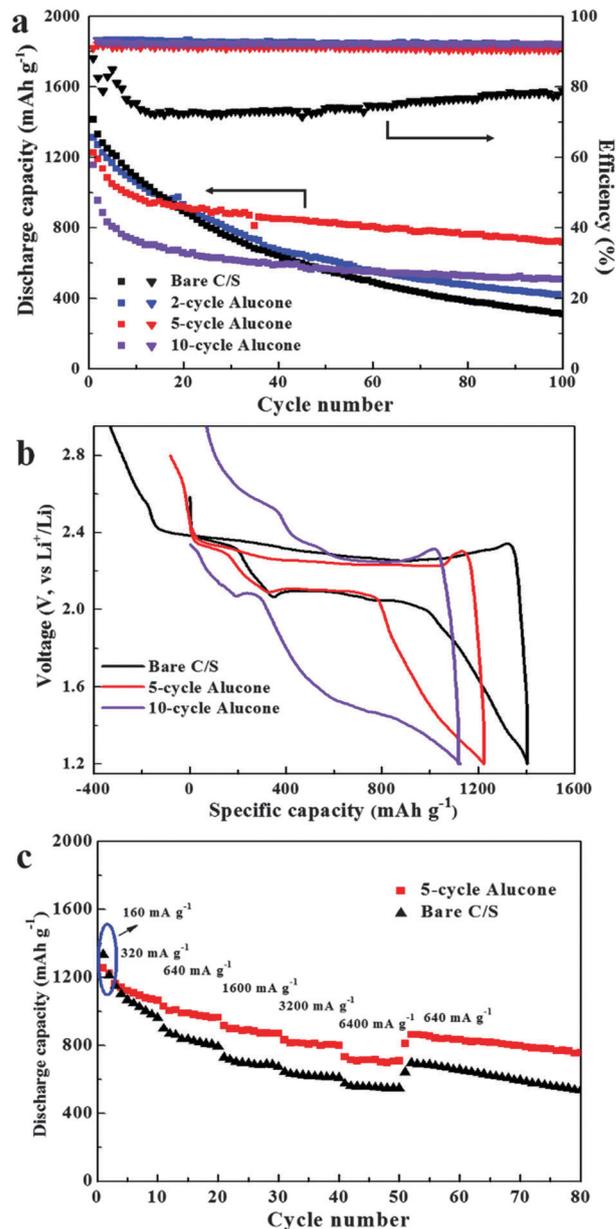


Fig. 2 (a) Cycle performance of bare, 2-, 5-, 10-cycle alucone coated C/S cathodes under 160 mA g^{-1} ; (b) typical discharge-charge profiles of sulfur cathodes with/without alucone coating; (c) comparison of rate performance between 5-cycle alucone coated and bare C/S electrodes.

discharge-charge profile, indicating effective alleviation of the “shuttle effect” by the alucone coating.^{4b} Furthermore, the sulfur cathode with 5-cycles of alucone coating shows flat potential plateaus, which are an indication of high reversibility of the Li-S redox reaction. On the other hand, the 10- and 20-cycle alucone coated cathodes show extreme potential polarization, suggesting limited conductivity and low reaction activity of sulfur cathodes with thicker alucone coatings (ESI[†], Fig. S4 and S5).

Fig. 2c demonstrates the rate performance of the 5-cycle alucone treated cathode against the bare C/S cathode. The electrodes are tested at 160 mA g^{-1} for the first 2 cycles and then subsequently increased to 6400 mA g^{-1} during cycling.

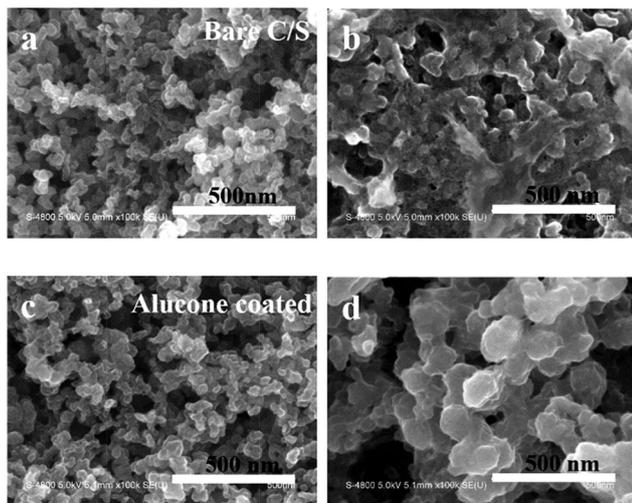


Fig. 3 FE-SEM images of the bare C/S electrode before (a) and after (b) cycling; and the alucone coated C/S electrode before (c) and after (d) cycling.

The 5-cycle alucone coated sulfur cathode demonstrates a discharge capacity of 700 mA h g^{-1} under 6400 mA g^{-1} , and returns to 750 mA h g^{-1} after 80 cycles. The improved rate performance confirms that the ultrathin layer of alucone not only relieves the “shuttle effect” from dissolved polysulfide but also allows lithium-ion fast diffusion under elevated test conditions.^{6c}

The morphology of electrodes with/without alucone coating was examined before and after battery cycling, in order to reveal the improved performance by alucone coating. As seen in Fig. 3, the morphology of the sulfur cathode with/without alucone coatings shows agglomeration of nanoparticles within sizes of 40–60 nm (Fig. 3a and c). After cycling, the bare C/S electrode is completely covered with discharge products due to the polysulfide dissolution (Fig. 3b), which is accountable for the reduced sulfur reversibility and elevated shuttle effect during cycling (Fig. 2).^{5a,15} Different from the bare C/S cathode, the alucone coated C/S cathode displays a limited amount of discharge products being deposited on the surface after cycling (Fig. 3d), suggesting that the dissolved polysulfides are restrained in the carbon matrix by alucone coating (ESI,† Fig. S8 and S9). The reduced dissolution of polysulfides by alucone coating leads to the greatly improved cycling stability and CE for the C/S cathode. Moreover, it is believed that the good mechanical properties of the alucone coating should contribute to the accommodation of volume expansion in the sulfur cathode during cycling,^{9b,11b,13} thus extending the durability of sulfur cathodes. In addition, the stable performance of the alucone coated C/S cathode is also attributed to the retained conductive network in the electrode after coating.

Previous studies have shown that ALD- Al_2O_3 coating could enhance the performance of C/S cathodes. In this work, we found that the performance of the C/S cathode with alucone coating by MLD is even better than the optimized ALD- Al_2O_3 coated C/S cathode. Fig. 4 compares the performance of MLD-alucone coated, ALD- Al_2O_3 coated, and bare C/S cathodes.

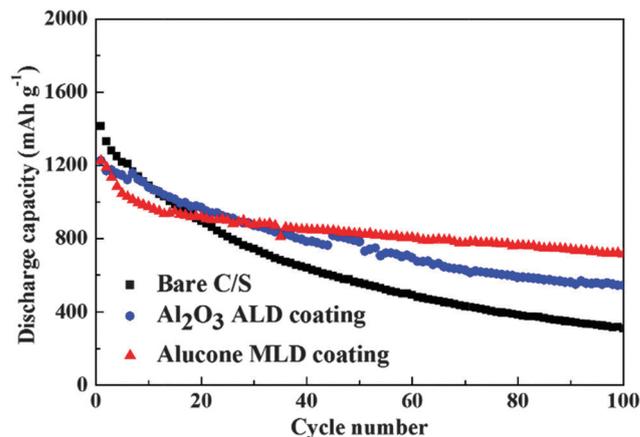


Fig. 4 Cycle performances of bare, ALD- Al_2O_3 coated, and MLD-alucone coated C/S cathodes at a current density of 160 mA g^{-1} .

Among these samples, it is obvious that the MLD-alucone coated C/S cathode demonstrates the most promising result with enhanced stability and prolonged lifespan, which delivers a capacity of 620 mA h g^{-1} after 150 cycles (ESI,† Fig. S7).

In summary, for the first time, inorganic–organic hybrid alucone coatings *via* MLD have been investigated on sulfur cathodes. The alucone coating layer provided not only solid protection of sulfur from dissolution, but also an ultrathin layer to allow fast Li-ion diffusion, resulting in improved cycling stability of Li–S cells. The 5-cycle alucone coated sulfur cathode delivered a discharge capacity of 710 mA h g^{-1} in 100 cycles under 160 mA g^{-1} , and about 700 mA h g^{-1} under 6400 mA g^{-1} over 50 cycles. The alucone coating demonstrated long durability during cell cycling, which explores a new direction in the protection of sulfur cathodes. Although the alucone film has limited conductivity, the introduction of carbon element in the MLD process holds the possibility to build an ideally conductive, long durable, as well as ultrathin conformal coating layer for sulfur cathodes in our future endeavours.

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