

INTERCONNECTED HOLLOW CARBON NANOSPHERES FOR STABLE LITHIUM METAL ANODES

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OVERVIEW

- Much less Li-S research conducted on the anode than cathode
- Central Li-S anode research topics:
 - Anode material
 - Coatings/SEI Layer
- This paper: coating anode with a thin monolayer of interconnected, amorphous, hollow carbon nanospheres
- Li dendrites do not form up to a practical current density of 1 mA cm^{-2}
- Demonstrated CE improvement to $\sim 99\%$ over more than 150 cycles

ARTICLES

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Interconnected hollow carbon nanospheres for stable lithium metal anodes

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For future applications in portable electronics, electric vehicles and grid storage, batteries with higher energy storage density than existing lithium ion batteries need to be developed. Recent efforts in this direction have focused on high-capacity electrode materials such as lithium metal, silicon and tin as anodes, and sulphur and oxygen as cathodes. Lithium metal would be the optimal choice as an anode material, because it has the highest specific capacity ($3,860 \text{ mAh g}^{-1}$) and the lowest anode potential of all. However, the lithium anode forms dendritic and mossy metal deposits, leading to serious safety concerns and low Coulombic efficiency during charge/discharge cycles. Although advanced characterization techniques have helped shed light on the lithium growth process, effective strategies to improve lithium metal anode cycling remain elusive. Here, we show that coating the lithium metal anode with a monolayer of interconnected amorphous hollow carbon nanospheres helps isolate the lithium metal deposits and facilitates the formation of a stable solid electrolyte interphase. We show that lithium dendrites do not form up to a practical current density of 1 mA cm^{-2} . The Coulombic efficiency improves to $\sim 99\%$ for more than 150 cycles. This is significantly better than the bare unmodified samples, which usually show rapid Coulombic efficiency decay in fewer than 100 cycles. Our results indicate that nanoscale interfacial engineering could be a promising strategy to tackle the intrinsic problems of lithium metal anodes.

When interest in secondary lithium batteries began to emerge more than four decades ago¹ it was clear that, to make viable Li metal anodes, two fundamental challenges would need to be resolved: (1) accommodating the large change in electrode volume during cycling (unlike graphite and silicon anodes, where lithiation produces volume changes of $\sim 10\%$ and 400% , respectively, Li metal is 'hostless' and its relative volumetric change is virtually infinite); and (2) controlling the reactivity towards the electrolyte (Li is one of the most electropositive elements)^{2–6}. Even today, there is still very little control over the thickness, grain size, chemical composition and spatial distribution of the solid electrolyte interphase (SEI), which, together, make the battery inefficient^{7,8}. One problem lies in the fact that the SEI layer cannot withstand mechanical deformation and continuously breaks and repairs during cycling. As a result, Li metal batteries have low Coulombic efficiency (80–90% for carbonate solvents and 90–95% for ether solvents)⁹ and low cycle life due to the rapid loss of Li and electrolyte in the continuous formation/dissolution of the SEI¹⁰. A second problem is that Li deposition is not uniform across the electrode surface and can form large dendrites that cause short circuiting of the battery^{11–13}. Third, reactions between the Li metal and the electrolytes are exothermic and large surface areas can pose risks of overheating (thermal runaway)¹⁴.

Considerable effort has been directed at addressing these problems using both solid and liquid electrolytes. As solid electrolytes, polymers and ceramics have been developed for their perceived ability to mitigate dendrite nucleation^{15,16} and block their growth^{17–20}. However, most solid electrolytes have low ionic conductivity, resulting in low power output. Moreover, Li polymer batteries

solid electrolytes with a framework structure, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and garnet type $\text{Li}_7\text{La}_2\text{Zr}_2\text{O}_{12}$, have been investigated for their high Li ion conductivity ($\sim 1 \times 10^{-2}$ to $1 \times 10^{-4} \text{ S cm}^{-1}$)^{15,23,24}, but, like their polymer counterparts, interfacial issues remain largely unresolved^{25,26}.

In the case of liquid electrolytes, a great deal of research has focused on using additives^{27–29} together with chemical passivation of the Li metal surface to reduce electrolyte decomposition^{30,31}. However, the thin films formed on the Li metal using these methods consist mainly of Li compounds, which are brittle and have limited cohesion with the metal surface³². Consequently, upon Li deposition, the film surface usually cracks as a result of volumetric expansion, exposing fresh Li metal for further reactions (Fig. 1a). Lithium dissolution then takes place, creating pits and crevices with low impedance³³, and Li ions flow at the defects, leading to rapid growth of metal filaments and dendrites. Stabilizing the interface between the Li metal and the electrolyte is therefore key in improving the cycling performance of Li metal batteries.

The ideal interfacial layer for the Li metal anode needs to be chemically stable in a highly reducing environment, and also mechanically strong. High flexibility is desired to accommodate the volumetric expansion of Li deposition without mechanical damage. In addition, the ability to control the flow of Li ions with the SEI inhomogeneities is essential to ensure uniform Li deposition³⁴. Here, we describe a flexible, interconnected, hollow amorphous carbon nanosphere coating with the aim of realizing such an ideal interfacial layer (Fig. 1b). The advantages of our approach are threefold: (1) amorphous carbon is chemically stable when in contact with Li metal; (2) the thin amorphous carbon layer does

THEORY

- Li metal anodes:

Benefits	High specific capacity (3860 mAh g ⁻¹)	Low anode potential (-3.04 V)	Low density (0.59 gcm ⁻³)
Challenges	Li dendrite growth	Extreme volume fluctuations	High reactivity with electrolyte

- Creating an ideal interfacial layer:
 - Chemically stable in highly reducing environment
 - High flexibility for volumetric expansion
 - Facilitates stable SEI formation
- Carbon nanosphere coating achieves this, suppressing Li dendrite growth by reducing Li ion flow to regions of SEI breakdown

THEORY

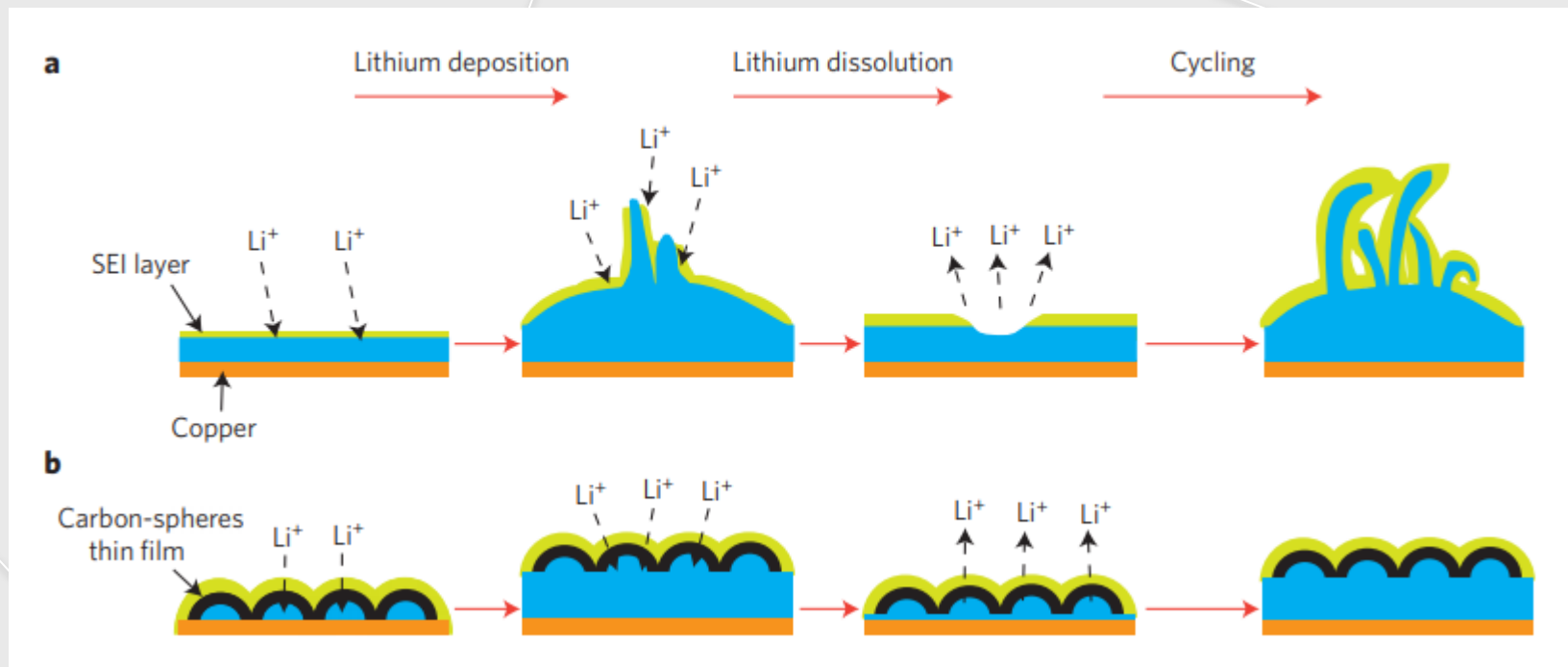
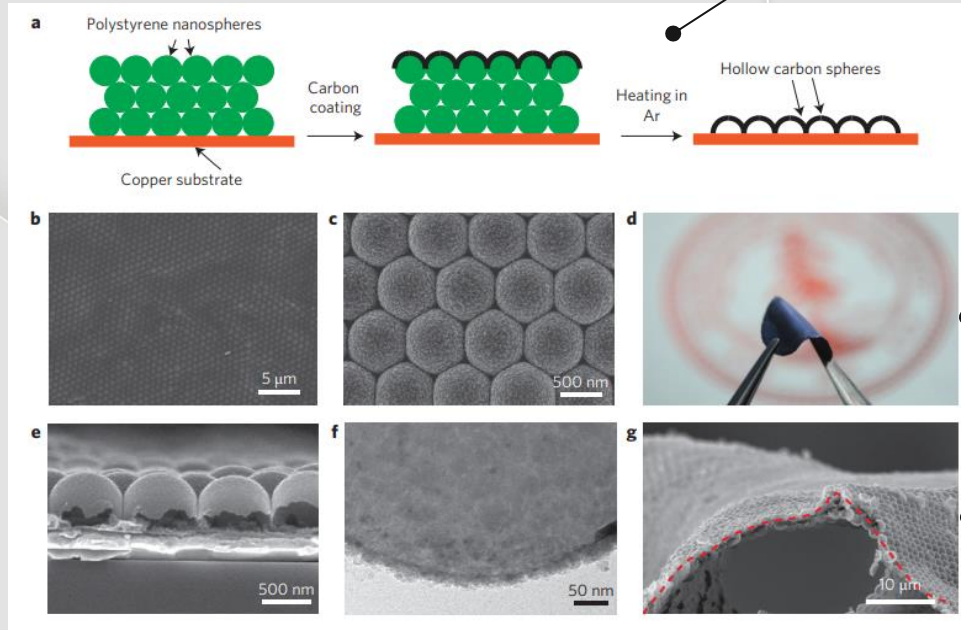


Fig.1

EXPERIMENTAL

(a) Vertical deposition of polystyrene: slowly evaporate 4% aqueous carboxylated polystyrene on Cu foil, then coat with amorphous carbon using flash evaporation, before heating in 400°C furnace



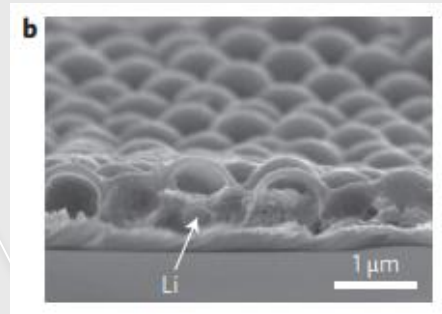
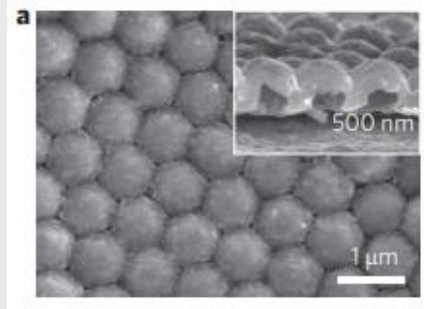
(b), (c) SEM top images of nanoparticle array structure; (d) digital camera image of nanosphere thin film

(e) SEM side/cross-sectional view; (f) TEM image showing 20nm wall thickness; (g) SEM image of nanosphere thin film peeled off Cu foil substrate

Fig.2

Li DEPOSITION

(a) SEM top image after initial cycling and SEI formation



(b) SEM side/cross-sectional image of interface after Li deposition

(c) SEM side image showing elevated film due to columnar deposition of Li (compare Fig.1b);

(d) SEM top image of smoother anode surface;

(e), (f) Similar SEM comparisons of anode surface without carbon nanosphere modification

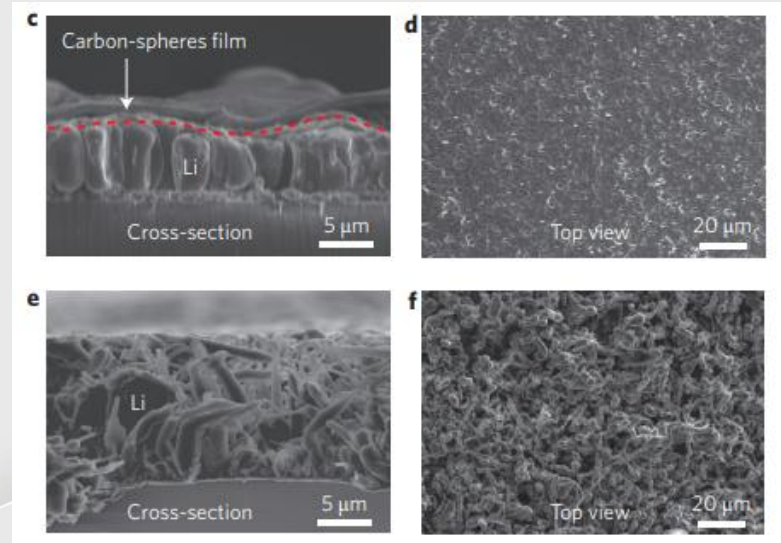
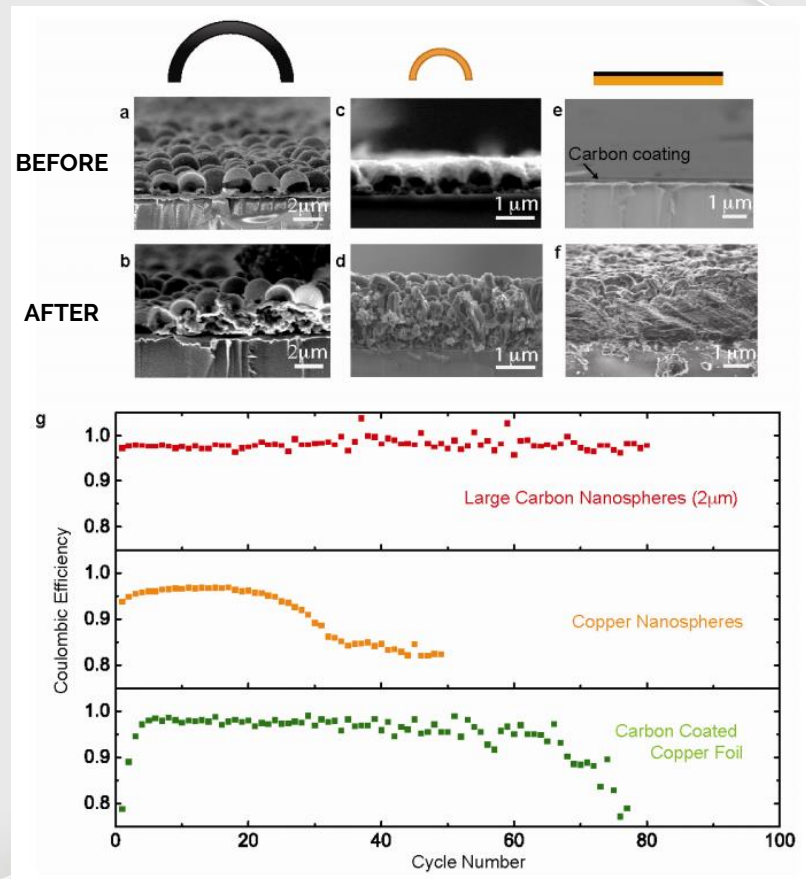


Fig.3

Li DEPOSITION: COMPARISON

SEM image comparison and cycling performance for carbon nanosphere coating tested against similar structures:

- (a, b, red line) Large carbon nanospheres (2 μm diameter): fairly successful
- (c, d, orange line) Copper nanospheres: Cu coating roughens anode surface, aggravating dendrite formation
- (e, f, green line) Carbon-coated Cu foil: no significant improvement from control electrode since film cracks



Supplementary Fig.6

RESULTS

- Experimental conditions:
 - Constant current polarization
 - 30 μl of electrolyte used between coin cells consistently to standardise performance
 - Li plated and stripped at 1 mA cm^{-2}
 - Li metal counter-electrode has excess Li so CE only reflect WE capacity

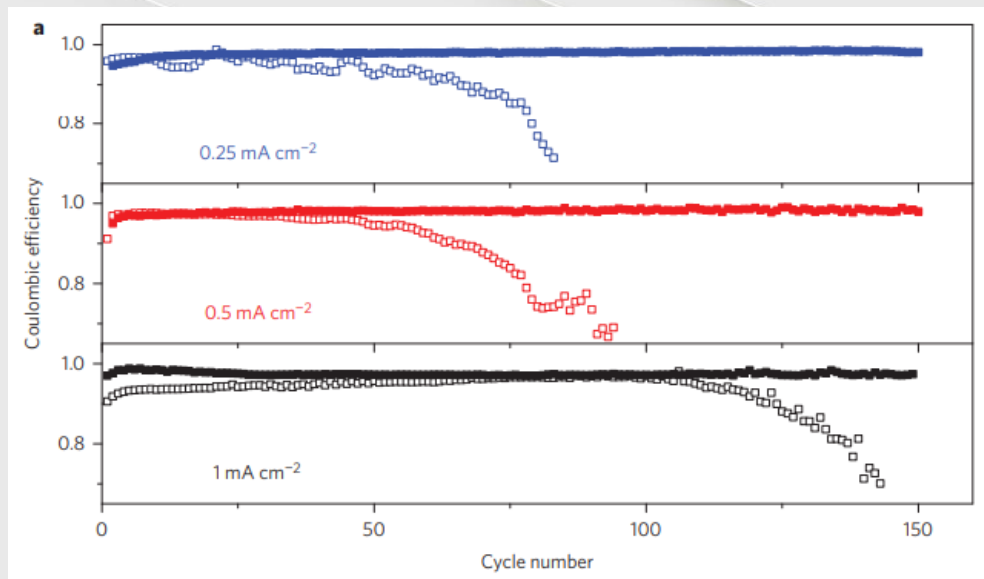


Fig.4

- Significantly improved cycling performance, with CE maintained at:
 - ~99% over 150 cycles at 0.25 mA cm^{-2} (v.s. control < 50% after 100 cycles)
 - ~98.5% over 150 cycles at 0.5 mA cm^{-2} (v.s. control < 50% after 100 cycles)
 - ~97.5% over 150 cycles at 1 mA cm^{-2} (v.s. control < 50% after 150 cycles)

CONCLUSION

Using an interfacial layer of hollow carbon nanosphere allows stable anode cycling up to a practical current density of 1 mAcm^{-2} with an areal capacity of 1 mAhcm^{-2}

Up to 99% CE over 150 cycles (at 1 mAcm^{-2} current density)

Success of this method attributed to:

- More uniform Li deposition under the hollow carbon nanospheres
- More stable SEI formation on top of the spheres
- Reduced of electrolyte decomposition

Looking ahead: improve CE even further to $>99.9\%$ for practical batteries/use electrolyte additives