Lithium-Metal Batteries

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# A Nano-shield Design for Separators to Resist Dendrite Formation in Lithium-Metal Batteries

*Jie Liang*[+], *Qiyuan Chen*[+], *Xiangbiao Liao*[+], *Pengcheng Yao*[+], *Bin Zhu*,* *Guangxin Lv*, *Xinyu Wang*, *Xi Chen*, and *Jia Zhu**

***Abstract:*** *Lithium dendrite growth during repeated charge and discharge cycles of lithium-metal anodes often leads to short-circuiting by puncturing the porous separator. Here, a morphological design, the nano-shield, for separators to resist dendrites is presented. Through both mechanical analysis and experiment, it is revealed that the separator protected by the nano-shield can effectively inhibit the penetration of lithium dendrites owing to the reduced stress intensity generated and therefore mitigate the short circuit of Li metal batteries. More than 110 h of lithium plating life is achieved in cell tests, which is among the longest cycle life of lithium metal anode and five times longer than that of blank separators. This new aspect of morphological and mechanical design not only provides an alternative pathway for extending lifetime of lithium metal anodes, but also sheds light on the role of separator engineering for various electrochemical energy storage devices.*

To meet the increasing demand of portable electronics and electric vehicles, it is critical to develop high-energy-density battery systems.[1] Lithium metal is the most attractive anode candidate for constructing high-energy-density batteries because of its high specific capacity (3860 mAh$g^{-1}$) and low electrochemical reduction potential (−3.04 V versus the standard hydrogen electrode).[2] However, there are many obstacles that hinder its application, such as Li dendrite formation,[3] large volumetric change,[4] and unstable solid electrolyte interface (SEI) during electrochemical cycles.[2c,5] In particular, Li dendrites can easily puncture the polymer separator after several cycles, leading to short-circuiting of the battery (Figure 1 d). The short circuit induced by Li dendrites could further initiate violent reactions between the electrodes and inflammable organic electrolyte, resulting in fire and even explosion.[6] Such potential safety problems severely limit the practical application of Li metal anodes. In the past decades, considerable efforts have been devoted to address the dendrite problems by designing and optimizing chemistry, structure, and engineering materials for electrodes,[7] electrolytes,[8] and their interphases,[9] respectively.

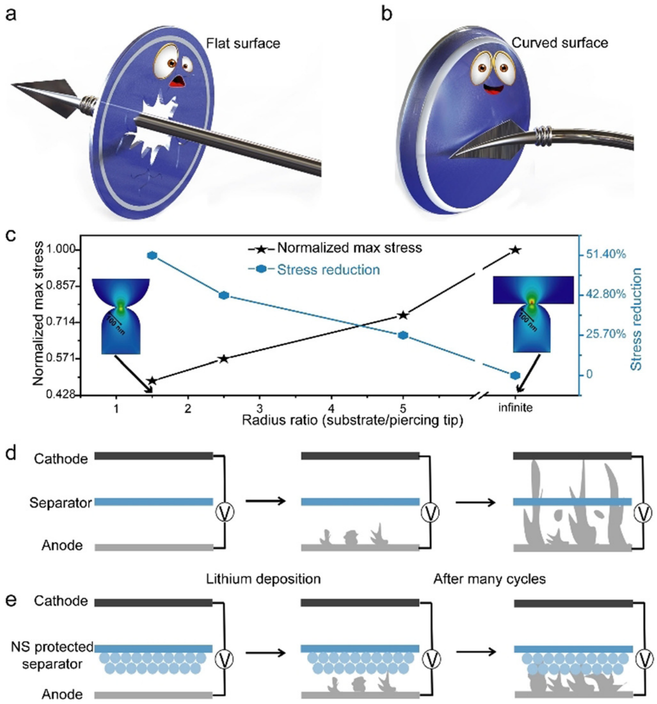


***Figure 1.*** Nano-shield (NS) design for separators to resist dendrite formation. a),b) Representation of shields with a) flat and b) curved surfaces being struck by a spear. c) Different maximum stress intensities and stress reduction by curved surfaces with different radius ratios (substrate/piercing tip), compared with a flat surface, when struck by a sharp tip. Less stress intensity is induced on the surface with larger curvature, especially when radius of shield is comparable to the piercing tip. d),e) Diagrams of Li deposition with d) a blank separator with a separator protected by e) a nano-shield: dendrites can easily puncture the blank separator after many cycles (d), while they can hardly puncture the separator with a nano-shield (e).

Improving the tolerance of the separator toward Li dendrites is considered as a promising way to extend the cycling life of Li metal battery, yet has received little attention.[10] Previous works demonstrated that ceramic particles, including $SiO_2$,[11] $Al_2O_3$,[12] and $TiO_2$[13] could enhance the wettability with organic electrolytes and thermal stability of separators. Liu et al.[11a] reported a novel sandwiched structure (PE/$SiO_2$/PE) as enhanced separators for Li-metal batteries, which delays the time for lithium dendrites to penetrate through the separator, thereby extending the life of battery. However, the morphological design of separators and

[*] J. Liang,[+] Q. Chen,[+] P. Yao,[+] Dr. B. Zhu, G. Lv, X. Wang, Prof. J. Zhu
National Laboratory of Solid State Microstructures
College of Engineering and Applied Sciences
Jiangsu Key Laboratory of Artificial Functional Materials
Nanjing University, Nanjing 210093 (P. R. China)
E-mail: binzhu@nju.edu.cn
jiazhu@nju.edu.cn
X. Liao,[+] X. Chen
Department of Earth and Environmental Engineering
Columbia University
New York, NY 10027 (USA)
[+] These authors contributed equally to this work.
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its influences on Li dendrites growth have not been investigated. Here, inspired from the design of shields, a piece of defensive armor commonly used in ancient warfare, we proposed a nano-shield design for separators. Both theoretical calculation and experiments confirmed that separators protected with this nano-shield can mitigate the short-circuit of Li metal batteries because of superior mechanical advantage.

For the design of a shield, it is well-known that compared to flat shield (Figure 1 a), the curved shield can not only offer more coverage for a soldier's body, but more importantly resist the strike of sharp weapons and even bend the sharp weapons,[14] resulting in less mechanical damage (Figure 1 b). To elucidate the curvature effect quantitatively, we numerically calculated stress levels distribution on surfaces of curved and flat shields against a piercing tip. As shown in Figure 1 c, when a constant displacement perpendicularly applied to the piercing tip, less stress intensity is induced on the substrate with larger curvature. Especially, for the shield with comparable radius as the piercing tip, the stress concentration it received is significantly reduced (less than half) compared to that received by flat shield. Furthermore, eccentrical piercing may deflect the movement of piercing tip and further protect the shield from damage (Supporting Information, Figure S1b). Therefore, it is clear that a curved shield with radius comparable to the piercing tip can effectively disperse interface stress and resist external forces.

Herein, inspired by the design of curved shield and considering the nanosize of lithium dendrites, we proposed that a separator with nano-shield (NS) design can effectively resist the puncturing of Li dendrites, extending the life of Li metal batteries.

It is expected that the design of the nano-shield has two effects on the separator when facing Li dendrites. First, when Li dendrites contact the nano-curved surface of the nano-shield, they will be flicked to change the growth direction other than penetrating the separator. Furthermore, this design of NS also provides the high tortuosity of the narrow channels among coating of $SiO_2$ nanoparticles. This high tortuosity diversifies the pathways for Li dendrite growth, and makes them difficult to penetrate. As a result, it is expected that Li dendrites will grow along the narrow and meandering channels formed by gaps among $SiO_2$ nanoparticles.

With this design of NS protected separators, more than 110 h battery lifespan without short-circuiting is achieved, approximately five times longer than that with traditional blank separator. Without changing either electrodes or electrolytes properties of battery systems, we anticipate that this convenient approach to be compatible and complementary with the other development of Li metal battery materials. Therefore, it opens up tremendous opportunities for advancing commercialization of Li-metal battery systems such as Li-air and Li-S batteries.

To realize this design of nano-shield, $SiO_2$ nanoparticles with diameters of 500 nm were chosen to be spin-coated on commercial polyolefin separators (see the Experimental Section). There are a few unique advantages for $SiO_2$ nanoparticles to construct a nanoshield. First, $SiO_2$ nanoparticles are common, low-cost, and easy to tune the appropriate radius. We chose $SiO_2$ nanoparticles with 500 nm diameter as a nano-shield, which is about twice the diameter of Li dendrites (200–300 nm),[15] which can minimize the formed stress according to the above calculation results (Figure 1 c). Second, the oxygen atom of $SiO_2$ has stronger electron-withdrawing property than other atoms of polymer separator, which forms stronger interaction force with electrolytes. Thus, $SiO_2$ can enhance the wettability between separator and electrolyte, which is critical for the performance of battery. Furthermore, as a ceramic material, $SiO_2$ has a good mechanical property and chemical stability,[11d,f] while it is easy to fabricate $SiO_2$-based nano-shield through the simple spin-coating method.

There is a notable morphology comparison between bare separator and NS protected separator (Figure 2 a,b). It is clear that about two layers of tightly arrayed $SiO_2$ nanoparticles with the thickness of about 1 μm are laid on the separator, suggesting the precise diameter of $SiO_2$ nanoparticles for

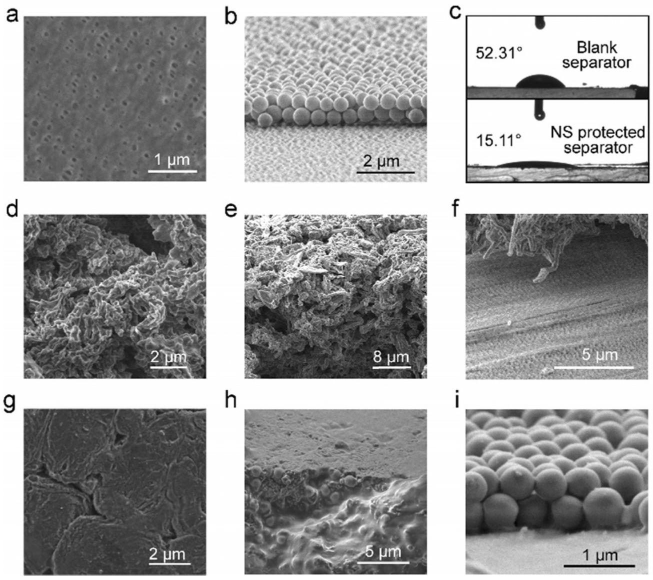


*Figure 2.* SEM images of the separators (blank/NS protected) and Li electrodes before and after cycles. a) Blank separator from top view and b) NS protected separators with $SiO_2$ spheres. c) Results of contact angle test: NS protected separator has smaller contact angle (15.11°) than blank separator (52.31°). d),e) Li foil showed many dendrites formed from top view and cross-section view after 200 cycles with blank separator. f) Blank separator against dendrites after 200 cycles. g),h) SEM images of Li foil from g) top view and h) cross-sectional view, demonstrating that Li foil was flat with few dendrites after 200 cycles with NS protected separators. i) NS protected separator with $SiO_2$ nanoparticles kept well and intact after 200 cycles.

500 nm. To investigate the wettability between electrolyte and separator, the electrolyte contact-angle tests were performed for a blank separator and a NS protected separator, respectively (Figure 2 c). The NS protected separator with $SiO_2$ nanoparticle covering presents a wetting angle of 15.11°, which is much smaller than that of blank separators (52.31°). The smaller wetting angle of the NS protected separator indicates that the NS protected separators with $SiO_2$ spheres

possess a better affinity with electrolyte than that of blank separators, which is beneficial for ion transport. We also tested the electrochemical impedance spectroscopy (EIS) for blank and NS protected separator. It is found that the corresponding resistance for the NS protected separator is about 3.5 Ohm, which is even lower than that of blank separator (5 Ohm; Supporting Information, Figure S2a). It is suggested that the resistance of separators does not increase significantly because of the NS protective layers. To further investigate the electrochemical stability of the $SiO_2$ nanoparticles, cyclic voltammetry test was carried out (Supporting Information, Figure S3).

To establish the function of NS during cycling, the morphological changes of Li foil and separators before/after 200 cycles were carefully characterized by SEM. After Li stripping/plating for 200 cycles, clear dendrite-like morphology of Li foil from cells with blank separators can be observed from the top view (Figure 2d) and side view (Figure 2e). In contrast, Li foil from cells with separators protected by NS presented a rather flat and smooth surface without obvious dendrites (Figure 2g,h). The distinctive morphological change of Li foil from different cells demonstrated that our NS layers effectively suppress the growth of Li dendrites during Li stripping/plating cycles. Furthermore, we can see that after 200 cycles, the separator with NS still maintained the $SiO_2$ nanoparticles closely packed without Li dendrites on it (Figure 2i). As for the blank separator, residual Li dendrites were clearly observed (Figure 2f).

To demonstrate the electrochemical performance improvement brought by NS protective layers, symmetric Li/Li coin cells with different separators were assembled and we conducted galvanostatic cycling tests under various current densities for 1 mAh cm$^{-2}$ Li deposition. Figure 3a–c show the voltage profiles of cells with blank and NS protected separators. At 0.25 mA cm$^{-2}$, stable cycling with low overpotential of about 80 mV and flat voltage plateaus was achieved for over 350 h. In comparison, the cell with blank separator shows a much more unstable overpotential variation during cycling (Figure 3a). When increasing the current density to 1 mA cm$^{-2}$ (Figure 3b), the cycling stability of cells with blank and NS protected separator diverged much more, where NS protected separator cell still afforded stable cycling with low overpotential but the blank exhibited significantly unstable voltage profiles. Even at 3 mA cm$^{-2}$ for higher areal capacity of 3 mAh cm$^{-2}$ (Figure 3c), cell with blank separator was short circuited soon, but the cell with NS protected separator kept stable over 400 h. It clearly illustrates that the NS-protected separator design can significantly improve the electrochemical performance of Li metal anode. Furthermore, from the EIS result (Supporting Information, Figure S2b), the impedance of cell with NS protected separator was also lower than that with blank separator, which can be attributed to a more stable cycling. Furthermore, a full cell test was also operated with blank/NS protected separators by using $LiFePO_4$ as the cathode, whereas the full cell with NS protected separator exhibits good cycle performance (Supporting Information, Figure S8). A comparison of this full cell performance with current, state-of-art works, illustrating the effectivity of our NS design, is presented in the Supporting Information, Table S1. In comparison with the used size and morphology of $SiO_2$ particles, we also carried out experiments in cells with separators protected by $SiO_2$ spheres of 1 μm diameter and 80 nm-thick $SiO_2$ film. It is seen that the cells with separator protected by

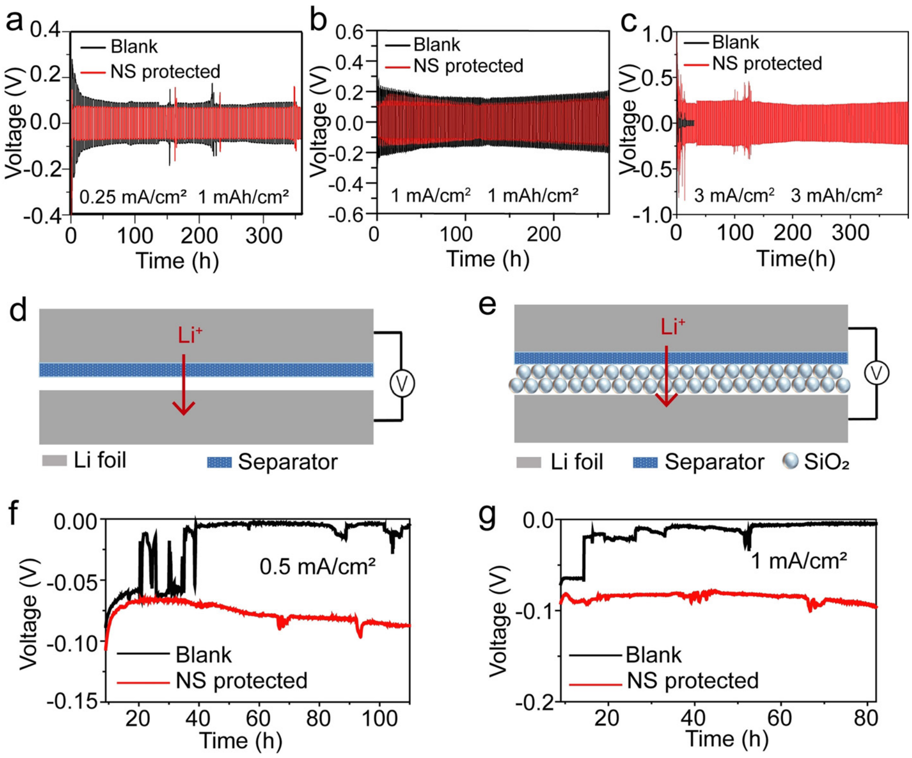


*Figure 3.* Electrochemical performance comparison of Li/Li symmetric cells with blank or NS protected separators. a)–c) Galvanostatic charge–discharge cycles at a) 0.25 mA cm$^{-2}$ 1 mAh cm$^{-2}$, b) 1 mA cm$^{-2}$ 1 mAh cm$^{-2}$, and c) 3 mA cm$^{-2}$ 3 mAh cm$^{-2}$: cells with NS protected separator exhibited more stable overpotential variation and lower overpotential at low current density than cells with blank separator, and at higher current density and areal capacity, cells with NS protected separator remained stable over 400 h while the blank went to short-circuit much earlier. d),e) Diagrams of Li/Li symmetrical cells used for long-time galvanostatic discharge tests: d) cells with blank separators, e) cells with NS protected separators. f),g) Voltage–time charts of cells with NS protected and blank separators at f) 0.5 mA cm$^{-2}$ and g) 1 mA cm$^{-2}$ during a long-time discharge experiment: cells with blank separator have been internally shorted after 23 h at 0.5 mA cm$^{-2}$ and after 14 h at 1 mA cm$^{-2}$, however cells with NS protected separator keep away from short-circuit for more than 110 h and 80 h, respectively.

larger diameter $SiO_2$ of 1 μm performed growing overpotential after repeated cycling at 1 mA cm$^{-2}$ and show short-circuiting after 280 h at 2 mA cm$^{-2}$ (Supporting Information, Figure S6b,c). For the cells with separators coated by flat $SiO_2$ layer with 80 nm thickness (Supporting Information, Figure S7b), at 1 mA cm$^{-2}$ the overpotential was not stable and generated short circuit only after 80 h. Combined with the above results, it clearly suggests that the spherical $SiO_2$ particles with 500 nm diameter is better.

To directly verify the dendrites-resisted effect of NS protected separators, a long time galvanostatic discharge was investigated with blank and NS protected separators in Li/Li symmetric cells, examining how long it takes to cause short circuit as the Li dendrites grow to puncture the separators (representations are depicted in Figure 3 d,e). Figure 3 f and Figure 3 g show the voltage profiles of different cells with blank/NS protected separators under the current densities of 0.5 mA cm$^{-2}$ and 1 mA cm$^{-2}$, respectively. When discharging at 0.5 mA cm$^{-2}$, after about 23 h, the voltage plateau of blank separator suddenly dropped from about 60 mV to nearly 10 mV, indicating that the cell has been internally shorted by Li dendrites (Figure 3 f). For comparison, the cell with blank separator sustained an even shorter life at 1 mA cm$^{-2}$, only after about 14 h the short circuit occurred (Figure 3 g). On the contrary, when the cell with NS protected separator discharged at 0.5 and 1 mA cm$^{-2}$, the life can be extended to more than 110 h and 80 h, respectively, without any short circuit observed (Figure 3 f,g), which is among the longest cycle life of Li metal anodes.[6c,10a] The five times longer lifespan obtained of NS protected separator obviously manifests that our design can effectively resist Li dendrite to mitigate short circuit. The Li foil morphology and the NS protected separator of the samples in Figure 3 g after the long time galvanostatic discharge are shown in the Supporting Information, Figure S10, which further suggests the suppression of Li dendrites growth with this NS design.

To clearly demonstrate the short circuit performance of blank separator and Li dendrite-resisted phenomenon of NS protected separator, in situ optical microscopy was employed to record the growth process of Li dendrites faced to a blank/NS protected separator during Li electrochemical deposition at constant current. To examine the dendrites growth in an optical microscope, we fabricated a special transparent cell (Figure 4 a,b), which was constructed by placing two Li foils on the Cu current collectors with one cladded with blank/NS protected separator. We investigated the dendrite-resisted performance of two separator from the top view of the transparent cell. Both Li deposition experiments were carried out under a current density of 10 mA cm$^{-2}$.

As depicted in Figure 4 c,d, with the continuous growth of dendrites, the blank separator was pierced and dendrites (highlighted by red circle in Figure 4 c) grew out through that hole after Li deposition at 100 min. Soon afterwards, the cell was short-circuited at 107 min, from dendrites contacting with the counter Li electrode. In contrast, the NS protected separator still stayed intact at 100 min as illustrated in Figure 4 d. Even after 270 min, none of dendrites piercing the NS protected separator was observed, indicating that our design is able to withstand the forces of dendrites growth rather than easily being impaled. Owing to the stripping of Li metal, the distance between separator and Li metal surface slightly increased after long time deposition. The in situ experiment results have shown that the NS protected separators possess an extraordinary ability to suppress Li dendrites growth and effectively mitigate short circuit.

To explore the process of how nano-shield protected separator effectively mitigates short circuit, phase-field simulations were carried out to model Li plating at the current density of 20 mA cm$^{-2}$. Figure 5 a shows the growth of Li

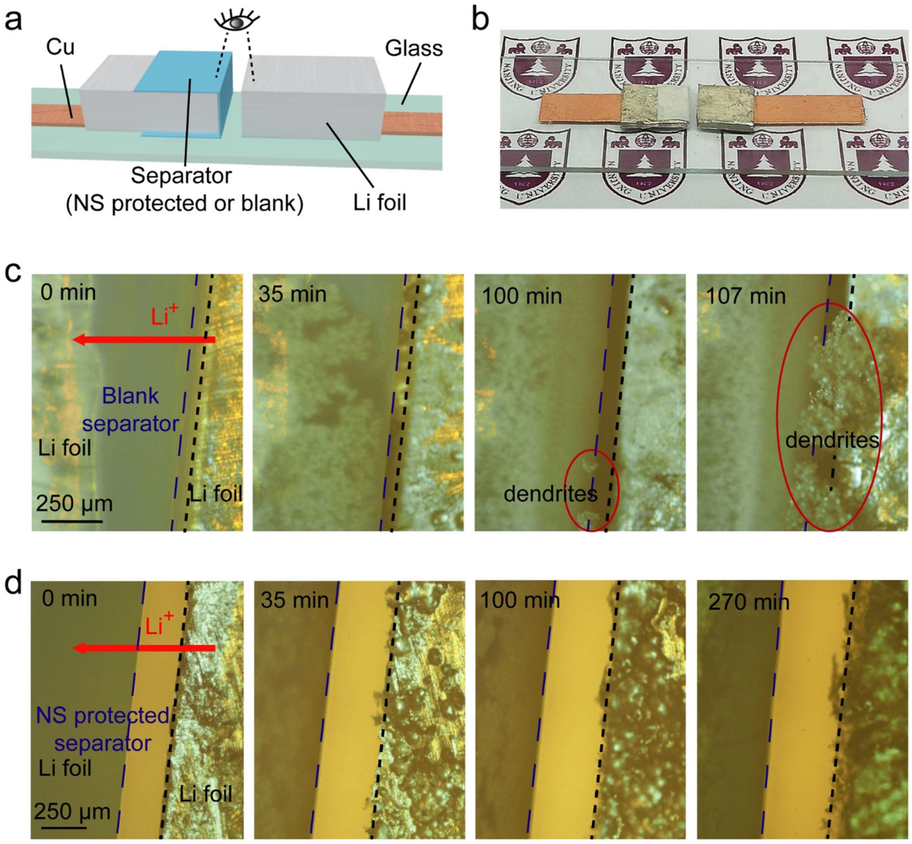


***Figure 4.*** In situ observation of the Li dendrite growth process. a) Representation and b) photograph of transparent Li/Li symmetrical cells for in situ investigation; c),d) Optical photographs (top view) of the discharged Li metal wrapped by separator c) with blank separator and d) with NS protected separator: dendrites grew to pierce the blank separator at 100 min and kept growing at 107 min (highlighted by red circles in c); while the decorated separator was not pierced by dendrites even after 270 min (d).

  

dendrites after plating for 1 s. As shown in Figure 5b, because the Li ions transport more slowly than electrons, concentration polarization occurred. Li dendrites can grow freely without the block of protective layers at a speed of $10\,\mu m\,min^{-1}$. On the other hand, separators with nanoparticles (500 nm diameter) NS protected can reduce the chance to form long dendrite to penetrate separator. Though concentration polarization is more severe than that with blank separator, tips of sharp dendrites are deflected once contacting with the curved surface of nanoparticle, and the high tortuosity provided by curved and narrow channels between $SiO_2$ nanoparticles increases the length of pathway for Li dendrites to grow, which protect the separator behind the layers of nanoparticles from puncturing. Figure 5c illustrates that for the battery with NS protected separator, the Li dendrites grow much more slowly after plating for 1 s. Even for 2 s (Figure 5e), the growth of Li dendrites is less than that with blank separator for 1 s. The corresponding modeling of

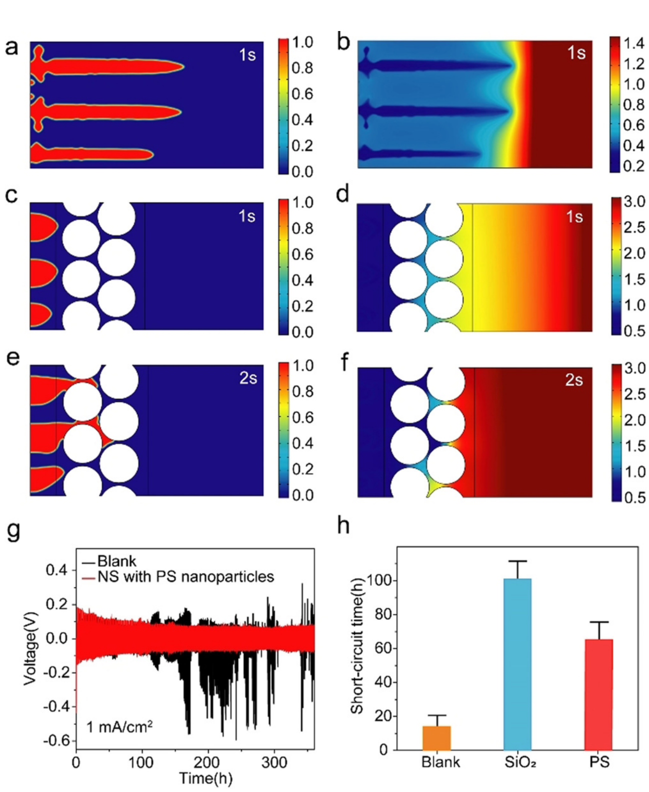


*Figure 5.* Simulation of Li dendrites growth with blank/NS protected separators. a)–f) Finite element simulations: a) the free and fast growth of Li dendrites against blank separator after Li plating for 1 s; b) the concentration distribution of Li ion after Li plating for 1 s with blank separator; c) the suppressed growth of Li dendrites against NS protected separator after Li plating for 1 s; d) the concentration distribution of Li ion after Li plating for 1 s with NS protected separator; e) the restricted growth of Li dendrites through the narrow channels among spheres after Li plating for 2 s; f) the concentration distribution of Li ion after Li plating for 2 s with NS protected separator; g),h) Electrochemical performance comparison of Li/Li symmetric cells with blank or PS nanoparticles NS protected separators: g) cell with PS nanoparticles NS protected was more stable during galvanostatic charge-discharge cycles and h) long-time discharge lifetime comparison among different NS protected separators.

Li ion concentration confirms it. SEM images of NS protected separators taken after cycles (Supporting Information, Figure S11) also provide obvious confirmation of the specific changes of Li dendrites growth. Dendrites were attached to the protective layer (Supporting Information, Figure S11a), and tips had been bent owing to the role of the shield-like layers, which elucidated by the simulation above. Furthermore, the remained Li particles in the channels between $SiO_2$ indicate our design successfully resist dendrites for mitigating short circuit (Supporting Information, Figure S11b).

As nano-shield is a generalized design, it can be applied to various other materials systems, such as polystyrene (PS) nanoparticles. It is found that cells with PS NS protected separators also exhibited stable cycle performance over 350 h, under a current density of $1\,mA\,cm^{-2}$ (Figure 5g). Furthermore, cells with PS NS protected separators exhibit a long lifetime without short-circuit during the long-time discharge experiment like $SiO_2$, which is more than three times longer than that of blank separator (Supporting Information, Figure S12). Figure 5h presents the average battery lifetime with different separators, clearly suggesting that our design of shield-like separator is remarkably effective for mitigating the short circuit of Li metal batteries.

In summary, inspired by a curved shield, we provide a nano-shield design for the separator of the lithium metal battery. Both theoretical simulation and experiment demonstrated that this nano-shield protected separator can effectively suppress the Li dendrites growth and mitigate the short-circuiting by reduced stress intensity owing to the curved surface effect and the increased growth pathway for Li dendrites because of the formed narrow channels. Separators protected by the nano-shield can validly extend the life of a charging test more than 110 h without short circuit, which is over five times longer than that of blank separators. This approach based on separator engineering is compatible with other developments of electrode/electrolyte modifications, which exhibits a great potential towards the development of high-energy-density storage systems.

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## Conflict of interest

The authors declare no conflict of interest.

  

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