A lithium passivated MoO₃ nanobelt decorated polypropylene separator for fast-charging long-life Li–S batteries†

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Dissolution of lithium polysulfide (LiPS) into the electrolyte during discharging, causing shuttling of LiPS from the cathode to the lithium (Li) metal, is mainly responsible for the capacity decay and short battery life of lithium–sulfur batteries (LSBs). Herein, we designed a separator comprising polypropylene (PP) coated with MoO₃ nanobelts (MNBs), prepared through facile grinding of commercial MoO₃ powder. The formation of LiS₈+MoO₃ during discharging inhibited the polysulfide shuttling; during charging, Li passivated Li₂MoO₃ facilitated ionic transfer during the redox reaction by decreasing the charge transfer resistance. This dual-interaction mechanism of LiPS—with both Mo and the formation of Li₂MoO₃—resulted in a substantially high initial discharge capacity at a very high current density of 5C, with 29.4% of the capacity retained after 5000 cycles. The simple fabrication approach and extraordinary cycle life observed when using this MNB-coated separator suggest a scalable solution for future commercialization of LSBs.

Introduction

Research into new high-energy batteries is thriving with the ever-growing worldwide demand for energy. In particular, lithium ion batteries (LIBs) are attracting most attention because their capacities are higher than those of conventional lead-acid and nickel-cadmium batteries.1,2 Many metal oxides, including LiCoO₂, LiFePO₄, V₂O₅, LiNiO₂, and LiMnO₂, have been used in LIBs as cathode materials, but, due to their low capacity (<300 mA h g⁻¹), next-generation battery research is seeking alternative high-capacity cathode materials.3–8 A high theoretical capacity of 1675 mA h g⁻¹, low cost, and abundance in nature have made sulfur a promising cathode material.9 Nevertheless, shuttling effects, the insulating nature of sulfur, and the large volumetric expansion of the active material upon discharging combine to result in low gravimetric energy densities and a short cycle life that has impeded the commercialization of lithium–sulfur batteries (LSBs).3,10 The formation of soluble LiPS (Li₂S₈; 3 < n ≤ 8) on the cathode side during the electrochemical reaction leads to an undesirable phenomenon known as shuttling. During the discharge process, the nucleophilic and soluble LiPS (Li₂S₈; 3 < n ≤ 8) can dissolve in the electrolyte and then undergo reduction to form lower-order non-conductive solid precipitates (e.g., Li₃S and Li₂S₂) on top of the anode, leading to the loss of the active material, a decrease in coulombic efficiency, a short cycle life, and a dramatic decay in the capacity of LSBs.11,12

To restrict the loss of the active material and increase the stability of LSBs, the shuttling effect should be curtailed by confining the polysulfides to the cathode side. Various techniques have been applied previously to modify the cathode such that it would act as an adsorbent of the polysulfides.13–20 Nevertheless, because of the large volume expansion of sulfur (by 80% during the discharge process), structural modification tends to have only a limited effect during a long cycling period. As a result, the focus has been shifted in recent years toward the modification of the separator, rather than that of the cathode, to improve the LSB performance.20–30 For example, Ghazi et al. deposited a highly Li⁺-conductive layer of MoS₂ onto a commercial separator through filtration of MoS₂ sheets; because MoS₂ interacts strongly with LiPS, the system exhibited a promising decay
in capacity of only 0.083% per cycle. Liu et al. reported a regenerative polysulfide-scavenging layer (RLS) comprising a layer of carbon nanotubes decorated with vanadium oxide nanowires; this RLS/polypropylene separator not only mitigated the shuttling effect but also provided a high gravimetric energy density of 365 W h kg\(^{-1}\). Zhou et al. prepared a heterogeneous structure of graphene and titanium carbide on the separator; it functioned well as both a LiPS binder and shuttling mitigator.

Abbas et al. coated an activated expanded graphite/chitosan (AEG/CH) composite onto the separator; here, the AEG interacted physically with the LiPS, with the CH helping the AEG bind to the separator while also interacting chemically with the LiPS; this structure formed a highly stable LSB for up to 3000 cycles, at a decay rate of 0.021% per cycle.

In this present study, we suppressed the shuttling effect and facilitated the redox transformation of LiPS back to sulfur by using a functional separator that featured a coating of MoO\(_3\) nanobelts (MNBs) facing the cathode side of a polypropylene (PP) separator. Two types of interactions occurred in this system: (i) interactions of Li\(^+\) ions with MoO\(_3\) to form Li\(_x\)MoO\(_3\), which is metallic in nature, observed using X-ray diffraction (XRD), further decreasing the internal resistance within the electrodes; (ii) the Mo atoms in MoO\(_3\) interacting with LiPS, confirmed using X-ray photoelectron spectroscopy (XPS). This dual-interaction mechanism was beneficial for the binding of LiPS to the cathode side of the separator; furthermore, live discharging of the sulfur cathode in an H-cell revealed that the MNB-coated separator was efficient at stopping the polysulfide shuttle. The use of the MNB-coated separator led to an excellent retention of capacity of 29.4% after 5000 cycles, with a decay rate of only 0.014% per cycle at the 5C rate (1C = 1675 mA h g\(^{-1}\)).

**Experimental**

**Material preparation**

MoO\(_3\) powder (99.5%, Sigma-Aldrich) was mixed with isopropyl alcohol (IPA, Sigma-Aldrich, 100 mL) at a concentration of 2 wt%. Approximately 50% of the grinding chamber was filled with micrometer-sized zirconia beads (bead size: 100 µm; density: 5.95 g cm\(^{-3}\); 600 g) and the remaining volume contained a suspension of particles to be ground. The mixture was stirred, using an electric stirrer, for 2 h at a rotation speed of 2000 rpm. The resultant dark-blue dispersion was purified without any contamination of zirconia beads, which precipitated rapidly after grinding to the bottom of the container, due to their high density. The as-prepared MNBs were mixed in IPA at a concentration of 1 wt% and spray-coated, using a spray gun, on one side of a polypropylene separator (BenQ, Taiwan). The MNBs were coated onto the separator at mass loadings of 0.1, 0.5, and 0.8 mg cm\(^{-2}\).

**Characterization**

An FEI Nova 200 scanning electron microscope was employed to observe the morphology of the MoO\(_3\) particles and the as-prepared MNBs. The crystallinity was characterized using X-ray diffraction (XRD, XPert3 Powder, PAN analytical) and Raman spectroscopy (Horiba Jobin Yvon HR-800). Tapping-mode atomic force microscopy (AFM, Veeco di Innovia) was employed to characterize the morphology of the MNBs. A JacobsV-670 UV–Vis spectrometer was employed to confirm the presence of absorption peaks of the polysulfides in the electrolyte.

**Electrochemical measurements**

A sulfur-loaded (1.5 mg cm\(^{-2}\)) cathode was prepared after infusing sulfur into expanded graphite flakes, following a procedure described previously. Next, 10 wt% carbon black and 10 wt% poly(vinylidene fluoride) (PVDF) were added in 80 wt% sulfur-expanded graphite (S-EG; i.e., 80% was sulfur and 20% was EG). The whole composition was subjected to ball-milling for 3 h in N-methyl-2-pyrrolidinone (NMP) to obtain a slurry, which was coated onto aluminum foil using a doctor blade. The film was dried at 50 °C overnight and then cut into a disk having a diameter of 12 mm. A lithium metal disk of 12 mm diameter was used as the anode. The electrolyte was prepared by adding 1 wt% LiNO\(_3\) to 1 M bis(trifluoromethane)sulfonamide lithium (LiTFSI) in dimethoxyethane (DME) and dioxolane (DOL) mixed in a 1:1 (v/v) ratio. 40 µL electrolyte was added to assemble the LSB while maintaining the electrolyte/sulfur ratio of 26.7 µL g\(^{-1}\). A pristine separator and an MNB-coated separator were used to assemble coin cells (CR2032) inside an argon (Ar)-filled glove box, in which the water and oxygen concentrations were maintained below 0.5 ppm. Galvanostatic cycling of the as-prepared LSBs was performed using an AcuTec system (Taiwan). Prior to the start of each galvanostatic charge/discharge measurement, each cell was activated at a current of 100 mA h g\(^{-1}\) for a few cycles. A potentiostat/galvanostat (Autolab PGSTAT302N, Eco Chemie) was used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). For EIS measurements, the frequency range extended from 0.01 Hz to 100 kHz, with an amplitude of 5 mV. CV tests were performed in a voltage window of 1.5–3 V, at a scan rate of 0.1 mV s\(^{-1}\). H-cell tests were performed to observe polysulfide diffusion through the pristine and modified separators. Lithium foil was used as an anode, maintained on one side of the cell, with the cathode on another cell, and the separator between the two cells. Later, both cells were filled with the electrolyte. H-cell discharge was performed at a rate of 0.1C (1C = 1675 mA h g\(^{-1}\)) in a voltage window of 1.5–3 V.

**Density functional theory (DFT) calculations**

The total energies and electronic structures of Li\(_2\)S\(_n\)-MoO\(_3\) systems were calculated using the Vienna **ab initio** simulation package (VASP), a plane-wave, pseudopotential package based on DFT. The ion–electron interaction was modeled using the PAW-PBE pseudopotential. The kinetic-energy cutoff was set at 400 eV, and the convergence criteria were set at 1 × 10\(^{-5}\) eV for SCF and 1 × 10\(^{-7}\) eV for energy. Population analyses were used to evaluate the charge redistribution. The electric field effect was also taken into account, using a saw-tooth
potential. Li₂S₈ and Li₂S₄ molecules were placed on the surface of a MoO₃ monolayer in this study.

Results and discussion

MoO₃ powder was ground in a mechanical grinder using zirconia beads (Fig. S1, ESI†); this mechanical process transformed the MoO₃ particles into a new microstructure. The bulk powder (Fig. 1a) was converted into nanobelts having widths of 100–200 nm and an average length of 2 µm (Fig. 1a and b). A thickness histogram of 50 different MNBs revealed that the majority of the MNBs had an average height of less than 8 nm (Fig. S2, ESI†). During the grinding process, hot spots were generated within the zirconia beads, where the temperature and pressure were maximized.35,39–41 Inside these hot spots, the MoO₃ was squeezed between two zirconia beads or between a bead and the wall of the grinder, resulting in mechanical cleavage of the bulk material. Shear and plastic deformation processes within the sample led to changes in the size and shape of the MoO₃.42 The resulting orthorhombic crystallized MNBs exhibited sharp diffraction peaks for the (110), (040) and (021) planes, confirming the presence of α-MoO₃ (Fig. 3a).43 Thus, the MoO₃ maintained a similar crystal structure and phase after its mechanical grinding. Sharp Raman spectral signals at 663, 817, and 991 cm⁻¹ confirmed the presence of α-MoO₃ (Fig. S3, ESI†).43 The as-prepared MNBs were dispersed into an isopropyl alcohol (IPA) solution and spray-coated to form a continuous film on the PP separator (Fig. S5a and S6, ESI†). In order to investigate the adhesion of the as-coated MNBs on top of the PP separator, the MNB coated separator bent at different angles and captured the images. Fig. S6b–d† show the MNB coated separator under different bending and folding conditions, and when it was unfolded (Fig. S6e†) the MNB-coated separator still shows a uniform coating, which further proves its good adhesion. Cross-sectional imaging revealed that the thickness of the coating of MNBs on top of the separator was approximately 1 µm (Fig. 1c). Fig. 1d provides a schematic representation of the spray-coating process of the MNB solution onto the PP separator, while Fig. 1e provides a schematic representation of an LSB incorporating an MNB-coated separator facing the cathode and its interactions with LiPS that inhibit the polysulfides from travelling toward the anode side.

A polysulfide diffusion test was performed in an H-cell to investigate the LiPS mitigation effect of the MNB-coated separator (Fig. 2). Lithium foil was placed in one cell (left side) and the cathode in the other (right side); between them was positioned either a pristine separator or a MNB-coated separator; the two cells were filled with the electrolyte. In the first

Fig. 1  (a) FESEM images of MNBs prepared by grinding (inset: commercial MoO₃). (b) AFM height image of a typical NB (inset: height profile of the NB). (c) Cross-sectional SEM image of an MNB-coated PP separator. (d) Schematic representation of the spray-coating of an MNB solution onto a PP separator. (e) Schematic representation of an LSB incorporating an MNB-coated separator and its trapping of polysulfides.
The pristine separator was positioned between the two cells; in the second, the MNB-coated separator was positioned facing the cathode, under identical experimental conditions. As time elapsed, polysulfide diffusion was observed and captured photographically. When using the pristine separator, the polysulfides began to diffuse through the separator after 30 min, as shown in Fig. 2a; after 60 min, the polysulfides were clearly visible on the left side; after 120 min, the left-hand-side electrolyte turned brownish-red, revealing the presence of polysulfides in the electrolyte. When using the modified separator, there was almost no change in the color of the electrolyte after 60 or 120 min (Fig. 2b); indeed, it took 5 h for a noticeable change, to brownish-red, in the color of the electrolyte on the left-hand side of the H-cell. Thus, the MNB-coated separator displayed excellent performance in mitigating the diffusion of the polysulfide through the separator. Video footage revealed the motion of LiPS diffusion when using the pristine separator (Media S1, ESI†) and LiPS shuttling when using the MNB-coated separator (Media S2, ESI†). After diffusion of the LiPS through the separator, the brownish-red LiPS solution was collected for UV–Vis spectral analysis. The UV–Vis absorption spectrum (Fig. 2c) featured a signal between 420 and 500 nm, consistent with a long-range LiPS, while the pristine electrolyte does not show any noticeable change in the UV–Vis spectra. This demonstration suggested that the MNB-coated separator might also suppress LiPS diffusion in LSBs. Fig. 2d presents a typical discharge voltage profile recorded while performing an H-cell diffusion test. At stage “a”, the cell began to discharge ($S_0$); the further stages confirmed the formation of soluble long-range and insoluble short-range polysulfides. Stages “a” to “c” are consistent with the formation of long-range polysulfides (e.g., $Li_2S_8, Li_2S_6$), while stages “c” to “e” suggest the formation of short-range polysulfides (e.g., $Li_2S_2, Li_2S$).

During the initial discharging of the battery, $Li^+$ ions would occupy the deep hollow sites of the Mo framework (Fig. S9, ESI†), resulting in the formation of $Li_xMoO_3$ ($Li_2MoO_3$). To investigate the presence of $Li_2MoO_3$ on top of the modified separator, a Li–S coin cell was dissembled inside a glove box after one discharge/charge cycle; the resulting XRD pattern confirmed the presence of $Li_xMoO_3$ on top of the MNB-coated separator (Fig. 3a). Lithium ions would be passivated on the surface of MNBs, rather than diffusing into the structure. Being metallic in nature, $Li_2MoO_3$ resulted in a rapid and smooth movement of $Li^+$ ions within the electrodes, leading to a decrease in the charge transfer resistance ($R_{ct}$) to
when using the MNB-coated separator, relative to that obtained (194 Ω) using the pristine separator (Fig. 3b). In the Nyquist plot, an additional large semi-circle appears for the LSB containing the MNB-coated separator. Until the end of the discharge process, the dimensions of the semi-circle continued to increase, indicating an increase in resistance within the cell resulting from the modified separator intercepting the LiPS units. Upon increasing the density of discharge, the formation of non-conductive/low-electrical-conductivity LiPS (especially Li2S) increased, with conglomerates being formed on the surface of the modified separator. Furthermore, XPS analysis of the separator after one discharge/charge cycle provided evidence for a second interaction mechanism of Mo with LiPS. The XPS spectra revealed (Fig. 4d) the changes in the binding energies of the Mo 3d orbitals after discharging the battery: the Mo 3d_{5/2} and 3d_{3/2} binding energies shifted from 232.4 to 231.9 eV and from 235.5 to 235.0 eV, respectively. The lower binding energies are indicative of interactions between the Mo atoms of MoO3 with the LiPS during the discharge process. To evaluate the surface diffusion of Li on Li2MoO3, a nudged elastic band (NEB) calculation was performed. The Li atoms moved from the shallow hollow sites to the bridge sites.
the charge redistributions of Li$_2$S$_8$/MoO$_3$ and Li$_2$S$_4$/MoO$_3$ and the total energy decreased after Li$_2$S$_8$ had attached to MoO$_3$. Furthermore, the total energy evolution of the resulting structures revealed that during the discharge process, Li$_2$S$_8$ would attach to the surface of MoO$_3$, forming Li-O bonds and changing the shape of the S$_8$ units (as adsorption, Fig. 4b). The central transition metal Mo (+6) was aggregated MNBs changed the conductivity from non-conductive to metallic. The two reduction peaks near 2.3 and 2.1 V correspond to the reduction of cyclooctasulfur (S$_8$) to soluble long-range LiPS (Li$_2$S$_n$) and Li$_2$S$_4$/MoO$_3$ systems when applying different charges. Significant charge transfer from Li to O occurred after adsorption, mainly resulting from the difference in electronegativity, in the Li$_2$S$_8$/MoO$_3$ system. In a system with positive charges, Li would tend to be more positive and, indeed, a significant charge transfer was observed. The behavior in the Li$_2$S$_8$/MoO$_3$ system was similar to that in the Li$_2$S$_4$/MoO$_3$ system, but with fewer electrons transferred from Li to O. The insertion of Li$^+$ ions into the aggregated MNBs changed the conductivity from non-conductive to metallic. The central transition metal Mo (+6) was reduced once Li$^+$ ions were incorporated into the MNB layer structure. As mentioned earlier, a very large binding energy between Li and MoO$_3$ was observed, indicating that Li would passivate MoO$_3$ instead of undergoing surface diffusion. Furthermore, XPS was performed to investigate the interactions between MoO$_3$ and the LiPS. Prior to performing the cycling process, the two fitted signals at 232.4 and 235.5 eV were characteristic of the spin–orbit splitting doublet of Mo 3d$_{5/2}$ and 3d$_{3/2}$ (Fig. 4d). After cycling, the binding energy shifted by 0.5 eV, presumably because of the strong interactions between the LiPS and the MNBs. The XPS signal at 229.8 eV suggested the presence of Mo–S bonds, further evidencing the chemical interactions between the polysulfides and MNBs.

Fig. 5a presents the cyclic voltammetry (CV) traces of a Li-S cell incorporating the MNB-coated separator during its first five discharge/charge cycles within a voltage window of 1.5–3 V, recorded at a scan rate of 0.1 mV s$^{-1}$. The two reduction peaks near 2.3 and 2.1 V correspond to the reduction of cyclooctasulfur (S$_8$) to soluble long-range LiPS (Li$_2$S$_n$, $3 \leq n \leq 8$) and to the further reduction of longer LiPS to insoluble lower LiPS (Li$_2$S$_4$/Li$_2$S), respectively. The oxidation peak near 2.5 V corresponds to the transformation of LiPS to sulfur. The complete overlapping of the reduction and oxidation peaks and the sharpness of these peaks suggest the high reversibility and fast kinetics of the electrochemical reactions. To investigate the rate performance of an LSB incorporating the MNB-coated separator, the cell was discharged at different C-rates, starting at 0.5C and followed by 2.5C, 5C, 7.5C, and 10C, then finally returning to 0.5C (Fig. 5b). Initially, at 0.5C, the cell exhibited a discharge capacity of 872 mA h g$^{-1}$; later, at 2.5C, 5C, 7.5C, and 10C, the Li-S cell discharged with capacities of 670, 605, 520, and 446 mA h g$^{-1}$, respectively. When the current was reverted to 0.5C, the cell exhibited a discharge capacity of 745 mA h g$^{-1}$, corresponding to 85.6% of its initial discharge capacity. This good retention of the discharge capacity suggested that the LiPS shuttling had been curtailed to a large degree by the MNB-coated separator. When the cell was discharged at a rate of 0.5C, the LSB incorporating the MNB-coated separator displayed an excellent retention of capacity of 82.25% after 500 cycles (Fig. 5c), while its coulombic efficiency was maintained at greater than 97%, revealing the feasibility of the electrochemical reaction. The initial discharge capacity was 1335 mA h g$^{-1}$; after 500 cycles, it was 1098 mA h g$^{-1}$, a rate of capacity decay of 0.0355% per cycle. Two discrete discharge plateaus of the MNB-coated separator were observed at 2.3 and 2.1 V after the 1st, 50th, 100th, 200th, 300th, 400th, and 500th cycles at the 0.5C-rate (Fig. 5d). These voltage plateaus represent the formation of higher- and lower-order LiPS from elementary S$_8$. In the voltage profile, the observed extreme reversibility suggested good utilization of sulfur in the cathode and the reversible chemical reaction of sulfur (LiPS). Furthermore, additional cycling tests were conducted at various C-rates to observe the effect of the MNB-coated separator; at 1C, 2C, 3C, and 4C, the system displayed excellent performance, with capacity retentions of 74, 72, 67, and 62%, respectively, after 1000 charge/discharge cycles (Fig. 5e). Fig. 5f presents the long-term cycling performance of a Li-S cell incorporating the MNB-coated separator, performed at a rate of 5C. The LSB began to discharge with a capacity of 696 mA h g$^{-1}$; after 5000 cycles, it ended with a capacity of 204 mA h g$^{-1}$. Thus, 29.4% of the discharge capacity was retained after 5000 cycles, giving a capacity decay rate of 0.014% per cycle; to the best of our knowledge, this cycling performance is the best ever reported at such a high C-rate. While the pristine separator starts to discharge with a capacity of 628 mA h g$^{-1}$ and after 1000 cycles, ended with a capacity of 114 mA h g$^{-1}$, a degradation rate of 0.082% per cycle (Fig. 5f). The long-term cycling stability of this system confirms that the MNB-coated separator confined the LiPS to the cathode side, with no observable hindrance of the Li$^+$ ions (Fig. 3b) and reversible reactions of the LiPS to the active material. Even at a low C-rate, the LSB exhibited outstanding performance, with a high discharge capacity and a low capacity decay rate per cycle. The excellent cycling stability of the LSB incorporating the MNB-coated separator supports two phenomena: (i) entrapment of LiPS (short- and long-range) on the cathode side and (ii) reutilization of the active material (i.e., a reversible electrochemical reaction). The stable performance at such a high C-rate might be due to the precipitation of solid and non-conductive LiPS and Li$_2$S crystallites that are small and more conformal when compared with the larger LiPS crystallites formed at low C-rates. At a higher discharge current, mainly smaller crystals were formed by Li$_2$S; these crystals were easier to oxidize during charging than were the corresponding larger crystals formed at lower discharged currents. The MNB-coated separa-
tor stopped the migration of LiPS and led to outstanding cycling performance at a rate of 5C. During the charging process, the as-precipitated LiPS tends to oxidize to form soluble LiPS in the cathode, but, due to the insulating nature of Li$_2$S, the oxidation of Li$_2$S is quite difficult. Not all of the precipitated material can be involved in the redox reaction, leading to a loss in capacity. Consequently, at the end of the charging process some of the Li$_2$S remain on the MNB surface; at the end of long-term cycling, stacking of these insulating layers leads to the death of the battery. Thus, our LSB modified with an MNB-coated separator performed outstandingly over 5000 cycles at 5C (Fig. 5f). At higher C-rates, the battery discharged so fast that none of the sulfur could participate in the reduction, and some as-formed LiPS remained within the electrolyte, leading to a lower discharge capacity acquisition. In a comparison study (Fig. 5e), we observed that decreasing the discharge current caused the initial capacity to increase, because a lower discharge current caused all of the sulfur to participate in the redox reaction. At a rate of 5C, we observed the lowest discharge capacity, but the highest stability at the same time. The MoO$_3$ loading on the PP separator had a great influence on the cell performance. Fig. S12 (ESI†) reveals that the LSB exhibited low capacity when the PP separator was loaded with relatively high amounts of MNBs (0.8 or 0.5 mg cm$^{-2}$). We suspect that a high MoO$_3$ loading probably hindered the movement of Li$^+$ ions within the cell, resulting in a lower discharge capacity. In contrast, a low MoO$_3$ loading of 0.1 mg cm$^{-2}$ was suitable to achieve a higher discharge capacity.

A high loading of sulfur in the cathode has a great influence on the electrochemical behavior of LSBs. We prepared the cathode with different amounts of active material
(1.5 mg cm\(^{-1}\), 3 mg cm\(^{-1}\) and 5 mg cm\(^{-1}\)) and tested at 5C rate for 500 cycles. On increasing the amount of sulfur in the electrode, the thickness of the electrode increases which reduces the utilization of the active material, especially at a high C rate like 5C [Fig. S11, ESI†]. Later cells were disassembled to investigate the influence of the MNB coated separator to mitigate the shuttle effect. The pristine separator fails to trap LiPS on the cathode side and the majority of the LiPS travel to the anode side and later deposit on top of the Li foil. EDS mapping of the pristine separator after 500 cycles shows a lower amount of S compared to the amount of S on top of the MNB-coated separator [Fig. S3b and S6a–e†]. This reaffirms the fact that the MNB-coated separator successfully trapped the LiPS on the cathode side of the separator; EDS mapping of the Li metal after 500 cycles further shows less dense S content on top of the Li foil in the case of using the MNB coated separator compared to the pristine separator (Fig. S8, ESI†).

The open circuit voltage (OCV) of an LSB incorporating the MNB-coated separator was recorded to observe the self-discharge phenomenon (Fig. S13, ESI†). After 5 h of resting, the OCV of the LSB featuring the pristine separator decreased dramatically, from 2.40 to 2.08 V, a decay of approximately 13.3%. In contrast, the LSB incorporating the MNB-coated separator exhibited outstanding stability, with the OCV decreasing by less than 1% after 1 h and the voltage remaining stable throughout 12 h of observation. These findings suggest that stable LSBs incorporating MNB-coated separators might be a promising technology for commercialization.

**Conclusion**

We have developed a bilayer separator, through the coating of MNBs onto a PP separator, that interacts with LiPS both physically and chemically to greatly mitigate the shuttling phenomenon in LSBs. The interfacial resistance of the cell decreased as a result of the formation of Li\(_2\)Mo\(_6\)O\(_{19}\), resulting in reversibility and rapid reaction dynamics. Mo\(_6\)O\(_{19}\) interacts strongly with LiPS, enabling a lower degree of decrease in capacity and an ultra-long cycle life: up to 5000 cycles with a degradation rate of 0.014% per cycle at a rate of 5C. We suspect that this facile design has the potential for the commercialization of functional separators for the mass production of LSBs at a low cost.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
