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Review Article

A roadmap of battery separator development: Past and future

Junghyun Choi[1] and Patrick Joohyun Kim[2]

Abstract

The battery separator is one of the most essential components that highly affect the electrochemical stability and performance in lithium-ion batteries. In order to keep up with a nationwide trend and needs in the battery society, the role of battery separators starts to change from passive to active. Many efforts have been devoted to developing new types of battery separators by tailoring the separator chemistry. In this article, the overall characteristics of battery separators with different structures and compositions are reviewed. In addition, the research directions and prospects of separator engineering are suggested to provide a solid guideline for developing a safe and reliable battery system.

Addresses

[1] Energy Storage Materials Center, Korea Institute of Ceramic Engineering and Technology, Jinju, 52851, South Korea

[2] Department of Applied Chemistry, Kyungpook National University, Daegu, 41566, South Korea

Corresponding author: Kim, Patrick Joohyun (pjkim@knu.ac.kr)

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Battery separator, Next-generation batteries, Battery safety, Polyolefin separator, Surface-modified separator, Ceramic-coated separator, Solid-state electrolyte.

Introduction

With the increasing demand for high-performing electronic devices and a global mission to reduce greenhouse gases created by fossil fuels, tremendous attention has been paid to the development of rechargeable energy storage systems, especially for lithium-ion batteries (LIBs) [1–4]. Since the advent of practical LIBs in our everyday life, numerous researches have been performed by replacing each of the battery components with new types of materials in order to improve the energy/power density, electrochemical stability, and cyclability of LIBs [5–9]. Among the essential components, a battery separator is the main component responsible for the overall safety of batteries [10–12]. The major role of the battery separator is to physically isolate the anode from the cathode while allowing mobile Li-ions to transport back and forth [13]. Unfortunately, two technical challenges associated with separator puncture and significant thermal shrinkage of polymer separators threaten the overall safety of batteries. In addition, most researches have mainly focused on reducing the total thickness of the battery separator and increasing the size of battery packs, i.e. putting large amount of active materials into the battery [14,15]. This approach also raises serious safety concerns with respect to short circuits [14,15].

In order to keep up with the recent needs from industries and improve the safety issues, the battery separator is now required to have multiple active roles [16,17]. Many tactical strategies have been proposed for the design of functional separators [10]. One of the representative approaches is to coat a functional material onto either side (or both sides) of the battery separator [18–21]. This conceptual idea has been already attempted by battery industries (Samsung SDI, LG Chem., etc.) in order to strengthen the mechanical–thermal properties, as well as improve the electrolyte wettability of polyolefin separators [22–24]. With the adoption of the ceramic-coated-separator (CCS), LIBs have delivered improved electrochemical performances even at elevated temperatures. In addition, the thermal stability and mechanical strength of CCSs are dramatically enhanced in comparison with a pristine polyethylene separator [22]. In this regard, the approach of tailoring the surface of the polyolefin separator can be an efficient and effective way to improve both electrochemical performance and stability of LIBs.

However, there are remaining issues to be resolved in the current battery system paired with CCSs. Furthermore, there would be more potential problems when moving on to an advanced battery system with Li anode. For instance, when metallic Li is introduced as an anode in the battery, unexpected events (e.g. Li dendrite growth) could result in even more serious safety issues [25,26]. In addition, it is no longer useful to use the

CCS after hundreds of cycles since the ceramic layer is fully covered by Li. The deposited Li would play a part as another Li source inside the cell. Considering these points, it is of importance to develop a stable and reliable battery separator compatible with high-performance LIBs. For a clear insight into the next-generation separator, the categories of membranes are classified into three phases according to the technological paradigm.

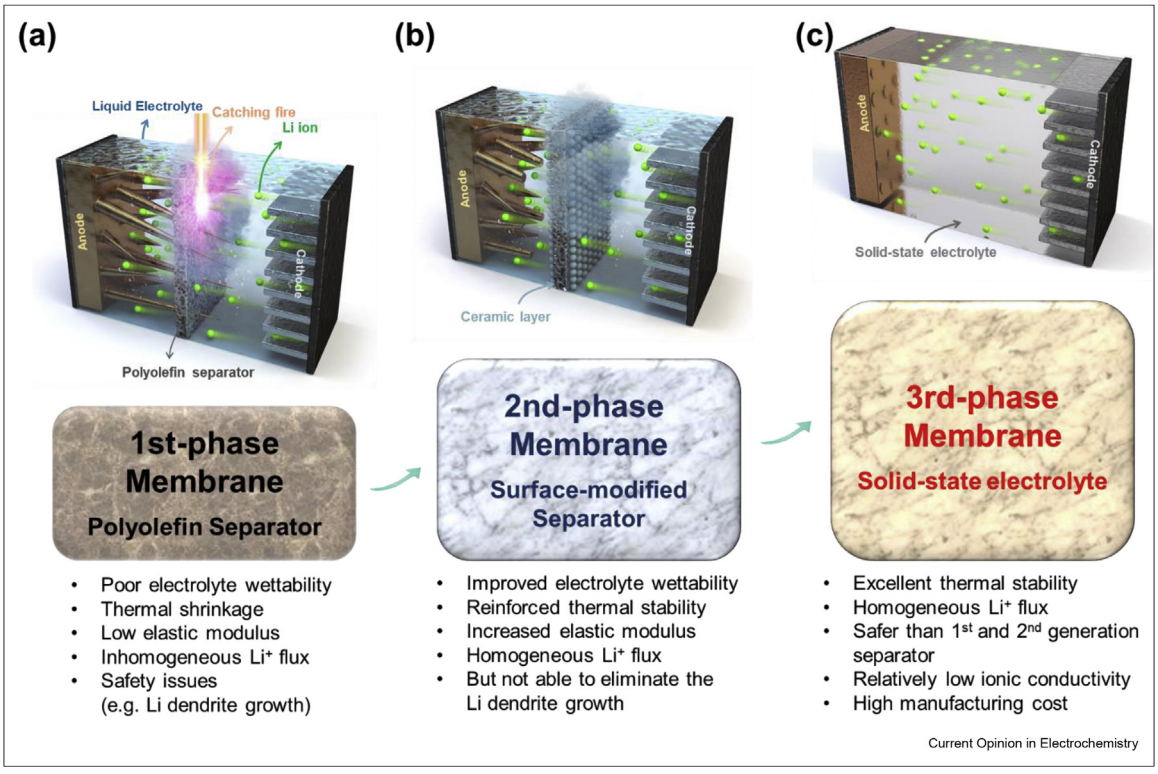
Separator design

Figure 1 illustrates how each phase of the battery separators plays a role in affecting the morphology of the deposited Li on the electrode and thus protecting the battery from safety hazards. Polyolefin separators (termed 'first-phase membrane') have high porosity and insulative properties [13]. But these are easily deformed by thermal or mechanical stress, which makes the polyolefin separator vulnerable to the penetration of growing Li dendrites (Figure 1a) [27]. Compared with the polyolefin separator, the surface-modified separator (termed 'second-phase membrane') is physically/thermally more stable and strong, which significantly reduces the risk of Li dendrite penetration (Figure 1b) [22]. However, since the fundamental causes of dendritic Li growth are not eliminated, and the penetration of Li dendrite across the surface-modified separator is realistically inevitable, it would eventually put the cell in danger after hundreds of cycles. In this regard, the utilization of solid-state electrolyte (termed 'third-phase membrane') served as an electrolyte and separator would be the feasible strategy to reduce potential safety issues originating from Li metal-based batteries (Figure 1c) [28].

First-phase membrane: polyolefin separator

Two representative polyolefins, i.e. polypropylene (PP) and polyethylene (PE), are typically used for fabricating battery separators [13]. Methodologies to fabricate battery separators are sorted into two methods: (1) wet method and (2) dry method [13]. The separator prepared by the wet method has interconnected pores through the entire area (Figure 2a). On the other hand, the separator fabricated by dry method has plenty of slit-like pores (Figure 2b). In general, the extensive uses of the polyolefin separator are limited by three major drawbacks. The first one is the huge thermal shrinkage at high temperatures (Figure 2e) [29]. The internal short-circuit

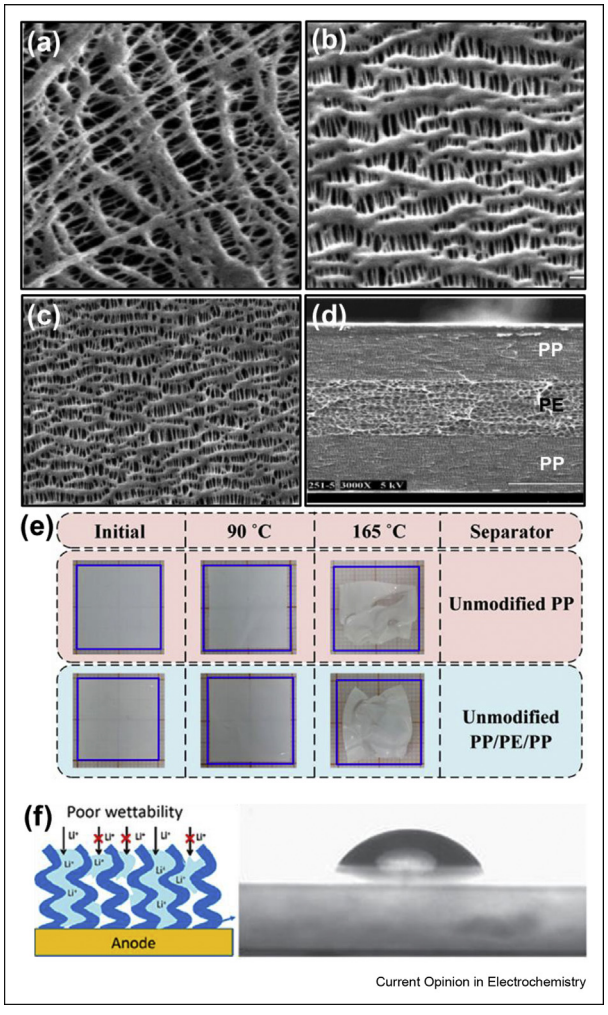
Figure 1



Schematics illustrating the roles of each membrane on Li deposition and battery safety. The categories of membranes are classified into three phases according to the technological paradigm: (**a**) first-phase membrane (Polyolefin separator), (**b**) second-phase membrane (Surfaced-modified separator), (**c**) third-phase membrane (Solid-state electrolyte).

caused by the contraction of the separator places the cell in a dangerous event such as a battery explosion [30]. For improving the thermal shrinkage problem of typical polyolefin separators, the tri-layered separator with PP/PE/PP architecture has been utilized (Figure 2c–d) [13,31]. The second one is the poor liquid electrolyte absorption and wettability, which affects the internal resistance of LIBs (Figure 2f) [32]. The last one is that the minimum modulus (6.4 GPa) to suppress the penetration of Li dendrite is larger than the elastic modulus of PP separators (2.1 GPa), inevitably allowing the piercing of Li dendrite across the separator [33]. Therefore, it would be highly desirable to develop a new membrane with improved thermal/mechanical properties and electrolyte wettability.

Figure 2



Polyolefin separators. Top-view scanning electron microscopy (SEM) images of separators made by (**a**) a wet method and (**b**) a dry method. (**c**) Top view and (**d**) cross-sectional SEM images of a tri-layered separator with PP/PE/PP architecture (Reproduced with permission from Ref. [13]. Copyright 2004 American Chemical Society). (**e**) Thermal shrinkage tests of a pristine PP separator and a tri-layer PP/PE/PP separator (Reproduced with permission from Ref. [29]. Copyright 2020 Multidisciplinary Digital Publishing Institute). (**f**) Poor wettability of a polyolefin-based separator with liquid electrolyte (Reproduced with permission from Ref. [34]. Copyright 2016 Elsevier).

Second-phase membrane: surface-modified separator

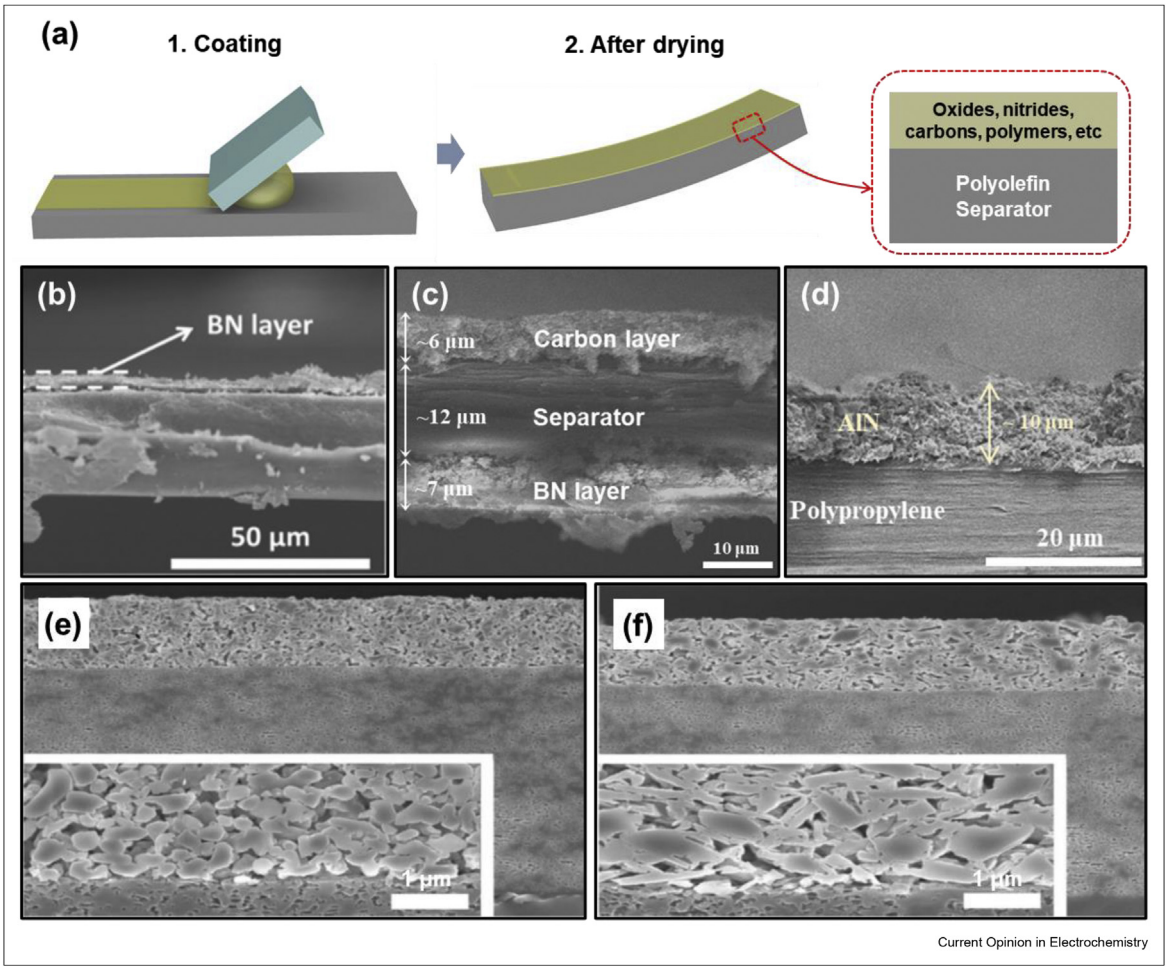
In order to address the latent issues with regard to thermal shrinkage and electrolyte wettability, a number of strategies have been proposed by coating a ceramic layer, depositing a metal layer, and forming a polymeric layer on the surface of polyolefin separators (Figure 3a) [35–41].

Nitrides, oxides, carbons, etc., can be employed as surface-coating materials for manufacturing surface-modified separators. A few research groups have demonstrated the effect of a nitride layer comprising either BN or AlN on managing the localized heat generated inside the cell and homogenizing Li^+ flux (Figure 3b–d) [21,42–44]. Under these influences, the formation of dendritic Li was noticeably suppressed, and the efficiency of Li plating/stripping was dramatically improved [42,43]. Oxides are known to be effective in improving the surface wettability with liquid electrolyte and the mechanical/thermal stability against high temperature when it is formed on the polymer separators [18,35,45]. For example, the CCS prepared by coating either Al_2O_3 or $Mg(OH)_2$ on the PE separator has exhibited improved thermal/mechanical stability and electrolyte wettability (Figure 3e–f) [22]. All these kinds of approaches have shown promising results in improving both stability and performance of LIBs.

Third-phase membrane: solid-state electrolytes

The adoption of solid-state electrolytes is the most promising option to eliminate the safety concerns with regard to the combination system of a polymer separator and liquid electrolyte [46,47]. The two basic roles of solid-state electrolytes are as follows: (1) a separator between electrodes and (2) a medium to transfer Li^+ between cathode and anode. For the practical use of solid-state electrolytes, it needs to meet the basic requirements for high mechanical/electrochemical stability and ionic conductivity [48]. Typically, solid-state electrolytes satisfying the above-described specifications can be classified into two major categories: (1) solid-polymer-electrolyte (SPE) and (2) solid-inorganic-electrolyte (SIE). Although there are numerous advantages of SPE (especially polyethylene oxide-based electrolyte), it could not circumvent fundamental safety issues (e.g. thermal runaway), which typically occur in the liquid-electrolyte system [48,49]. On the contrary, SIE is a strong candidate that can ameliorate many safety problems in terms of thermal/electrochemical stability [50–52]. The configuration and thermal/electrochemical stability of each battery with each polymer separator, oxide-based solid electrolytes,

Figure 3

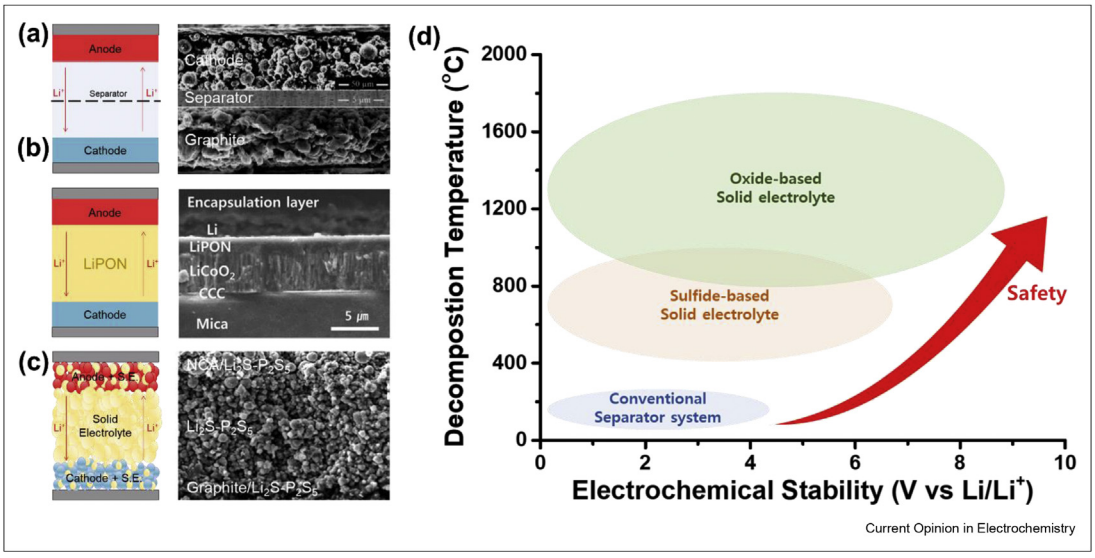


Surface-modified separators. (**a**) Schematic illustration of separator coating process and configuration of the surface-modified separator. Cross-sectional SEM images of nitride material-coated separator: (**b**) a BN-coated separator (Reproduced with permission from Ref. [43]. Copyright 2015 American Chemical Society), (**c**) a BN|PP|Carbon separator (Reproduced with permission from Ref. [21]. Copyright 2017 Springer Nature), and (**d**) an AlN-coated separator (Reproduced with permission from Ref. [42]. Copyright 2019 American Chemical Society). Cross-sectional SEM images of (**e**) an Al_2O_3-coated separator and (**f**) an $Mg(OH)_2$-coated separator (Reproduced with permission from Ref. [22]. Copyright 2019 Elsevier).

and sulfide-based solid electrolytes are illustrated in Figure 4a–d.

Among oxide-based solid electrolytes, LiPON and garnet-type lithium electrolytes are considered the promising solid electrolytes for practical all-solid-state-batteries (ASSBs), due to their excellent thermal stability and decent ionic conductivity [50]. Lithium phosphorous oxynitride (LiPON) is an amorphous-type oxide-based solid electrolyte [53,54]. The main features of LiPON are its high stability against metallic lithium, a wide potential window of 0–5.5 V vs. Li/Li^+, and an extremely high shear modulus of 77 GPa. However, it has relatively low ionic conductivity ($1–3 \times 10^{-6}$ S cm^{-1} at R.T.), which limits its application to thin-film micro-batteries [47,55]. Garnet-type lithium electrolyte is a crystalline oxide-based solid electrolyte. It has a decent ionic conductivity (0.1–1 mS cm^{-1}), excellent compatibility with Li, a wide potential window, and high stability under chemical/electrochemical conditions [56–58]. Unfortunately, garnet-type solid electrolytes have several critical issues inhibiting the practical use for commercial batteries, such as a poor solid–solid interface contact and a phase transformation from cubic to tetragonal [52,59]. In addition, the polycrystalline microstructure of SIE undermines the battery safety because it allows the propagation of Li dendrites through structural heterogeneities [60,61]. The high manufacturing cost and the sample preparation steps, i.e. sintering at high temperatures, also restrict the mass production of ASSBs [62].

Figure 4



Schematic illustration of the configuration of each battery with different membrane. (**a**) Polymer-based separator (Reproduced with permission from Ref. [74]. Copyright 2019 Elsevier), (**b**) amorphous thin-film solid-state electrolyte (LiPON) (Reproduced with permission from Ref. [54]. Copyright 2012 American Chemical Society), and (**c**) crystalline solid-state electrolyte (Sulfide, oxide, etc.) (Reproduced with permission from Ref. [75]. Copyright 2014 Elsevier). (**d**) Comparison of each separator/membrane in terms of thermal/electrochemical stability.

Sulfide-based solid electrolytes have been regarded as the most practical solid-state electrolyte for high-power applications (e.g., EVs) because of a high ionic conductivity comparable to typical liquid electrolyte and a high Li transference number [63]. In addition, the soft and deformable feature and relatively favorable manufacturing process (i.e., cold pressing) of sulfide-based electrolytes would be able to overcome the inherent weaknesses of oxide-based solid electrolytes [64,65]. Basically, sulfide-based solid electrolytes suffer from a rapid decomposition at the interface between Li metal and sulfide electrolyte, giving rise to the formation of an interphase layer [66]. Among sulfide-based electrolytes, Li-argyrodites (Li_6PS_5X (X = Cl, Br, I)) have drawn special attention due to a relatively slow reaction at the Li metal-solid electrolyte interface, a high ionic conductivity ($10^{-5} - 10^{-3}$ S cm^{-1}), and a wide potential window (up to 7 V vs. Li/Li^+), rendering it as a practical solid electrolyte close to commercialization [67–70]. However, these are particularly vulnerable to the exposure of moisture in the air, leading to the generation of toxic H_2S gas, and thus, the breakup of metal-sulfide bonds [63]. In addition, it is observed that Li dendrites are formed even in the sulfide electrolyte system [71–73]. All these unwanted events would cause serious safety issues like battery explosion and require a rigorous battery assembly process, i.e., processing and handling of sulfide electrolytes under a strictly controlled inert atmosphere [28]. To address the challenges of sulfide electrolytes, further studies would be inevitable as follow-up works.

Conclusion and outlook

Despite the remarkable advancement of separator technology, it is still not able to eliminate the root cause of unexpected threats such as dendritic Li formation. The adoption of solid-state electrolytes would be the feasible solution to circumvent most of the safety hazards with regard to thermal runaway and short-circuit. However, the relatively low ionic conductivity and high interfacial resistance of solid-state electrolytes are the two biggest obstacles for facilitating the operation of high-power electronic devices. Considering these points, it would be necessary to sort each type of the batteries in terms of specific purposes of use. For instance, solid-state batteries would be more suitable for applications requiring high energy density and long-term durability. In contrast, liquid-electrolyte LIBs with an advanced separator would be more appropriate for applications requiring high-power densities. In this regard, extensive researches on both surface-modified separator (second-phase membrane) and solid-state electrolyte (third-phase membrane) should be conducted in parallel to meet each of the requirements from the different applications.

In the future, the most important part of the advanced separator research is how to reduce the thickness of the coating-layer on the separator without sacrificing the electrochemical performance and stability. The studies on scaling-up the solid-state electrolyte from laboratory to industrial level, establishing a cost-effective manufacturing process, and exploring the fundamental

solution to safety problems in the liquid-electrolyte LIB would become even more important. To keep up with this trend and make the current LIB system safer and better, a concerted effort has to be made for advanced separator development.

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Author contributions

All authors wrote the manuscript. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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