

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/139254/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Hong, John, Jang, A-Rang, Park, Woon Bae, Hou, Bo , Lee, Jeong-O, Sohn, Kee-Sun, Cha, SeungNam, Lee, Young-Woo and Sohn, Jung Inn 2021. Thermodynamically and physically stable dendrite-free Li interface with layered boron nitride separators. ACS Sustainable Chemistry and Engineering 9 (11) , pp. 4185-4193. 10.1021/acssuschemeng.1c00040

Publishers page: <http://dx.doi.org/10.1021/acssuschemeng.1c00040>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



# 1 **Thermodynamically and Physically Stable Dendrite-Free** 2 **Li Interface with Layered Boron Nitride Separators**

3

4 John Hong<sup>a,b,†</sup>, A-Rang Jang<sup>c,†</sup>, Woon Bae Park<sup>d</sup>, Bo Hou<sup>e</sup>, Jeong-O Lee<sup>f</sup>, Kee-Sun Sohn<sup>g</sup>,  
5 SeungNam Cha<sup>h</sup>, Young-Woo Lee<sup>i,\*</sup> and Jung Inn Sohn<sup>j,\*</sup>

6

7 <sup>a</sup> Energy Storage & Distributed Resources Division, Lawrence Berkeley National Laboratory,  
8 1 Cyclotron Rd, Berkeley, CA 94720, USA

9 <sup>b</sup> School of Materials Science and Engineering, Kookmin University, 77 Jeongneung-Ro, Seoul  
10 02707, Republic of Korea

11 <sup>c</sup> Department of Electrical Engineering, Semyung University, 65 Semyung-ro,  
12 Chungcheongbuk-do 27136, Republic of Korea

13 <sup>d</sup> Department of Printed Electronics, Sunchon National University, 291-19 Jungang-ro,  
14 Sunchon, Jeollanam-do 57922, Republic of Korea

15 <sup>e</sup> Department of Physics and Astronomy, Cardiff University, 5 The Parade, Newport Road,  
16 Cardiff CF24 3AA, United Kingdom

17 <sup>f</sup> Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT),  
18 141 Gajeong-Ro, Daejeon 34114, South Korea

19 <sup>g</sup> Department of Nanotechnology and Advanced Materials Engineering, Sejong University, 39  
20 Sejong-Daero Seoul 05006, Republic of Korea

21 <sup>h</sup> Department of Physics, Sungkyunkwan University (SKKU), 2066 Seobu-Ro, Suwon,  
22 Gyeonggi-Do 16419, Republic of Korea

23 <sup>i</sup> Department of Energy Systems, Soonchunhyang University, 2 Soonchunhyang-Ro, Asan,  
24 Chungcheongnam-Do 31538, Republic of Korea

25 <sup>j</sup> Division of Physics and Semiconductor Science, Dongguk University-Seoul, 30 Pildong-Ro  
26 Seoul 04620, Republic of Korea

27

28 **Corresponding Author** (Prof. Young-Woo Lee and Prof. Jung Inn Sohn)

29 E-mail address: ywlee@sch.ac.kr, junginn.sohn@dongguk.edu

30 <sup>†</sup> Those authors contributed equally to this work.

1 **Abstract**

2 The development of promising separator candidates, offering both great physical rigidity and  
3 high thermal resistance, is still a global challenge to guarantee high-performance  
4 electrochemical cells. Freestanding hexagonal boron nitride (*h*-BN) separators are developed  
5 using the strategically combined synthetic steps with liquid and thermal-expansion exfoliation  
6 methods, which can simply fabricate the largely yielded *h*-BN nanosheets. The as-prepared  
7 freestanding *h*-BN nanosheet separator presents the better ionic conductivity than commercial  
8 polymer separators, and furtherly provides the excellent stability of Li-ion cells by suppressing  
9 the protruding dendritic Li growth during cycles on the electrodes as well as the high thermal  
10 and electrochemical stability of *h*-BN nanosheet separators even after aging process at high  
11 temperature 80~120 °C. Furthermore, the lithium titanate (LTO) batteries with the freestanding  
12 *h*-BN separators maintain an outstanding reversible coulombic efficiency of ~ 99 % after 600  
13 cycles as well as high cycling retention, indicating the significant improvement on battery  
14 performance compared to the LTO batteries with commercial polymer separators. Thus, the  
15 freestanding *h*-BN separators may provide a new strategic way for the efficient storage of  
16 charge in next-generation rechargeable batteries and high-safety energy storage applications.

17

18 **Keywords:** hexagonal boron nitride, two-dimensional atomic crystal, layered separator,  
19 thermal stability, lithium metal anode

20

## 1 **Introduction**

2       Currently, to meet the ever-increasing demands of electrical energy delivery,  
3 electrochemical lithium ion batteries (LIBs) are a primary class of energy storage and delivery  
4 sources in portable electronic applications [1-4]. Particularly, in order to optimize and further  
5 improve the overall energy-storing performance of LIBs, the rational selection and design of  
6 each conventional battery component (such as electrodes, electrolyte, and separators) are very  
7 essential [5-7]. In fact, many studies on LIBs have intensively focused on the improvement of  
8 energy storage capacitance and cyclability by the optimization of electrode and electrolyte  
9 materials [8-9]. However, there are more crucial factors which may limit the overall  
10 performance of LIBs such as the growth of protruding Li dendrites during cycling and the  
11 physical and chemical damage through internal and external heat environments [10-11]. Such  
12 factors can induce the serious deformation of separator membranes and cause drastic  
13 performance failure as well as severe problems on battery safety [12]. Commercial separators  
14 are largely consisted of polymer-based compounds, which can be certainly damaged by the  
15 aforementioned factors during cycling. Therefore, the development of novel separators with  
16 high electrochemical, physical, and thermal stability is important not only for viable long-term  
17 and high-performance LIB applications but also for the use of Li metal as the anode, possessing  
18 a high theoretical specific capacity of 3860 mAh g<sup>-1</sup> and a low redox potential (-3.04 V vs.  
19 standard hydrogen electrode) [13-17]. Recently, to suppress Li dendrite growth, the deposition  
20 of some nanomaterials (such as silicone nanofilaments, dopamine and mesoporous silica thin  
21 films) on commercial separators has been reported and presented the high electrochemical  
22 stability [15-16]. Moreover, the coated Prussian blue and reduced graphite oxides on  
23 commercial separator also show the ultra-long-term stability of Li plating/stripping [17].  
24 However, instead of focusing on new coating materials on commercial separators, the  
25 development of freestanding materials candidates for separators may be a crucial way to solve  
26 Li dendrite problems which are usually originated from polymer-based commercial separators.

1 Hexagonal boron nitride (h-BN), as a typical two-dimensional (2D) insulating material  
2 with a wide band gap (5-6 eV), has been considered to be a promising candidate for separator  
3 membranes in LIBs because of its outstanding ion permeability as well as superior thermal,  
4 chemical and physical stability [18-20]. h-BN films have recently revealed great success as  
5 stable coating materials on electrodes and polymer membranes, which can lead to the great  
6 strides in increasing the performance and stability of LIBs. For example, Yan et al. and Xie et  
7 al. reported that the 2D h-BN layers were directly synthesized on a Cu foil using a chemical  
8 vapor deposition (CVD) method [21-22]. The 2D h-BN layers can effectively suppress the  
9 growth of Li dendrites and hence, improve the cycling stability. Furthermore, Kim et al. and  
10 Luo et al. reported that the commercial polymer separators coated with the h-BN materials can  
11 improve the coulombic efficiency and ensure the reliability of Li metal anodes [23-24].  
12 Nevertheless, the CVD-grown h-BN films are not practical to utilize as commercial and  
13 practical products due to its low reproducibility and limitation of large-scale fabrication. Indeed,  
14 the h-BN coated commercial polymer separators can be also damaged by any internal or  
15 external heat sources, resulting in the issues of dramatic performance degradation or safety  
16 failure. Therefore, it is highly desirable to fabricate freestanding h-BN separators, which are  
17 made of h-BN itself from new practical and scalable synthetic routes.

18 In this work, freestanding h-BN nanosheet (BNN) separators represent the outstanding  
19 thermal endurance under high-temperature conditions and possess the excellent physical  
20 rigidity against the dendritic Li growth after long cycling test as well as provide the favorable  
21 Li ion permeability, which is also theoretically calculated by a density function theory (DFT)  
22 model. The high quality and nanosized h-BN sheets were fabricated by employing both the  
23 simple liquid and thermal expansion exfoliation method, which might give the great scalability  
24 and processability. The freestanding BNN separators (BNN-Ss) can successfully suppress the  
25 formation of protruding Li dendrites and possess the high thermal stability even at the high  
26 thermal conditions at  $\sim 120$  °C, where the commercial polymer separators cannot handle those

1 thermal conditions. In addition, the spinel lithium titanate (LTO) batteries with the freestanding  
2 BNN-Ss maintain a reversible coulombic efficiency of  $\sim 99\%$  after the 600 cycles. These  
3 electrochemical and physical results imply the great potential of freestanding BNN-Ss as a key  
4 separator component for the future battery technology in stability and cyclability against  
5 internal and external surrounding environments.

6

## 1 **Results and Discussion**

2       The exfoliated *h*-BN nanosheets (BNNs) were prepared by using the combination of liquid  
3 exfoliation and thermal expansion techniques. The synthetic methods to yield the BNNs are  
4 schematically illustrated in **Fig. 1a** and **S1**. First, the bath and ultrasound probe sonification  
5 (liquid exfoliations) methods for *h*-BN bulk powders with a concentrated alkaline solution were  
6 carried out. These physical exfoliation methods can convert the bulk *h*-BN powders to the  
7 hydroxyl functionalized and small-sized thin *h*-BN layers. The hydrodynamic forces during the  
8 bath and ultrasound sonification can lead to the dramatic breakdown of the bulk BN powders  
9 into the thin BN layers. Simultaneously, the edge sites of the BN layers are simultaneously  
10 attacked by hydroxyl ions, and the hydroxyl ions are attached to the edge sites of thin *h*-BN as  
11 a functional group. Moreover, as shown in **Fig. S1**, during the gravimetric filtration process,  
12 the *h*-BN nanosheets can be stacked and laminated together with multiple layered structure.  
13 Moreover, during the lamination, the sheet-to-sheet van der Waals interactions become more  
14 effective. As shown in **Fig. S2**, X-ray photoelectron spectroscopy (XPS) spectra of both pristine  
15 BN powder and exfoliated BN have no difference. Especially, there are no split peaks and peak  
16 shift on the B1s and N1s of the both pristine BN powders and exfoliated BN layers,  
17 demonstrating the clear crystallinity of the exfoliated BN layers. Next, the secondary hydrogen  
18 ( $H_2$ )-assisted thermal expansion treatment was applied on the functionalized thin *h*-BN layers  
19 so as to further cleave the interlayers of the thin *h*-BN layers and to yield the nanosized BNNs.  
20 The finally obtained optimized BNNs were dispersed in an isopropyl alcohol (IPA) solution for  
21 the filtration process (**Fig. S3**). The freestanding BNN-Ss were further filtered by the vacuum  
22 filtration of the prepared exfoliated BNNs in the IPA solution. The vacuum filtration method  
23 enables the scalable fabrication of freestanding *h*-BN nanosheet-separators (BNN-Ss). Due to  
24 the fixed size of 2032-coin cells, the diameter and thickness of the freestanding BNN-Ss were  
25 carefully controlled by adjusting the amount and concentration of the BNN solution during

1 filtration. The thickness of BNNs was about 20 ~ 30  $\mu\text{m}$ , which is close to that of the  
2 commercial polymer separators.

3 It should be noted that the ion ( $\text{H}^+$  and  $\text{Li}^+$ ) permeability through the in- and out-plane of  
4 thin layer *h*-BN at the level of mono- and few-layers has been already demonstrated by other  
5 research groups [19,25,26]. The BNNs are successfully exfoliated into the mono- to few-layers  
6 of *h*-BN. Therefore, when the BNNs are further applied to the separator application, their thin  
7 in-plane structure can successfully provide the Li ion diffusion paths. **Fig. 1b** presents the  
8 morphologies and height profiles of the exfoliated BNN samples examined by atomic force  
9 microscopy (AFM). The thicknesses of representative BNNs were determined to be the mono-  
10 and bilayers, which are about 0.48 nm, and 0.90 nm, respectively [27]. **Fig. S4a** presents the  
11 Raman peak of bulk BN powders centered at near 1366  $\text{cm}^{-1}$  (the  $\text{E}_{2\text{g}}$  mode (G band), B-N  
12 vertical vibrational mode within layers). Distinctly, the Raman peak of BNNs exhibits the  
13 relatively slight blue shift up to 4  $\text{cm}^{-1}$ , which is a clear signature of the thin thickness of BNNs  
14 [28]. Note that the shift of the G band of *h*-BN is strongly correlated to its thickness: the thin  
15 thickness of *h*-BN presents an upshifted G band, while the thicker *h*-BN shows the downshift  
16 of the Raman peak position. **Fig. S4b** presents the Small-angle X-ray Scattering (SAXS) results  
17 of BNNs. The slope of the SAXS scattering intensity profile at very low  $q$  values is found to be  
18 2.14, indicating the perfect dispersion of BNNs before the filtration process [29-30]. High-angle  
19 annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of  
20 BNNs were also performed as shown in **Fig. 1c**. The inset TEM image of **Fig. 1c** represents the  
21 thin layers of BNNs. Moreover, the crystal images of BNNs include the well-organized  
22 honeycomb structure. The magnified HAADF-STEM image also clearly depicts the atomic  
23 structural characteristic of BNNs along with the distribution of B and N atoms. The hexagonal  
24 symmetric selective area electron diffraction (SAED) patterns in **Fig. 1d** imply that the BNNs  
25 are well matched with theoretical *h*-BN crystal structure [31]. Likewise, the STEM height line  
26 profiling of BNNs further indicates the existence of the N atoms and B atoms along with the

1 in-plane direction of the BNN crystals. **Fig. S5** shows the TEM images of the exfoliated BNNs  
2 with few layered thicknesses. The most exfoliated BNNs have the diameters from few hundred  
3 nanometers to micrometers. These results indicate that the separator with the thin layers and  
4 small sizes of *h*-BN can guarantee the favorable ion diffusion paths through the in- or out-plane  
5 of BNNs. **Fig. 1e** depicts the freestanding BNN-Ss fabricated by the vacuum filtration method.  
6 The BNN-Ss can maintain its original structure even when it is strongly subjected to the  
7 different bending forces.

8 In order to evaluate and compare the heat-resistant properties of BNN-Ss and commercial  
9 polymer separators, thermal shrinkage tests were carried out at a temperature range from room  
10 temperature to 550 °C. The visual images of BNN-Ss and commercial polymer separators after  
11 heat treatment at various temperatures are presented in the bottom and top of **Fig. 2a**,  
12 respectively. Shrinkage (%) is defined as the ratio of undamaged area to the area of an original  
13 separator and is also plotted as a function of increased temperature. The photo images clearly  
14 indicate that the commercial polymer separators started its volumetric degradation after the heat  
15 exposure about 80 °C and lost over 70% of their original area upon the high temperature  
16 treatment (200 °C), which is in good agreement with previously reported literatures [32-34]. On  
17 the other hand, the thermal shrinkage of BNN-Ss is negligibly small or not identified even up  
18 to 200 °C. The more detailed shrinkage images of the commercial polymer separators and BNN-  
19 Ss are shown in **Fig. S6** and **S7**, respectively. Even at 550 °C, the BNN-Ss well maintain its  
20 original round shape without any surface and volume degradation. These results indicate that  
21 the strong thermal durability of BNN-Ss can be strongly attributed to the superior intrinsic  
22 physical and chemical properties of *h*-BN. In addition, the wettability tests with an electrolyte  
23 solution and ionic conductivity tests were performed. Compared to the commercial polymer  
24 separators, the BNN-Ss exhibits the better wettability and electrolyte uptake, as shown in **Fig.**  
25 **2b, 2c** and **S8**. The variation of contact angles using droplets of the electrolyte solution was  
26 measured between the commercial polymer separators and the BNN-Ss. Specifically, the

1 electrolyte uptake of BNN-Ss is found to be 256%, which is approximately 2 times higher than  
2 that of the commercial polymer separators. In addition, the ionic conductivity of BNN-Ss,  
3 evaluated by bulk resistance from electrochemical impedance spectroscopy (EIS) results (**Fig.**  
4 **S9**), exhibits the reasonable value of  $0.496 \text{ mS cm}^{-1}$ , which is similar to that of the commercial  
5 polymer separators ( $0.461 \text{ mS cm}^{-1}$ ).

6 The distinct structural, thermal and ionic characteristics of *h*-BN properties and the as-  
7 prepared BN separators can be beneficial for the overall stability of Li ion cells during cycling.  
8 Especially, its extremely thermal stability can overcome any external thermal resources and the  
9 following malfunctions such as the deformation and decreased ionic conductivity of polymer  
10 separators. Also, the high rigidity of *h*-BN can handle all negative outcomes in cells by the  
11 natural growth of Li dendrites and the corresponding physical damage on polymer separators  
12 during cycling. To investigate the both ionic advantages of BNN-Ss from its physical and  
13 chemical properties, the BNN-Ss and commercial polymer separators were employed in the Li  
14 ion cells for the Li plating/stripping electrochemical experiment. It can be seen from **Fig. 3a**  
15 that a Cu plate (substrate), a Li foil and a 1.0 M  $\text{LiPF}_6$  electrolyte were used as the working  
16 electrode, counter/reference electrode and electrolyte, respectively. The total Li plating capacity  
17 was set to be  $1.0 \text{ mAh cm}^{-2}$  on the Cu working electrode at a rate of  $0.5 \text{ mA cm}^{-2}$ . The Li  
18 stripping was then cycled to a cutoff potential of 2.0 V at the same rate of  $0.5 \text{ mA cm}^{-2}$ .  
19 Specifically, after 10 cycles, the electrochemical tests of the Li cells with the BNN-Ss and  
20 commercial polymer separators were paused and resumed after the 1hr thermal aging process  
21 in an oven to identify the experimental thermal stability of those separators. The coulombic  
22 efficiency was defined as the ratios between total Li plating and stripping capacity. As shown  
23 in **Fig. 3b**, before the aging process, the coulombic efficiencies (CE) on the Cu substrate during  
24 the Li plating/stripping are similar between the cells with the both separators. All cells can well  
25 maintain its initial CE values until first 10 cycles. After the aging process (the heat treatment  
26 while Li plating/stripping is stopped), the CE of the cells with the commercial polymer

1 separators dropped to about 50% of its initial CE after 20 cycles. After aging at 80 °C, the CE  
2 for commercial polymer separators is lowered due to the physical damage and shrinkage on the  
3 commercial separator. In contrast, the Li plating/stripping cells with the BNN-Ss can  
4 continuously guarantee its initial electrochemical properties, which are similar to the initial CE  
5 before the aging process. The dramatic CE differences right after the aging process can strongly  
6 represent that the high thermal stability of BNN-Ss might be essential to protect the stability of  
7 Li ion cells. Even in the severe conditions (after the aging process up to the 125 °C, **Fig. S10**),  
8 the CE of the cells with BNN-Ss is close to ~ 80 % after 20 cycles. After aging at 125 °C, the  
9 CE for the h-BN separators is well maintained, but slightly lowered. However, the CE for the  
10 commercial polymer separators is dramatically lowered due to the large physical damage and  
11 shrinkage on the commercial separator. It has been reported that the LiPF<sub>6</sub> electrolyte solution  
12 in organic carbonates is thermally stable up to 140 °C with non-electrochemical  
13 charge/discharge process [35]. Thus, these results are strongly attributed to the high thermal  
14 stability of *h*-BN while the degradation of commercial polymer separators occurs after thermal  
15 aging process.

16 The electrochemical behaviors of the Li plating/stripping cells with the BNN-Ss and  
17 commercial polymer separators were further characterized by the over-potential (voltage)  
18 versus capacity (time) results after 1<sup>st</sup> cycle and 20<sup>nd</sup> cycle (including the aging process) (**Fig.**  
19 **3c and 3d**, respectively). For the first Li plating/stripping cycle, the Li metal is deposited on  
20 the Cu foil during the Li plating, but some of the Li metal is left over on the Cu foil while the  
21 stripping processes (C.E. is not 100%). After a few cycles, the initial nucleation barrier on the  
22 Li/Cu foil is lower than that of the pristine Cu foil. The high nucleation density leads to a  
23 comparatively low plating overpotential. The Li plating/stripping over-potential of the cells  
24 with the BNN-Ss is slightly lower than that of the cells with the commercial polymer separators  
25 at 20<sup>th</sup> cycle. The Li stripping over-potentials of the commercial polymer separator and BNN-  
26 S is 312 mV and 129 mV at the time of 0.75 h, respectively. Over-potential values can indicate

1 the status of Li plates on the Cu substrate which might result from the different structural and  
2 physical conditions of Li metal during cycling. The lower over-potentials of the cells with the  
3 BNN-Ss can representatively indicate the favorably deposited Li plates on the Cu substrate to  
4 continue the stable cycling performance of Li ion cells [22,24]. Moreover, there is a large  
5 voltage hysteresis (over-potential differences) at the cells with the commercial polymer  
6 separators, which is usually determined by the unfavorable interfacial charge-transfer properties.  
7 Those differences on the voltage versus capacity results might be strongly attributed to the  
8 morphologies of Li on the Cu substrate. The curve of the cells with the BNN-Ss after 20 cycles,  
9 after the aging process, indicates the longer capacitance (time) before reaching the cutoff  
10 potential of 2.0 V compared to the commercial polymer separators, subsequently demonstrating  
11 the CE with the BNN-Ss. The morphologies of the Li plates on the Cu substrate were visually  
12 investigated using scanning electron microscopy (SEM). The SEM images were taken after the  
13 heat treatment of 80 °C after 10 cycles and then the electrochemical test was continued for  
14 additional 10 cycles. As shown in **Fig. 3f**, the Li plates on the Cu substrate with the commercial  
15 polymer separators present the typical protruding and dendritic Li metal, including many one-  
16 dimensional Li wires. Such protruding structures can cause the failure of separator component  
17 in LIB. Using the BNN-Ss, however, the resulting Li granules show the smooth and uniform  
18 formation on the Cu substrate (**Fig. 3e**). The BNN-Ss show the high physical stability against  
19 the tensile strain from the Li dendrites after the electrochemical cycling. Due to the rigid and  
20 high physical stability of BNN-Ss, the cells with the BNN-Ss can physically inhibit protruding  
21 Li dendrite growth and successfully maintain its original electrochemical performance  
22 compared to the polymer-based separating materials as shown in schematically in **Fig. 3g** and  
23 **3h**. Collectively, the BNN-Ss can successfully provide the good thermal and physical stability  
24 of Li ion cells against the external and harsh heat environment as well as the physical  
25 deformation by the strain from dendritic Li growth. Therefore, in real LIB system, the BNN-Ss  
26 can decrease the risk of overall capacitance degradation and improve the cycling stability.

1 For the real application testing with the BNN-Ss, as shown in **Fig. 4a**, the electrochemical  
2 performance of BNN-Ss with lithium titanate (LTO) and Li metal electrodes was further tested.  
3 The spinel LTO ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) electrode has been used as the electrode because LTO possesses  
4 high power processability, a unique zero-strain effect, stable charge and discharge voltage ( $\sim 1.6$   
5 V vs.  $\text{Li}/\text{Li}^+$ ), and excellent cycling stability. The LTO electrodes were used due to its high rate  
6 capability and long cycle life. **Fig. 4b** presents a cyclic voltammetry of the LTO electrode with  
7 the BNN-Ss [36]. The LTO electrode exhibits a pair of sharp peaks at about 1.50 V and 1.65 V,  
8 which are characteristic of the Li insertion/extraction on LTO. The charge–discharge curves of  
9 BNN-Ss at a current density of  $100 \text{ mA g}^{-1}$  are shown in **Fig. 4c**. A pair of distinct and flat  
10 voltage plateau at around 1.50 V and 1.65 V reflects the well-known two-phase Li  
11 insertion/desertion equilibriums between  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  [37]. During the first cycle,  
12 the plateau at around 1.5 V (vs.  $\text{Li}/\text{Li}^+$ ) would be related to the Li ion insertion/deintercalation  
13 of LTO and the small plateau at around 1.7 V (vs.  $\text{Li}/\text{Li}^+$ ) is induced by Li ion  
14 insertion/deintercalation of  $\text{TiO}_2$  phase. During the initial insertion, the unexpected side  
15 insertion of Li ion into the  $\text{TiO}_2$  dominant phase can make the following additional reduction  
16 plateau [38–41]. However, after the 1<sup>st</sup> cycle, the observed small plateau is negligible. The LTO  
17 with the BNN-Ss delivers an initial discharge capacity of  $171.2 \text{ mAh g}^{-1}$ . The LTO electrode  
18 with the BNN-Ss exhibits better long-term cycling stability than that of the commercial polymer  
19 separators even in the room temperature (**Fig. S11**). As shown in **Fig. 4d**, the LTO electrode  
20 with the BNN-Ss present a high coulombic efficiency of  $\sim 99 \%$  up to 600 cycles, whereas that  
21 of the commercial polymer separators drops to  $\sim 78 \%$ . **Fig. 4e** presents the rate-capability test  
22 of BNN-Ss and commercial polymer separators. At a current density of  $1500 \text{ mA g}^{-1}$ , the  
23 retention of the charge storage capacities of the LTO electrode with the BNN-Ss can reach a  
24 higher value of  $\sim 60\%$  than that of the commercial polymer separators. These results might be  
25 attributed to the high wettability and ionic conductivity of BNN-S and further suggest that the  
26 BNN-Ss play a pivotal role for the enhanced energy storing kinetics and stable

1 operation/cyclability of LIBs (Table S1). Due to the thickness difference, the ionic conductivity  
2 of BNN-Ss, calculated using  $R_b$  and thickness of separator, shows the value of  $0.496 \text{ mS cm}^{-1}$ ,  
3 which is slightly higher than or comparable to that of the commercial polymer separators ( $0.461$   
4  $\text{mS cm}^{-1}$ ). Moreover, the contact angle and electrolyte uptake results obtaining from the droplets  
5 of the electrolyte solution on the separators samples represent the high interface interaction  
6 between the solution and BNN-S as shown in Figure 2b and 2c. As illustrated in **Fig. 4f** and **4g**,  
7 similar to previous results,[21,22,24] the commercial polymer separators are not proper  
8 candidates to block the piercing Li dendrites growth on the Li metal electrode. In contrast, the  
9 uniform and smooth deposition of the additional Li dendrites by the BNN-Ss with superior  
10 thermal and physical stabilities can induce the better cyclability than the commercial polymer  
11 separators. The possible diffusion mechanism of Li ions through BNN-Ss might be attributed  
12 to the mitigation through atomic defects which are formed during the exfoliation steps. The  
13 feasibility of those defects working as the potential ion diffusion paths is demonstrated by  
14 density-functional theory (DFT) calculations (**Fig. S12**). **Fig. S12d** also shows the auxiliary  
15 DFT calculations for input models obeying the exact charge neutrality. On the exfoliated *h*-BN  
16 sheets, there can be two possible atomic defects which are placed in the location where the  
17 nitrogen or borone atomic bonding is broken. Based on the activation barrier energy calculation,  
18 the diffusion paths thorough those two defects show the lower activation barrier energy of Li  
19 electrolyte ions compared to the pristine BN structure.

20

## 21 **Conclusion**

22 In summary, new synthetic methods of thin *h*-BN nanosheets are developed and have  
23 successfully resulted in the *h*-BN nanosheets as the freestanding separators for electrochemical  
24 energy storage applications. The resultant freestanding *h*-BN nanosheet separators exhibit the  
25 excellent physical rigidity during the cycling and thermal endurance against the high-  
26 temperature environments without the dramatic performance degradation as well as show the

1 good Li ion diffusion kinetics. The *h*-BN separators can handle ~ 120 °C external heat without  
2 the structural collapse and also well maintain its initial coulombic efficiency during the Li  
3 deposition on the Cu substrate. The free-standing *h*-BN separators can maintain a reversible  
4 coulombic efficiency of ~ 99% after the 600 cycles with the LTO electrodes. The strong thermal  
5 and physical durability of the freestanding *h*-BN nanosheet separators can be strongly correlated  
6 to the superior intrinsic physical and chemical feasibility of *h*-BN. Moreover, the density  
7 functional theory (DFT) calculation reveals that the small defect sites on the *h*-BN nanosheets  
8 can induce the much favorable Li ion penetration along with the sheets and corresponding  
9 separators. Thus, based upon these findings, the facile and efficient processability of the *h*-BN  
10 nanosheets and the corresponding freestanding separators can further extend the applicability  
11 of energy storage applications in near future.

12

1 **ASSOCIATED CONTENT**

2 **- Supporting Information**

3 Experimental methods, Schematic illustration of the exfoliation process, XPS spectra before and after  
4 exfoliation method, Real image of exfoliated h-BN nanosheets, Raman spectra of pristine h-BN powder  
5 and exfoliated h-BN, SAXS analysis of BNNs, TEM images, Thermal stability tests of commercial  
6 separators and BNN-S, Electrolyte wettability test, Impedance plots, Coulombic efficiency (CE) versus  
7 cycle plots after 125 °C thermal aging step, Capacity cycling retention of LTO//Li cells, DFT crystal  
8 models of h-BN defects, Parameters for ionic conductivity calculation.

9  
10 **- Author Information**

11 **Corresponding Authors**

12 E-mail: ywlee@sch.ac.kr

13 E-mail: junginn.sohn@dongguk.edu

14  
15 **- Author Contributions**

16 J.H and A.-R.J. equally contributed to this work. J.H, A.-R.J., Y.-W.L. and J.I.S. conceived the idea.  
17 J.H, A.-R.J., and Y.-W.L. synthesized the samples, analyzed the data, and wrote the manuscript; W.B.P.  
18 and K.-S.S. analyzed the DFT data. B.H. analyzed the TEM data. K.-S.S., J.-O. L. S.N.C., Y.-W.L, J.I.S.  
19 contributed in reviewing the manuscript and provided scientific input.

20  
21 **- Notes**

22 The authors declare no competing financial interest

23  
24 **- Acknowledgements**

25 This research was supported by the National Research Foundation of Korea grant funded by the Korea  
26 government (MSIT) (2019R1F1A1041407, 2019M1A2A2065616, 2019R1A4A1021237, and  
27 2019R1A2C1007883) and by the Soonchunhyang University Research Fund.

## 1 **References**

- 2 [1] Tarascon, J.-M.; Armand, M. Issues and challenges facing rechargeable lithium batteries.  
3 *Nature* **2001**, *414*, 359-367.
- 4 [2] Li, M.; Lu, J.; Chen, Z.; Amine, K. 30 Years of lithium-ion batteries. *Adv. Mater.* **2018**, *30*,  
5 1800561.
- 6 [3] Wang, K.-X.; Li, X.-H.; Chen, J.-S. Surface and interface engineering of electrode  
7 materials for lithium-ion batteries. *Adv. Mater.* **2015**, *27*, 527-545.
- 8 [4] Liu, J.; Bao, Z.; Cui, Y.; Dufek, E.; Goodenough, J.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu,  
9 P.; Manthiram, A.; Meng, S.; Subramanian, V.; Toney, M.; Viswanathan, V.; Whittingham,  
10 S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X.-Q.; Zhang, J.-G. Pathways for practical high-energy  
11 long-cycling lithium metal batteries. *Nat. Energy* **2019**, *4*, 180-186.
- 12 [5] Nitta, N.; Wu, F.; Lee, J.; Yushin, G. Li-ion battery materials: present and future. *Mater.*  
13 *Today* **2015**, *18*, 252-264.
- 14 [6] Alias, N.; Mohamad, A. Advances of aqueous rechargeable lithium-ion battery: A review. *J.*  
15 *Power Sources* **2015**, *274*, 237-251.
- 16 [7] Lee, H.; Yanilmaz, M.; Toprakci, O.; Fu, K.; Zhang, X. A review of recent developments  
17 in membrane separators for rechargeable lithium-ion batteries. *Energy Environ.*  
18 *Sci.* **2014**, *7*, 3857-3886.
- 19 [8] Lee, Y.-W.; An, G.-H.; Kim, B.-S.; Hong, J.; Pak, S.; Lee, E.-H.; Cho, Y.; Lee, J.; Giraud,  
20 P.; Cha, S.; Ahn, H.-J.; Sohn, J.; Kim, J. Synergistic effects of a multifunctional graphene  
21 based interlayer on electrochemical behavior and structural stability. *ACS Appl. Mater.*  
22 *Inter.* **2016**, *8*, 17651-17658.
- 23 [9] Gauthier, M.; Carney, T.; Grimaud, A.; Giordano, L.; Pour, N.; Chang, H.-H.; Fenning, D.;  
24 Lux, S.; Paschos, O.; Bauer, C.; Maglia, F.; Lupart, S.; Lamp, P.; Shao-Horn, Y. Electrode–  
25 electrolyte interface in Li-Ion batteries: current understanding and new insights. *J. Phys.*  
26 *Chem. Lett.* **2015**, *6*, 4653-4672.

- 1 [10] Li, L.; Li, S.; Lu, Y. Suppression of dendritic lithium growth in lithium metal-based  
2 batteries. *Chem. Commun.* **2018**, *54*, 6648-6661.
- 3 [11] Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward safe lithium metal anode in  
4 rechargeable batteries: A review. *Chem. Rev.* **2017**, *117*, 10403-10473.
- 5 [12] Woo, J.-J.; Zhang, Z.; Rago, N.; Lu, W.; Amine, K. A high performance separator with  
6 improved thermal stability for Li-ion batteries. *J. Mater. Chem. A* **2013**, *1*, 8538-8540.
- 7 [13] Liu, B.; Zhang, J.-G.; Xu, W. Advancing lithium metal batteries. *Joule* **2018**, *2*, 833-845.
- 8 [14] Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.-G. Lithium metal  
9 anodes for rechargeable batteries. *Energy Environ. Sci.* **2014**, *7*, 513-537.
- 10 [15] Yang, Y.; Wang, W.; Li, L.; Li, B.; Zhang, J. Stable cycling of Li-S batteries by  
11 simultaneously suppressing Li-dendrite growth and polysulfide shuttling enabled by a  
12 bioinspired separator. *J. Mater. Chem. A* **2020**, *8*, 3692-3700.
- 13 [16] Yang, J.; Wang, C.-Y.; Wang, C.-C.; Chen, K.-H.; Mou, C.-Y.; Wu, H.-L. Advanced  
14 nanoporous separators for stable lithium metal electrodeposition at ultra-high current  
15 densities in liquid electrolytes. *J. Mater. Chem. A* **2020**, *8*, 5095-5104.
- 16 [17] Wu, X.; Liu, N.; Guo, Z.; Wang, M.; Qiu, Y.; Tian, Y.; Tian, D.; Guan, B.; Fan, L.; Zhang,  
17 N. Constructing multi-functional Janus separator toward highly stable lithium batteries.  
18 *Energy Storage Mater.* **2020**, *28*, 153-159.
- 19 [18] Zhang, K.; Feng, Y.; Wang, F.; Yang, Z.; Wang, J. Two dimensional hexagonal boron  
20 nitride (2D-hBN): synthesis, properties and applications. *J. Mater. Chem. C* **2017**, *5*,  
21 11992-12022.
- 22 [19] Hu, S. Lozada-Hidalgo, M.; Wang, F. C.; Mishchenko, A.; Schedin, F.; Nair, R. R.; Hill,  
23 E. W.; Boukhvalov, D. W.; Katsnelson, M. I.; Dryfe, R. A. W.; Grigorieva, I. V.; Wu, H.  
24 A.; Geim, A. K. Proton transport through one-atom-thick crystals. *Nature* **2014**, *516*, 227-  
25 230.

- 1 [20] Mortazavi, B.; Yang, H.; Mohebbi, F.; Cuniberti, G.; Rabczuk, T. Graphene or h-BN  
2 paraffin composite structures for the thermal management of Li-ion batteries: A multiscale  
3 investigation. *Appl. Energy* **2017**, *202*, 323-334.
- 4 [21] Yan, K.; Lee, H.-W.; Gao, T.; Zheng, G.; Yao, H.; Wang, H.; Lu, Z.; Zhou, Y.; Liang, Z.;  
5 Liu, Z.; Chu, S.; Cui, Y. Ultrathin two-dimensional atomic crystals as stable interfacial  
6 layer for improvement of lithium metal anode. *Nano Lett.* **2014**, *14*, 6016-6022.
- 7 [22] Xie, J.; Liao, L.; Gong, Y.; Li, Y.; Shi, F.; Pei, A.; Sun, J.; Zhang, R.; Kong, B.;  
8 Subbaraman, R.; Christensen, J.; Cui, Y. Stitching h-BN by atomic layer deposition of LiF  
9 as a stable interface for lithium metal anode. *Sci. Adv.* **2017**, *3*, eaao3170
- 10 [23] Kim, P. J. H.; Seo, J.; Fu, K.; Choi, J.; Liu, Z.; Kwon, J.; Hu, L.; Paik, U. Synergistic  
11 protective effect of a BN-carbon separator for highly stable lithium sulfur batteries. *NPG*  
12 *Asia Mater.* **2017**, *9*, e375.
- 13 [24] Luo, W.; Zhou, L.; Fu, K.; Yang, Z.; Wan, J.; Manno, M.; Yao, Y.; Zhu, H.; Yang, B.; Hu,  
14 L. A thermally conductive separator for stable Li metal anodes. *Nano Lett.* **2015**, *15*, 6149-  
15 6154.
- 16 [25] Kroes, J. M. H.; Fasolino, A.; Katsnelson, M. I. Density functional based simulations of  
17 proton permeation of graphene and hexagonal boron nitride. *Phys. Chem. Chem. Phys.*  
18 **2017**, *19*, 5813-5817.
- 19 [26] Tian, H.; Seh, Z. W.; Yan, K.; Fu, Z.; Tang, P.; Lu, Y.; Zhang, R.; Legut, D.; Cui, Y.;  
20 Zhang, Q. Theoretical investigation of 2D layered materials as protective films for lithium  
21 and sodium metal anodes. *Adv. Funct. Mater.* **2017**, *7*, 1602528.
- 22 [27] Falin, A.; Cai, Q.; Santos, E.; Scullion, D.; Qian, D.; Zhang, R.; Yang, Z.; Huang, S.;  
23 Watanabe, K.; Taniguchi, T.; Barnett, M.; Chen, Y.; Ruoff, R.; Li, L. H. Mechanical  
24 properties of atomically thin boron nitride and the role of interlayer interactions. *Nat.*  
25 *Commun.* **2017**, *8*, 15815.

- 1 [28] Li, L. H.; Chen, Y. Atomically thin boron nitride: unique properties and applications. *Adv.*  
2 *Funct. Mater.* **2016**, *26*, 2594-2608.
- 3 [29] Hoda, N.; Antoni, S.-F.; Jozef, A.; Stephan H.; Hossein, M.; Nader, Q.; Raffaele, M.  
4 Gelatin–Graphene Nanocomposites with Ultralow Electrical Percolation Threshold. *Adv.*  
5 *Mat.* **2016**, *28*, 6914-6920.
- 6 [30] Thomas, M.; Liliana, C.; Anna, S.; Isabelle, G.; Ekaterina, I.; Rico, T. Bulk properties of  
7 aqueous graphene oxide and reduced graphene oxide with surfactants and polymers:  
8 adsorption and stability. *Phys. Chem. Chem. Phys.* **2018**, *20*, 16801-16816.
- 9 [31] Oh, H.; Jo, J.; Tchoe, Y.; Yoon, H.; Lee, H. H.; Kim, S.-S.; Kim, M.; Sohn, B.-H.; Yi, G.-  
10 C. Centimeter-sized epitaxial h-BN films. *NPG Asia Mater.* **2016**, *8*, e330.
- 11 [32] Wu, D.; Shi, C.; Huang, S.; Qiu, X.; Wang, H.; Zhan, Z.; Zhang, P.; Zhao, J.; Sun, D.; Lin,  
12 L. Electrospun nanofibers for sandwiched polyimide/poly (vinylidene fluoride)/polyimide  
13 separators with the thermal shutdown function. *Electrochim. Acta* **2015**, *176*, 727-734.
- 14 [33] Liao, H.; Zhang, H.; Qin, G.; Li, Z.; Li, L.; Hong, H. A macro-porous graphene oxide-  
15 based membrane as a separator with enhanced thermal stability for high-safety lithium-ion  
16 batteries. *RSC Adv.* **2017**, *7*, 22112-22120.
- 17 [34] Blake, A. J.; Kohlmeyer, R. R.; Hardin, J. O.; Carmona, E. A.; Maruyama, B.; Berrigan, J.  
18 D.; Huang, H.; Durstock, M. F. 3D printable ceramic–polymer electrolytes for flexible  
19 high-performance Li-ion batteries with enhanced thermal stability. *Adv. Energy Mater.*  
20 **2017**, *7*, 1602920.
- 21 [35] Gnanaraj, J. S.; Zinigrad, E.; Asraf, L.; Gottlieb, H. E.; Sprecher, M.; Schmidt, M.; Geissler,  
22 W.; Aurbach, D. A. detailed investigation of the thermal reactions of LiPF<sub>6</sub> solution in  
23 organic carbonates using ARC and DSC. *J. Electrochem. Soc.* **2003**, *150*, A1533-A1537.
- 24 [36] Krajewski, M.; Hamankiewicz, B.; Michalska, M.; Andrzejczuk, M.; Lipinska, L.;  
25 Czerwinski, A. Electrochemical properties of lithium–titanium oxide, modified with Ag–

- 1 Cu particles, as a negative electrode for lithium-ion batteries. *RSC Adv.* **2017**, *7*, 52151-  
2 52164.
- 3 [37] Chen, C.; Agrawal, R.; Wang, C. High performance  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Si}$  composite anodes for Li-  
4 ion batteries. *Nanomaterials* **2015**, *5*, 1469-1480.
- 5 [38] Lou, S.; Zhao, Y.; Wang, J.; Yin, G.; Du, C.; Sun, X. Ti-based oxide anode materials for  
6 advanced electrochemical energy storage: Lithium/sodium ion batteries and hybrid  
7 pseudocapacitors. *Small* **2019**, *15*, 1904740
- 8 [39] Gangaja, B.; Nair, S. V.; Santhanagopalan, S. nterface-engineered  $\text{Li}_4\text{Ti}_5\text{O}_{12}-\text{TiO}_2$  dual-  
9 phase nanoparticles and CNT additive for supercapacitor-like high-power Li-ion battery  
10 applications. *Nanotechnol.* **2018**, *29*, 095402.
- 11 [40] Liao, J.-Y.; Chabot, V.; Gu, M.; Wang, C.; Xiao, X.; Chen, Z. Dual phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}-\text{TiO}_2$   
12 nanowire arrays as integrated anodes for high-rate lithium-ion batteries. *Nano Energy* **2014**,  
13 *9*, 383-391.
- 14 [41] Lukman, N.; Rais, F.; Haniffudin, N.; Hariyati, P.; Achmand, S.; Joko, T.; Bambang P.  
15 Synthesis of dual-phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}-\text{TiO}_2$  nanowires as anode for lithium-ion battery. *Ionics*  
16 **2019**, *25*, 1505-1511.
- 17

## 1 **Figure Captions**

2 **Figure 1.** (a) A schematic image of exfoliated *h*-BN nanosheets. (b) AFM images of mono- and  
3 bi-layer BNNs & Linear AFM depth profiles of mono- and bi-layer BNNs. (c) A HAADF-  
4 STEM image of BNNs. The inset image shows a TEM image of BNNs. (d) A high resolution  
5 STEM image, SAED pattern and atomic line profile of BNNs. (e) Optical images of BNN-Ss.

6 **Figure 2.** (a) Thermal deformation tests of BNN-Ss and commercial polymer separators up to  
7 300 °C (b) Contact angle (CA) of BNN-Ss and commercial separators with electrolyte solvents.  
8 (c) Electrolyte uptake (EU) calculation of BNN-Ss and commercial separators.

9 **Figure 3.** A schematic illustration of (a) Li plating/stripping experiment cells with BNN-Ss and  
10 commercial polymer separators. (b) Coulombic efficiency (CE) versus cycle plots with BNN-  
11 Ss and commercial polymer separators after 80 °C thermal aging process. Potential versus time  
12 plots during Li plating/stripping cycling with (c) BNN-Ss and (d) commercial polymer  
13 separators. SEM characterization of Li plating on the Cu substrate with (e) BNN-Ss and (f)  
14 commercial polymer separators. Schematic illustrations of deposited Li dendrites with (g)  
15 BNN-Ss (flat structures) and (h) commercial polymer (protruding structures).

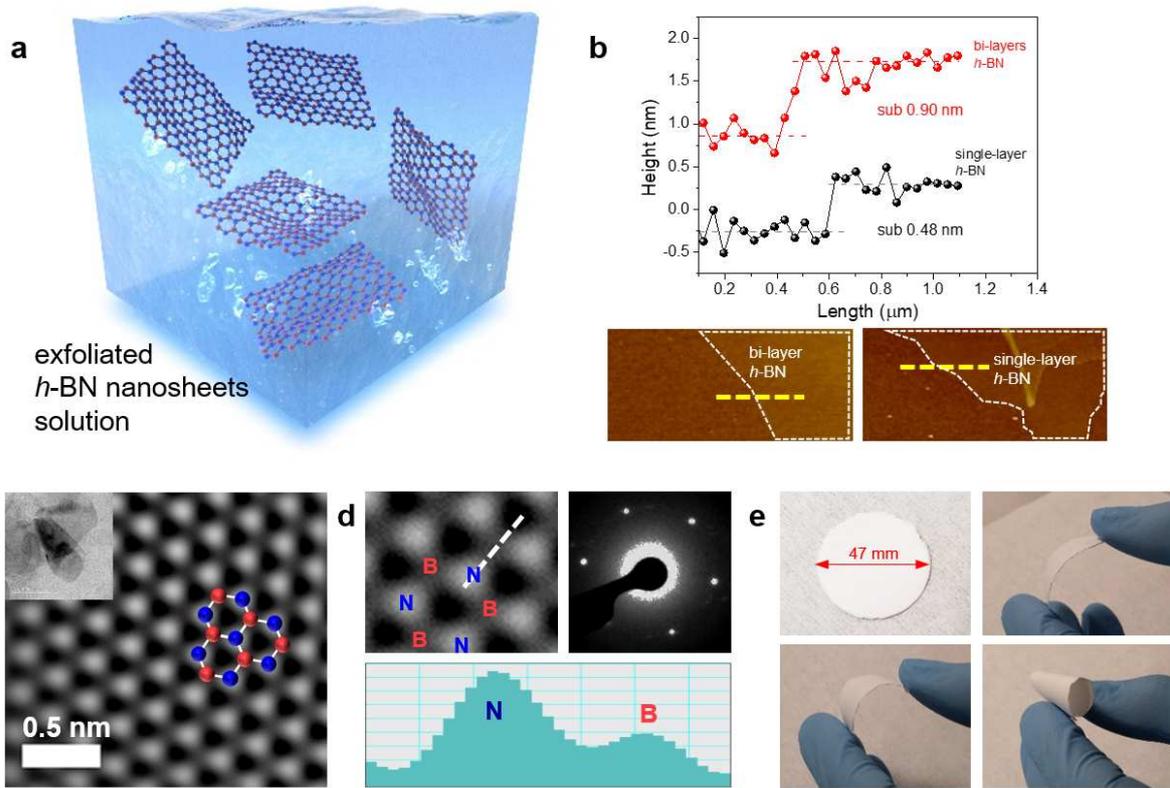
16 **Figure 4.** (a) A schematic ion diffusion illustration of LTO//Li cells with BNN-Ss. (b) Cyclic  
17 voltammetry of LTO//Li cells. (c) Charge-discharge curves of LTO//Li cells with BNN-Ss. (d)  
18 Coulombic efficiency of LTO//Li cells with BNN-Ss and commercial polymer separators. (e)  
19 Capacity rate retention of LTO//Li cells with BNN-Ss and commercial polymer separators.  
20 Schematic characterization of cycled Li metal electrodes in LTO//Li cells with (f) BNN-Ss and  
21 (g) commercial polymer separators.

22

1

Fig. 1. J. Hong et al.

2



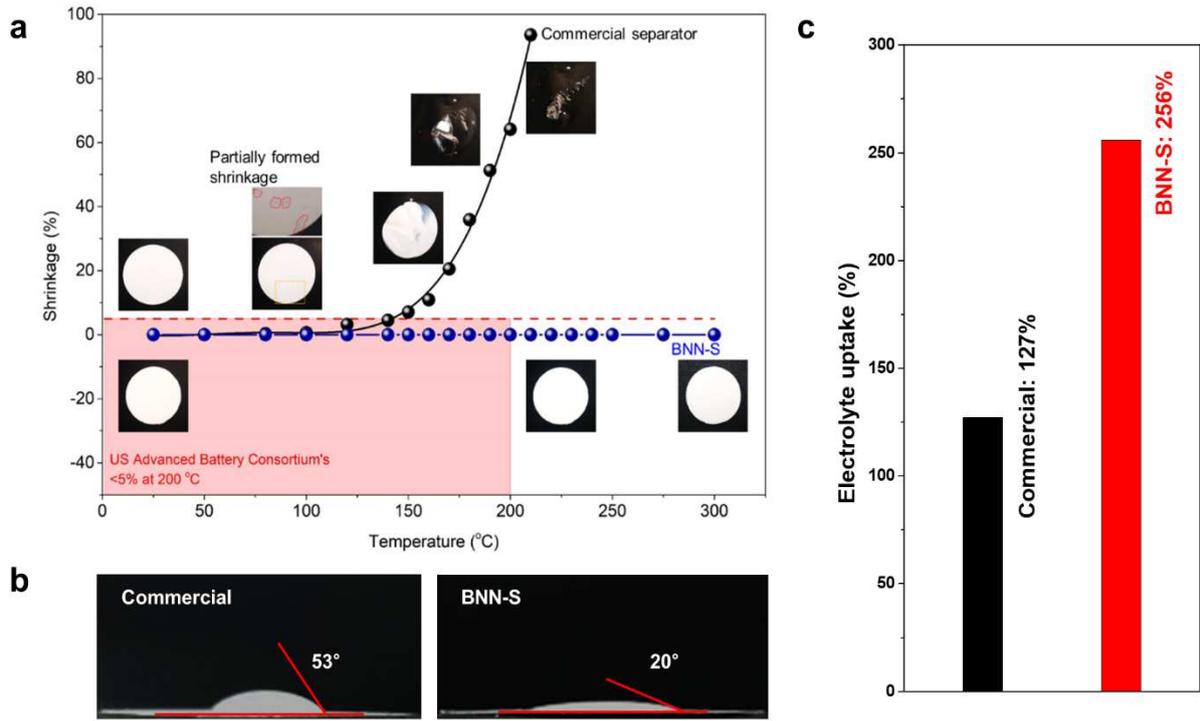
3

4

5

1

Fig. 2. J. Hong et al.



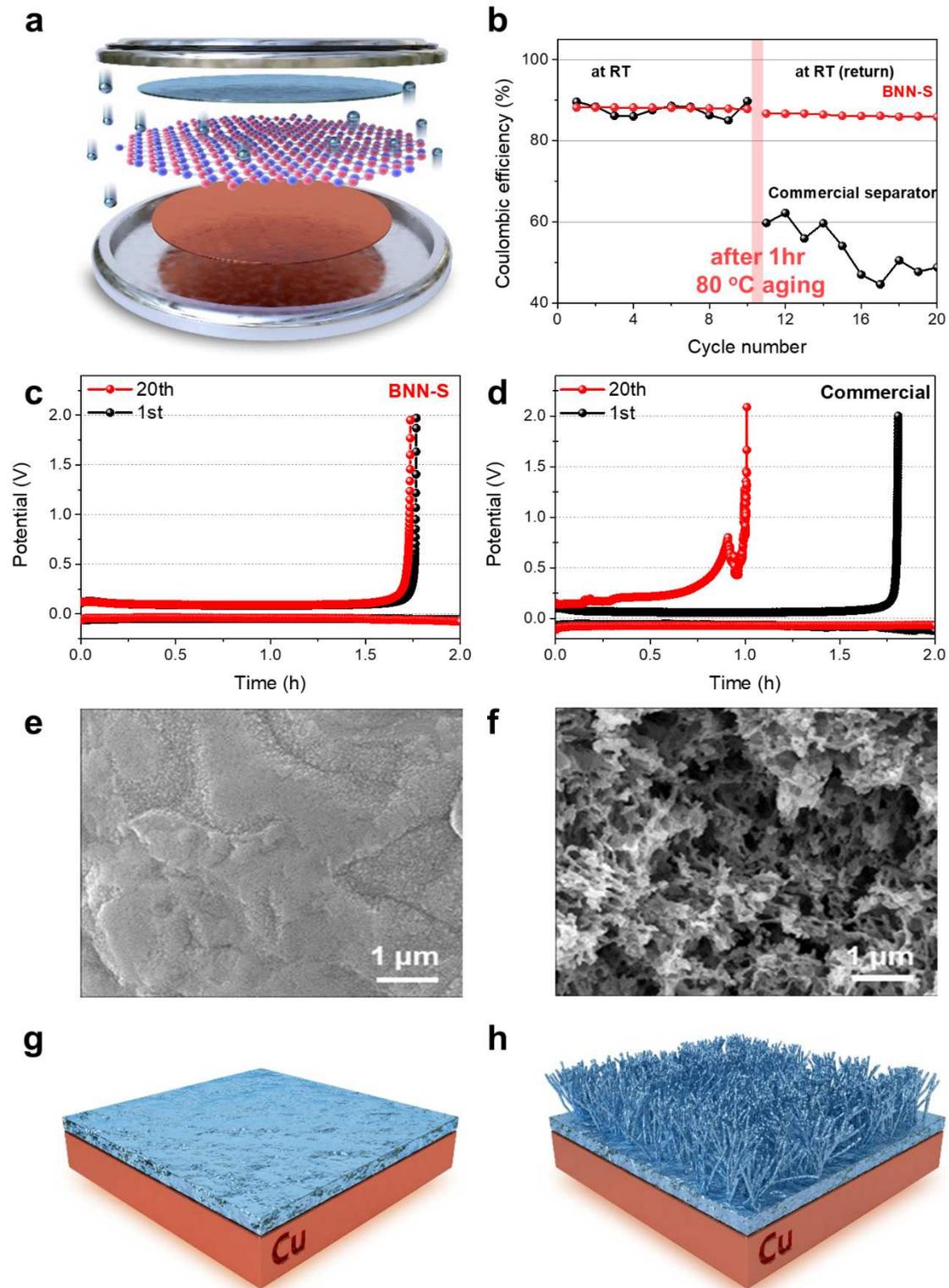
2

3

4

1

Fig. 3. J. Hong et al.



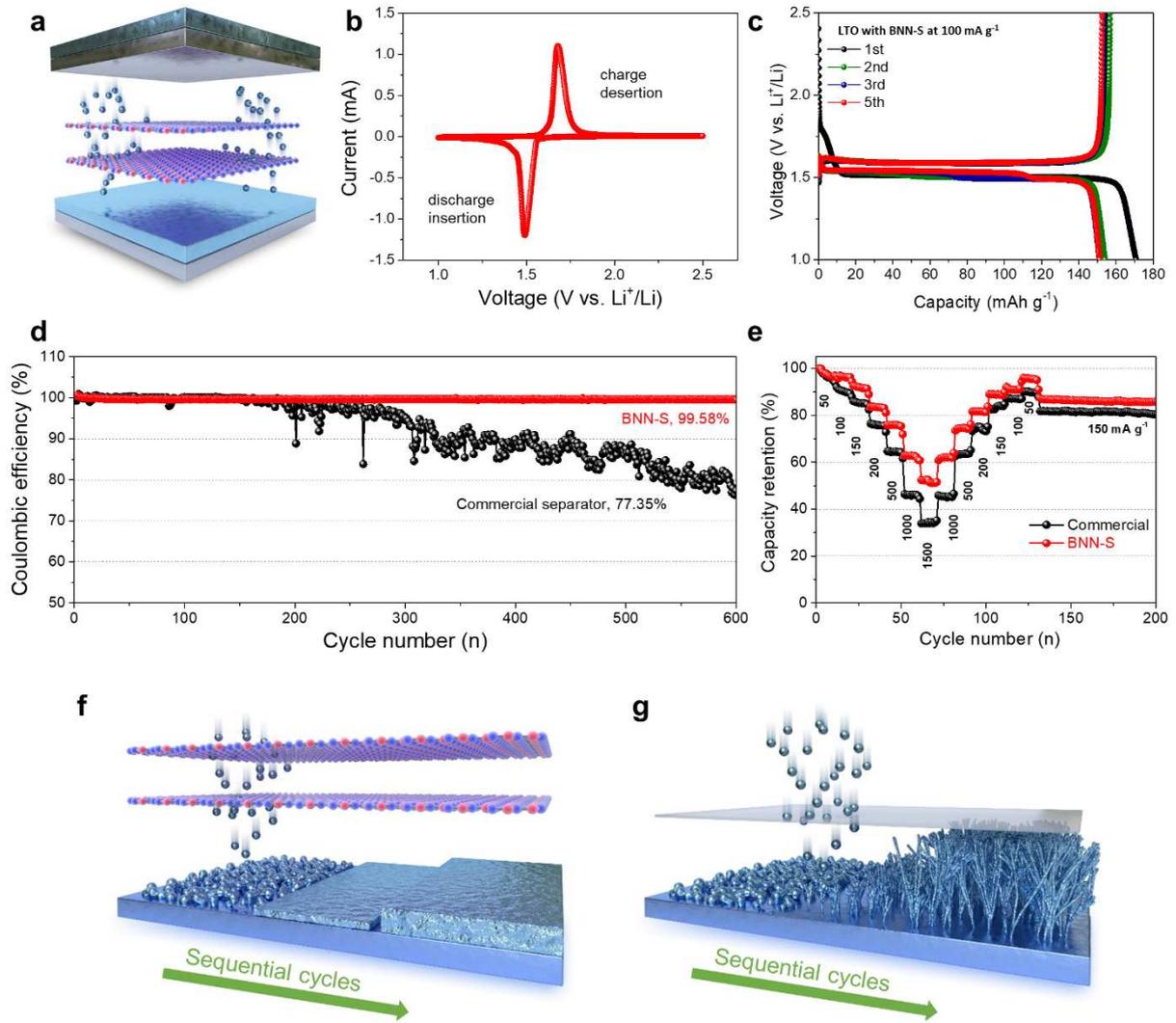
2

3

4

1

Fig. 4. J. Hong et al.

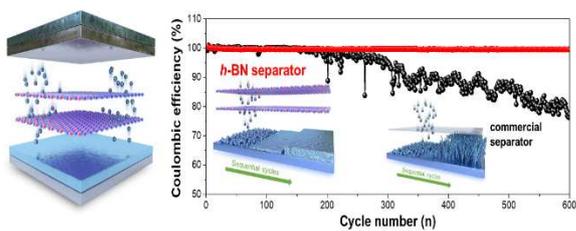


2

3

1 **For Table of Contents Use Only**

2



3

4

5 Freestanding *h*-BN nanosheet separator show the high electrochemical performance in Li ion  
6 battery including high physical and thermal stability.

7