Chapter 5

5. Hexagonal Boron Nitride Decorated PP Separator

5.1 Introduction

In the age of growing demand for electrochemical energy storage devices and depleting lithium reserves, sodium metal batteries (SMB) hold significant promise as a cost-effective and environmentally friendly alternative to lithium-ion batteries. Sodium metal, with its impressive electrochemical properties, including a high specific capacity of 1166 $mAhg^{-1}$ and a low redox potential of -2.71 V vs SHE, emerges as a compelling option for battery anodes[218–220]. Additionally, sodium's abundant availability provides a clear advantage over lithium metal[221,222]. However, the realization of commercial room-temperature SMBs faces several interconnected technical challenges, namely, fragile solid electrolyte interface, dendrite growth, and the associated efficiency and safety concerns. The sodium dendrites formed during subsequent charging/discharging cycles severely limit the practical implementation of sodium metal batteries. This results in low columbic efficiency, accelerated electrolyte degradation, increased sodium consumption, and premature battery failure. Moreover, these dendritic growths often penetrate the separator material to cause short-circuiting, posing the ever-impending danger of thermal runaway and fires[223–225]. Although the mechanics behind dendrites in sodium metal is not clearly understood, the growth of these dendritic structures has been found to be impacted by factors such as ionic concentration and composition of the electrolyte, uniformity of the Na^+ flux, chemo-mechanics of the SEI, operating currents and many more[220,226]. To date, several strategies have been deployed to suppress the dendrite formation in metal batteries. Some strategies that have successfully subdued the dendritic growth in Li/Na metal anodes are electrolyte modulation, electrode-electrolyte interfacial engineering, or 3D current collectors.

However, these strategies tend to be expensive, instrument-intensive, and difficult to scale up[227–229].

Another strategy explored for mitigating the issue of dendrite growth is the functionalization of the separator material[230,231]. Separators, which act as a physical barrier between the two electrodes, play an essential role in controlling ion mobility within the battery. In a full-cell configuration, these separators, while maintaining electrical insulation, also act as a pouch for holding the electrolyte in place, facilitating the movement of sodium metal in and out of the cell. Given the direct link between dendrite growth and ionic conductivity and interactions at the electrolyte-electrode interface, the surface functionalization/modification of the separator holds the potential to effectively impede the growth of dendritic structures. However, it is imperative that any modification, in conjunction with enhanced cycling performance, does not negatively affect its key functioning, such as electrolyte wettability, mechanical strength, electrical insulation, and ionic conductivity, and rather ameliorate these properties. For this purpose, the material selected for the surface functionalization must be lightweight and exhibit insulating properties, porous/ layered structure, and thermal and chemical stability.

Considering the requisite properties, hexagonal boron nitride (hBN) caters to all the requisite needs and emerges as a compelling option for its utilization in separator engineering. hBN is an insulating material with a structure analogous to graphene, where alternate boron and nitrogen atoms are bonded in a honeycomb structure. Its two-dimensional structure bestows it with a considerably high surface area, and the partial ionic bonding between boron and nitrogen imparts very high mechanical strength, superior thermal stability and conductivity, and excellent chemical stability[232,233].

Owing to these excellent properties, hBN has been previously investigated for separator modification in lithium-based batteries. Boron nitride nanotubes have been reported for coating polypropylene separators, demonstrating elevated stability at high temperatures and high current operation[234]. The coating of the PP separator with the ultrathin hBN/polyimide layer is reported to stabilize the SEI and suppress the Li dendrite growth. The full cell showed extreme stability after long cycling and high temperature[235]. hBN/PI separators also displayed good wettability, superior thermal conductivity, enhanced thermal stability, and excellent electrochemical performance[236]. hBN nanosheet-based free standing separators have shown promising results in lithium batteries, showcasing suppressed Li dendrite growth, and better rate capability and cycling stability at elevated temperatures (80 - 120°C)[237,238]. Boron nitride-modified separators have also been explored for application in lithium-sulfur batteries with great success. The modification successfully suppresses the shuttle effect at the cathode, dendrite formation at the anode and increased ion transport through the separator, leading to high capacity and long-term stability of the battery[239–241]. Although there have been significant achievements in improving the electrochemical performance of lithium batteries, more research needs to be conducted to enhance the performance of sodium batteries in this area. Nevertheless, several computational reports have proposed hBN to possess significant sodiophilic characteristics that might be conducive to modulate the Na^+ flux when applied as a layer over the separators[242–244]. The results showcasing hBN's ability to mitigate the dendritic deposition of lithium and its sodiophilic character motivated us to investigate hBN as a separate modifier for application in SMBs.

This chapter report that boron nitride nanoplatelets can be utilized for the modification of commercial polypropylene separators to enhance their mechanical, thermal, and electrochemical performance in SMBs. The hBN decorated separator demonstrated superior thermal stability, enhanced electrolyte wettability, suppressed dendrite growth, and improved columbic efficiency compared to the same separator without hBN decoration. This work intends to showcase the possible application of hBN for improving Na-metal batteries. However, a detailed optimization of the surface layer real-time application of this approach in Na-S or Na-O_2 batteries is required and will be studied as the next problem statement.

5.2 Results and discussion

5.2.1 Chemo-mechanical Characterization:

We utilized scanning electron microscopy to investigate the morphological changes brought about by coating the separator surface with boron nitride. **Figure 5.1** presents the SEM images of the pristine and BNNP coated PP separator. Unlike the uncoated PP, the BNNP coated PP (BN-PP) exhibits uniformly distributed nanoplatelets all over the separator. The nanoscale structures of the BN were found to be stacked onto one another, offering the 3D voids onto the porous network for facile electrolyte movement. The hBN coating did not result in any significant increase in the separator weight. The average weight of three hBN coated separators punched in circles of 18 mm diameter was found to be 5.14 mg compared to the 4.50 mg of the uncoated separator of the same dimensions.

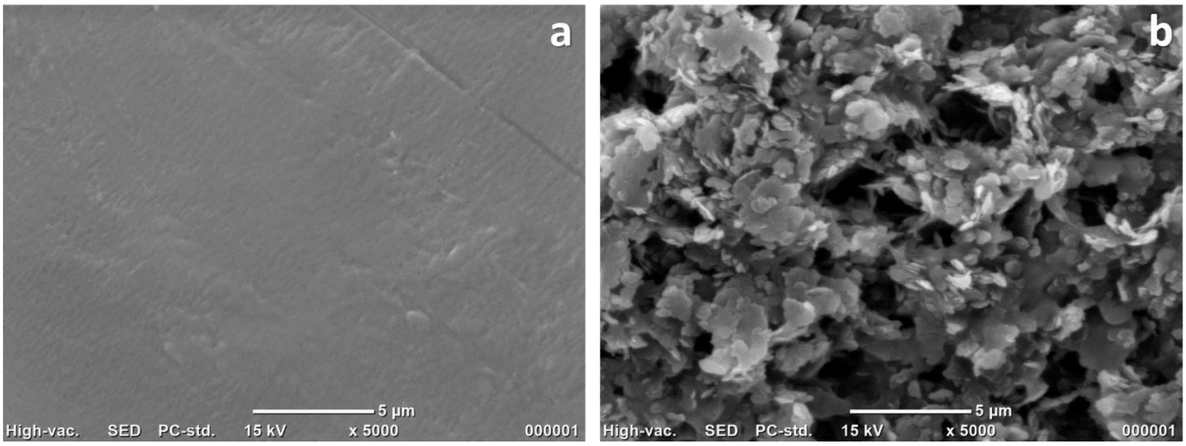

Figure 5.1: Top view SEM images of **(a)** uncoated and **(b)** hBN coated separator.

The wetting capacity of the coated and uncoated separator with respect to the electrolyte was next investigated. To do so, films of coated and uncoated separators were cut and attached to the stage of the goniometer (Biolin Scientific) (**Figure 5.2**). These acted as substrates over which contact angles of sessile electrolyte droplets having a volume ~ 1 µL were measured. The coated separator films show a ~ 30 ° decrease in the contact angle, indicating substantially increased wettability by the introduction of the thin hBN coating. The increased wettability can be ascribed to the connected network of hBN nanoplatelets offering enhanced room for spreading and imbibition of the electrolyte compared to the conventional porous substrate. The improved electrolyte wettability is expected to be conducive for providing uniform ion flux during deposition/stripping cycles, which is known to be one of the primary factors controlling the non-uniform/ dendritic deposition of the metal.

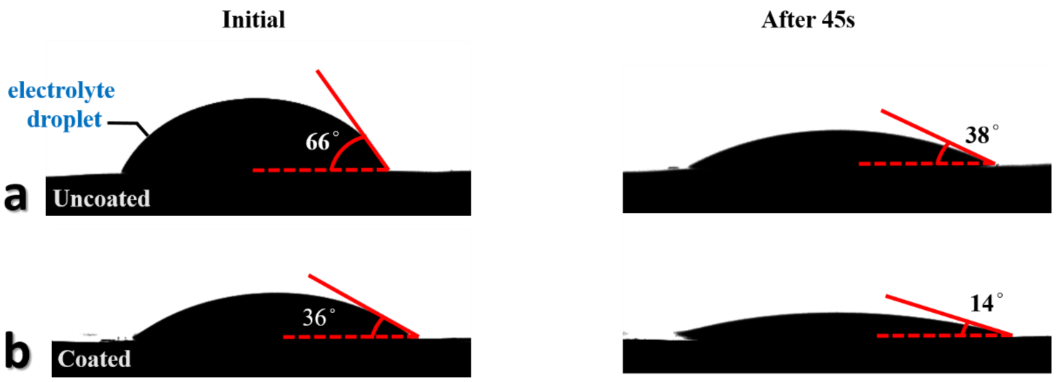

Figure 5.2: Contact angle of electrolyte droplet at **(a)** uncoated and **(b)** hBN coated separator.

Another factor that dictates a battery's safety is the separator's thermal stability. Being a polymer, polypropylene based separators shrink with the increasing temperature, bringing the cathode and anode in direct contact, leading to a short circuit, battery failure, and ultimately thermal runaway[225]. Therefore, the impact of hBN coating on the thermal stability of the separator was investigated by employing thermal gravimetric analysis (TGA). Essentially, the weight loss in response to increasing temperature was monitored to compare the thermal stability of the coated and uncoated separator (**Figure 5.3**). The careful TGA analysis manifests the superior thermal stability of the hBN coated separator. The bare PP separator started shrinking around 240 °C, whereas the shrinking of hBN coated PP was observed only after 280 °C. Furthermore, BN PP exhibits a higher decomposition temperature than the bare PP separator. The PP separator was decomposed to an 80% weight ratio at 420 °C and to a 100% weight ratio at 470 °C. On the contrary, the hBN coated separator got to an 80% weight ratio at 470 °C. Moreover, it decomposed only to 85% weight ratio even at 575 °C. The enhanced thermal stability is ascribed to the outstanding thermal stability of boron nitride material[232,245].

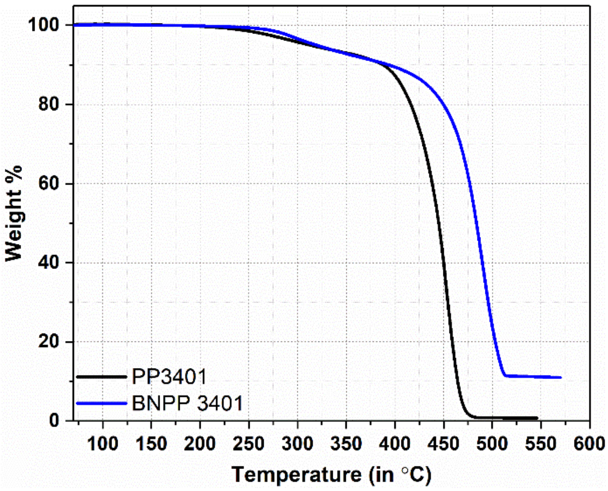

Figure 5.3: TGA analysis of uncoated and hBN coated separator

5.2.2 Electrochemical performance

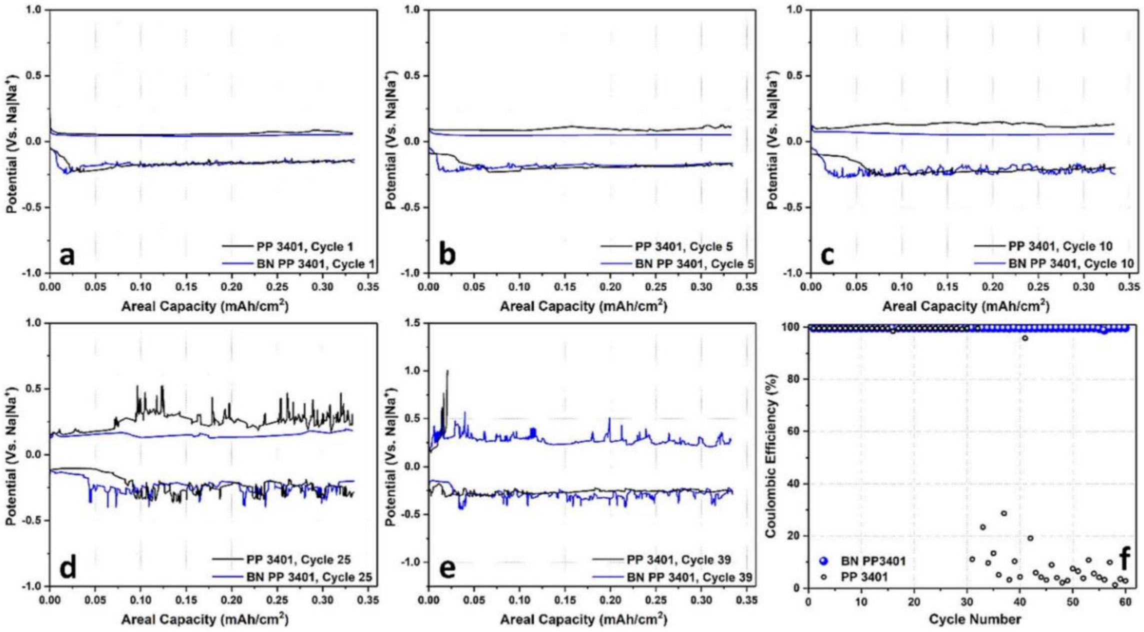

Figure 5.4: Voltage profile corresponding to 15% stripping of total sodium (2 mAh cm^{-2}) at 1 mAcm^{-2} for **(a)** 1st, **(b)** 5th, **(c)** 10th, **(d)** 25th, and **(e)** 39th cycle. **(f)** Coulombic Efficiency of Na|Na symmetrical cells constructed using uncoated and hBN coated separator.

Currently, the reversibility of the Na-metal batteries is severely plagued by the dendritic deposition of Na, resulting in inferior columbic efficiency. Repeated deposition-stripping of sodium becomes a primary cause of microscopic cracks in the SEI layer. This not only exposes the fresh sodium for the irreversible consumption of electrolyte for rupture-repair cycles of SEI but also offers less energetic and preferential nucleation sites for sodium plating. These nucleation sites act as breeding points for the non-uniform, mossy, or dendritic growth of sodium. The whole process irreversibly consumes the electrolyte, impedes the Na+ transfer, and increases the voltage hysteresis[246,247]. Here, the effect of hBN coated separator on the reversibility of the Na deposition/stripping was investigated by monitoring the plating-stripping characteristics of symmetrical cells. It is worth mentioning that in contrast to using Na-foil, which offers an indefinite supply of Na^+, the study relies on investigating the reversibility under limited Na loading (2mAhcm^{-2}).

The galvanostatic cycling tests in Na|Na symmetrical cells with hBN coated and uncoated separator were conducted and the Na stripping platting behavior was studied. Firstly, the effect of hBN coating on the electrochemical reversibility of Na plating and stripping of 15% of the total sodium at a current density of 1 mA cm^{-2} was evaluated. **Figure 5.4a–e** demonstrates the voltage profiles of 1st, 5th, 10th, 25th, and 39th cycles. For the initial 10 cycles, the cells with coated and uncoated separators behaved similarly, however, in subsequent cycles an increased polarization was observed. After 30 cycles, a substantial decrease in coulombic efficiency was observed for the cell having uncoated separator which lately showcases less than 10% coulombic efficiency. In contrast, the cell with the hBN coated separator shows coulombic efficiency >99.6% till 60 cycles under identical cycling conditions as presented in **Figure 5.4f**. However, the polarization was found to increase for the hBN coated separator as well, hinting toward a sluggish stripping behavior. To further evaluate the ability of hBN coating to improve the reversibility of Na stripping/plating behavior, the cyclability was investigated under more aggressive conditions. To do so, the galvanostatic cycling for stripping/plating of 80% of the total sodium (2 mAhcm^{-2}) equivalent was tested at a current density of 1 mA cm^{-2}.

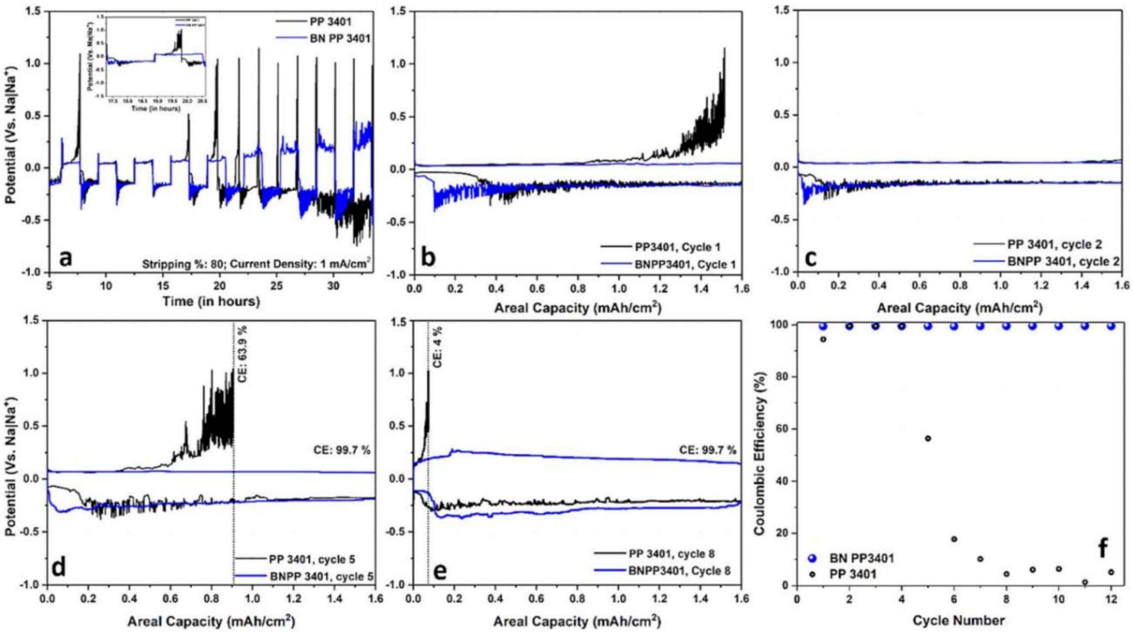

Figure 5.5a) Cyclability study, voltage profile corresponding to 80% stripping of total sodium (2 mAhcm^{-2}) at 1 mAcm^{-2} for **(b)** 1st, **(c)** 2nd, **(d)** 5th cycle**, (e)** 8th cycle, **(f)** Coulombic Efficiency of Na|Na symmetrical cells constructed using uncoated and hBN coated separator.

Figure 5.5a demonstrates the electrochemical profile observed in successive stripping/plating for the two cells, comprised of hBN coated and uncoated separators. The cell with an uncoated separator showcased a sharp upsurge during the first stripping (**Figure 5.5b**), which can be ascribed to the formation of SEI and other parasitic reactions at the metal/electrolyte interface. The subsequent plating/stripping for the successive two cycles exhibited stable stripping and plating with a coulombic efficiency >99% for both cells (**Figure 5.5c**). However, an increase in stripping potential was observed from the fifth cycle with a significant drop in coulombic efficiency. Interestingly, the cell with hBN coated separator manifested stable cycling, exhibiting a coulombic efficiency of 99.7%, as visible in **Figure 5.5d**. In contrast to the cell with an uncoated separator, which showed almost no stripping in the 8th cycle, the cell with hBN coated separator demonstrated CE > 99% with a minimal increment in potential (**Figure 5.5e**). The observations manifest the ability of hBN to stabilize the sodium deposition/stripping behavior. The primary reason is expected to be a non-dendritic sodium deposition, which helps mitigate the accumulation of dead Na. Furthermore, due to the direct contact of the hBN layer and Na-metal, a chemically inert artificial SEI layer will form, which will impede the electrolyte degradation at the metal surface, thereby increasing the CE as well as the cycle life of the cell as witnessed from **Figure 5.5f**. To validate the proposed reasoning, the cycled cells were de-crimped inside the glovebox using a de-crimping dye, and the used electrodes were taken for scanning electron microscopy.

Figure 5.6a showcases the SEM images of Na-anode cycled for 10 cycles in a cell containing an uncoated PP 3401 separator. Dendritic growth and non-uniform deposition of Na can be clearly seen, which very well explains the CE < 5%. The upward growth of Na results in loss of contact, making the Na unavailable for further stripping and thus becoming the reason for poor CE. On the other hand, the Na-anode cycled in a cell having hBN coated separator showcases uniform Na deposition, as represented in **Figure 5.6b**. However, in some places, the Na-anodes were found to bulge out, which indicates that there is still scope for improvement, which can be achieved by optimizing the coating parameters like composition, thickness, etc. We believe that the hBN-coated separator ensured a uniform Na^+ flux, exploiting the chemical and mechanical benefits of the material. The sodiophilic nature of hBN is expected to facilitate the uniform sodium ion passage through the separator. It might also result in Na pre-nucleation at uniformly distributed hBN ascribed to its sodiophilic nature and Na^+ adsorption affinity. The synergistic role of both possibilities is expected to result in uniform Na-platting instead of mossy dendritic growth at the metal surface.

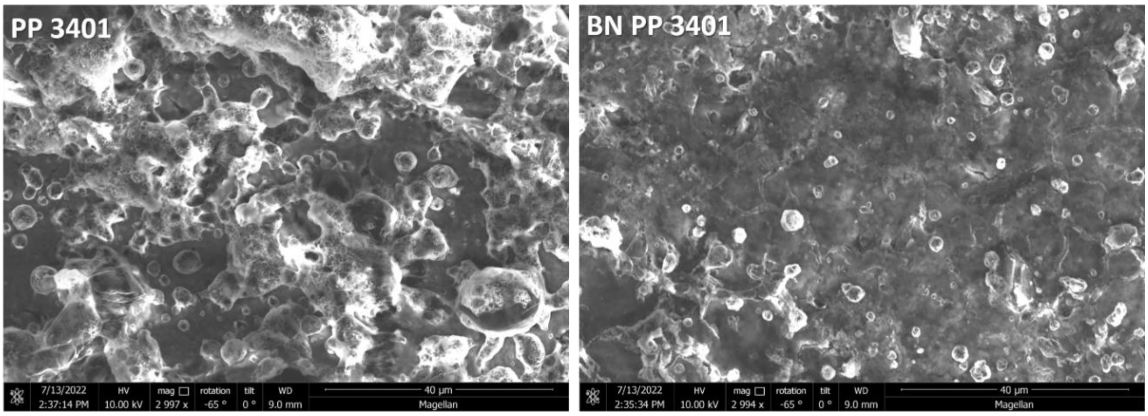

Figure 5.6: SEM images of post cycled Na anode disassembled after 10 cycles.

5.3 Conclusion

This study presents a strategy to achieve dendritic-free sodium deposition using an hBN nano-platelets coated polypropylene separator. The coating resulted in a tailored Na/separator interface, improving wettability and uniform Na^+ flux. The direct contact of the hBN layer and Na-metal resulted in dendritic-free Na deposition/stripping, ascribed to the hydrophilic character of hBN. The increased coulombic efficiency of the hBN-coated separator can be explained based on the uniform Na^+ flux and formation of a chemically inert artificial SEI layer. The uniform Na^+ flux ascribed to the sodiophilic nature of hBN will provide guided nucleation sites for uniform metal deposition. Meanwhile, the chemical inertness of hBN is expected to impede electrolyte degradation at the metal surface, thereby increasing the CE and cycle life of the cell. Though this study provides a strategy to mitigate the dendritic deposition, the approach is in its infancy. A comprehensive study investigating the effect of coating composition, thickness, and method is required for practical applications. Furthermore, a pragmatic application in metal batteries like Na-S and Na-O_2 should be carefully studied to decipher the efficient use of the proposed strategy.