Chapter 4

4. Hexagonal Boron Nitride as Anode for Sodium-ion Battery

4.1 Introduction

For the past few decades, rechargeable lithium-ion batteries (LIBs) have been predominantly used for most of the energy storage requirements ranging from electronic devices and electric vehicles to grids[183–186]. Nevertheless, depleting and unevenly distributed lithium ore reserves pose a challenge to LIB's suitability for future ESS. Reports suggest that around a quarter of all globally excavated lithium metal is used in the manufacturing of LIBs, which is turning out to be a bottleneck for the energy industry[187,188]. For these reasons, there has been an ongoing search for an alternative battery system that can share the load. Sodium-ion batteries (SIB) have been proposed as one such system, which has attracted much attention due to similar working principles as LIBs. One major reason for enthusiastic interest in SIBs was the expectation that the well-matured technology and electrode material could be employed in the fabrication of SIBs. Unfortunately, due to thermodynamically unfavorable sodium intercalation, graphite has been found to be incompatible with the SIBs, which has blocked its path to speedy commercialization[189,190].

To tackle this challenge, there has been widespread theoretical and experimental research for the discovery of novel materials that can be employed as SIB anodes. A number of materials have been investigated for this purpose, including carbon-based materials, alloying compounds, conversion, and organic compounds. Although these materials have promised to impart high energy density to the battery, several major issues still lurk in their practical usage, such as high-volume expansion, low-temperature operation, low cyclability, and irreversibility[191–193]. In recent periods, the superb properties of 2D

nanomaterials such as graphene, graphene oxide, transition metal di-chalcogenides (MoS_2, WS_2, etc.), transition metal carbides, boron carbon nitride and hexagonal boron nitride (hBN), including ultra-high specific surface area, negative adsorption energy, great thermal and chemical stability have brought them in limelight for their potency as novel anode materials[194–196]. hBN, a two-dimensional structure analogous to graphene with boron and nitrogen bonded alternatively in a honeycomb pattern, has particularly been under theoretical radar for this purpose[197]. Lately, hBN has been reported to provide great protection layer at the anode/electrolyte interface for enhancing the lifetime of lithium-ion batteries[198,199].

Numerous theoretical reports have recently portrayed hBN as a superb candidate for potential application as anode material in SIBs. ***Nejati et al*** investigated the adsorption of atomic sodium and sodium ion on the boron nitride nanosheet theoretically using hybrid B3LYP functional augmented with empirical dispersion term[200]. Performed over the sheet consisting of 36 boron and 36 nitrogen atoms, DFT calculations showed that the adsorption energy of sodium ion is -34.2 kcal/mol, which is significantly more negative than the adsorption energy of atomic sodium (1.4 kcal/mol), indicating a favorable interaction with Na^+ ion. Similar theoretical predictions were made by Hossenien and others, where adsorption energies were found to be -33.7 and -0.08 kcal/mol for Na+ ion and atomic Na, respectively, and the cell voltage for hBN was predicted to be 1.46V[201,202]. ***Kansara and group*** studied the electrochemical properties of the h-BN monolayer as a new anode material for sodium and lithium-ion batteries[203]. Conducted over a group of 18 atoms (B_9N_8), The theoretical study predicted a maximum capacity of 571.698 mAh/g and an electrode potential of 0.009 V for the adsorption of sodium ions. Notably, all the computational studies performed focused on the sodium ion adsorption energy on hBN, and there is a clear gap in understanding of the formation of the intercalation compound of

Na-hBN. Moreover, various functionalization strategies including halide doping[204], carbon doping[205] and hetero-structure assemblies involving hBN[206–208] have also been devised and theoretically investigated.

Despite all these theoretical works predicting the great potential of hBN as anode material for SIBs, we could not find any experimental work validating the same in the literature. Discerning this large gap between theoretical and experimental work motivated us to fill in this void of information for future reference. Thus, we hereby investigate the use of bulk hexagonal boron nitride (BNB), and hexagonal boron nitride nanoplatelets (BNNP) as the anode material in SIBs.

4.2 Results and Discussion

The need for experimental evidence supporting several recent computational reports showcasing hBN as a potential sodium-ion battery anode material motivated us to examine its pragmatic viability in hosting Na^+ ions. The following sections will present and discuss the structural and electrochemical behavior of hBN bulk (BNB) and hBN nanoplatelets (BNNP) toward hosting Na^+ in SIBs.

4.2.1 Material characterization

Before the electrochemical evaluation, structural and morphological characteristics of the hBN material were first investigated using X-ray diffraction (XRD) spectroscopy and scanning electron microscopy (SEM).

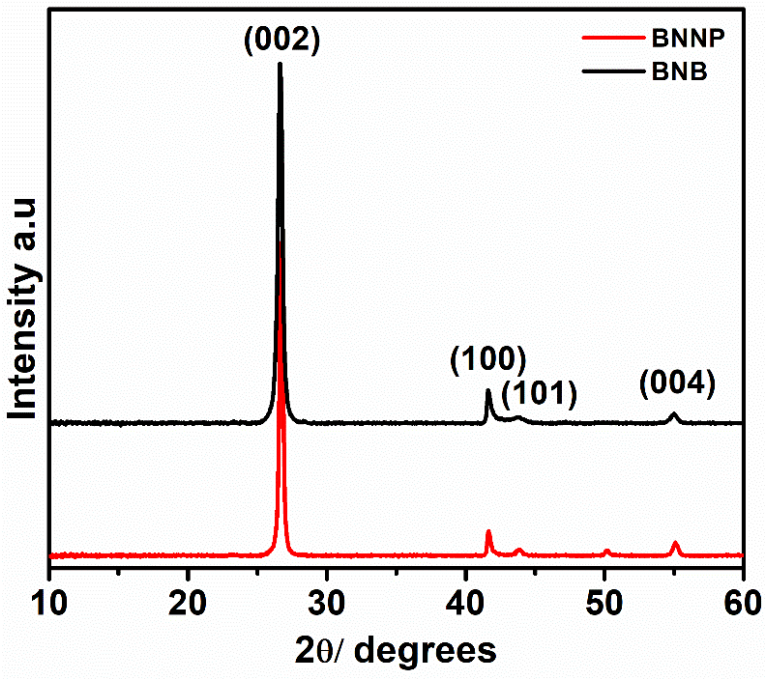

Figure 4.1: XRD diffraction patterns for BNB and BNNP.

Figure 4.1 presents the X-ray diffractogram of BNB and BNNP, respectively. As evident from the figure, both the materials exhibited sharp and well-defined peaks at 26.67^{o}, 41.62^{o}, 43.77^{o}, and 55.00^{o} corresponding to the (002), (100), (101) and (004) facets of hexagonal boron nitride, respectively, in accordance to JCPDS file 034-0421. The interlayer spacing for BNB and BNNP was 0.339 nm, as calculated for the (002) plan. The d-spacing of 0.339 nm for hBN is similar to that of graphite (0.34nm), which might not be conducive to Na^{+} insertion[209,210].

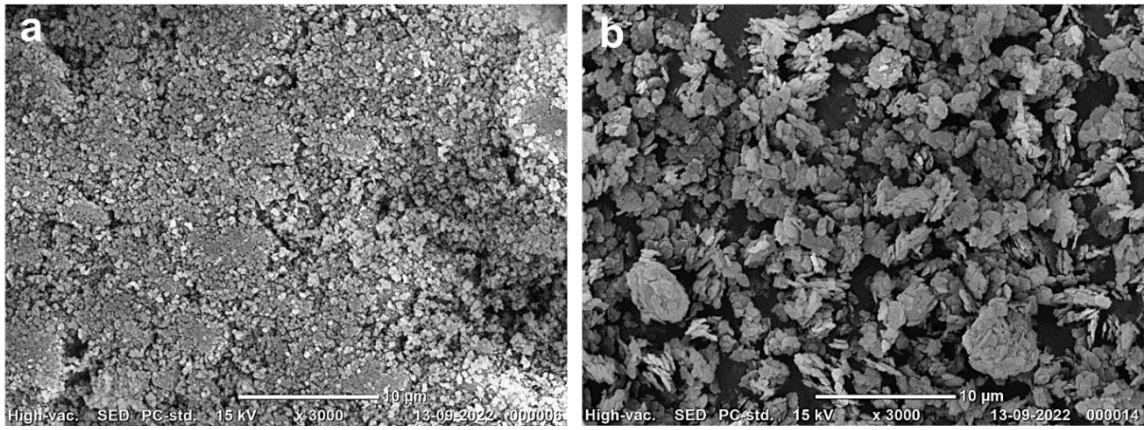

Figure 4.2 SEM images showcasing the morphology of **a)** BNB and **b)** BNNP**.**

Figure 4.2 showcases the morphology of BNB and BNNP. The figure shows that BNB does not have any defined morphology; instead, irregular islands with a high particle polydispersity index can be witnessed. On the other hand, BNNP exhibits well-defined plate-like morphology that is stacked onto one another. With a lateral dimension of < 5µm, these platelets showcase smooth edges, which are expected to provide adsorption sites for Na^+ ions.

4.2.2 Electrochemical performance

After finding substantial differences in the morphologies of BNB and BNNP, the ability of both materials to reversibly host Na^+ ions were investigated. **Figure 4.3a** shows the comparative first charge-discharge cycle for the BNB and BNNP at a current of 15 mAg^{-1} in the potential range of 0.10 to 2.40V. From the first discharge, at least two plateaus/sloping regions were observed, indicating the involvement of different charge storage processes. The first region in the voltage region of 1.00 – 0.75 V corresponds to the irreversible electrolyte degradation and formation of SEI at the anode surface[211,212]. This process was the major contributor to the first discharge capacity ~ 40 $mAhg^{-1}$ for BNNP and ~ 30 $mAhg^{-1}$ for BNB. Compared to BNB, an additional sloping region from ~

0.75 – 0.60 V was observed for BNNP, which can be assigned to the Na^+ adsorption on the easily accessible surfaces and edges of BNNP, which are expected to be much more due to nano-dimensions of the particles. The low voltage sloping region was common to both materials and represents the sodiation of pores, voids or interlayer regions. A total specific discharge capacity of ~ 90 and 50 $mAhg^{-1}$ were observed in the first cycle for BNNP and BNB, respectively. Nevertheless, on careful analysis of the first charge and discharge profiles, it can be inferred that the capacity obtained from the processes in the potential range of 1.25 – 0.60 V originated through irreversible Na^+ adsorption or parasitic processes. On the other hand, a capacity of ~ 34 $mAhg^{-1}$ and 22 $mAhg^{-1}$ contributed by the low voltage sloping region was found to manifest reversible sodiation/desodiation leading to a charge capacity of ~ 18 $mAhg^{-1}$ and 13 $mAhg^{-1}$ in the subsequent charging cycles for the BNNP and BNB, respectively. The poor coulombic efficiency indicates substantial irreversibility in the involved electrochemical processes. Notably, the BNNP anode exhibits greater irreversibility than BNB. This irreversibility is ascribed to the large surface-to-volume ratio of BNNP, offering more edges, defects, and adsorption sites leading to enhanced electrolyte degradation during SEI formation and more Na^+ adsorption compared to BNB[213]. The positive sodium adsorption on hBN, especially on BNNP, validates the computational results, which predicted high negative adsorption energy for sodium ion interaction with boron nitride nanosheets[214–217]. Nevertheless, the favorable adsorption seems to involve strong interaction, which limits the desorption, resulting in the associated irreversibility. Similar inferences can be made from the voltage profile of 3rd cycle, as represented in **Figure 4.3b**. As can be seen, only the low voltage sloping region was witnessed during discharging, confirming its participation in the reversible sodiation/desodiation as discussed above. Both the hBN exhibited a low charge capacity of ~ 18 $mAhg^{-1}$ and 12 $mAhg^{-1}$ after the first cycle, demonstrating their inability to host

Na^+ ions effectively. The electrochemical behavior of hBN was further investigated at different rates to understand the charge storage ability at slow and fast ion-transfer rates.

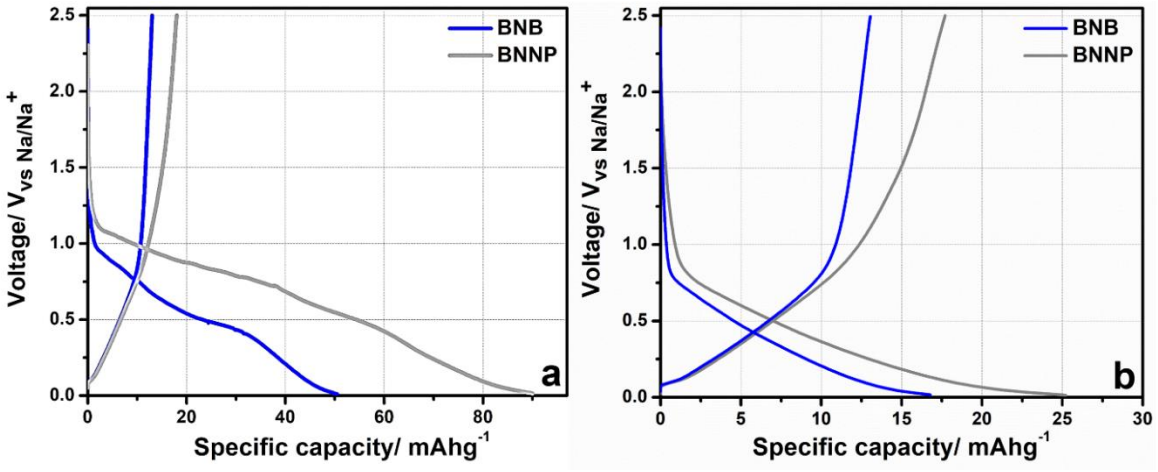

Figure 4.3: Comparative voltage profiles of BNB and BNNP during **a)** 1st cycle, **b)** 3rd cycle.

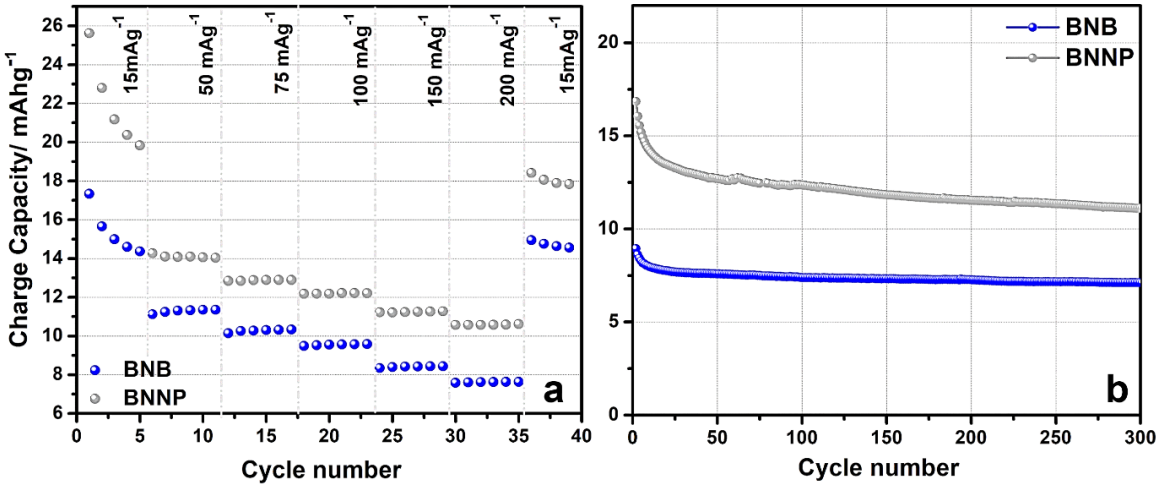

Figure 4.4 a) Rate study for the BNB and BNNP at various current rates **b)** Long cycle study for BNB and BNNP at 150 mAg^{-1} current rate.

The rate capability of both the hBN materials was investigated by varying current densities in the range from 15 mA/g to 200 mA/g (**Figure 4.4a**). The specific charge capacities obtained for BNNP were found to be 21.95, 14.26, 12.88, 12.17, 11.23, and 10.57 $mAhg^{-1}$ at current densities of 15, 50, 75, 100, 150, and 200 mAg^{-1}, respectively. While for BNB, the values were 15.38, 11.72, 10.14, 9.55, 8.43, and 7.60 $mAhg^{-1}$. No substantial change

in the capacities, even at faster rates, indicates the involvement of Na^+ adsorption and pore-filling rather than intercalation, as adsorption and pore-filling tend to follow faster diffusion. BNNP and BNB showcase abysmal performance at all rates and indicate that the hexagonal boron nitride is inappropriate for Na-ion storage, irrespective of the particle morphology/dimensions. The cycling performance of both materials was also investigated at 150 $mAhg^{-1}$ for 300 cycles, as demonstrated in **Figure 4.4b.** After 300 cycles, recorded capacities for BNB and BNNP anodes were 7.38 and 12.35 $mAhg^{-1}$, respectively, where the insignificantly better capacity by BNNP can be attributed to its increased surface area. On the other hand, the high surface area of BNNP is a cause for its relatively low-capacity retention (66.5% compared to BNB's 76.7% after 100 cycles). While the nano-dimension particles in BNNP provide more active sites for stronger bonding of sodium atoms, these ions seem sluggish desorption, causing irreversibility and capacity loss. The cycling study further confirms the incompetence of hBN in serving as an anode for sodium-ion batteries.

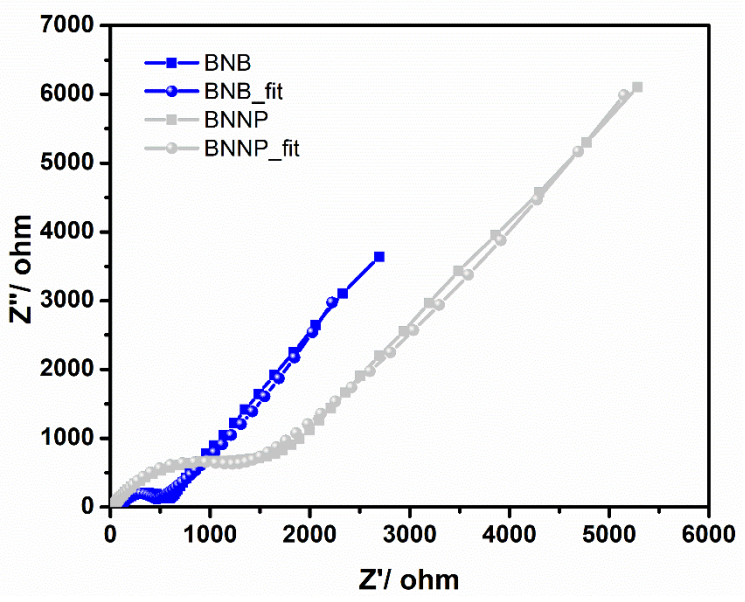

Figure 4.5 Electrochemical impedance spectra for the BNB and BNNP active material**.**

To understand the transport of sodium ions in the two electrodes, AC impedance spectra for the two active materials were recorded and examined in the frequency range of

1-10^6 Hz. **Figure 4.5** showcases the typical Nyquist impedance plots for the two materials. The spectra present two distinct semicircles in the high and intermediate frequency range respectively along with a 45^o line in the low frequency region attributed to the Warburg impedance. A larger sloping line for the BNNP anode indicates slower sodium ion diffusion in nano-dimensional boron nitride. Moreover, we observe larger interface impedance in case of BNNP which can be attributed to either SEI layer or charge transfer impedance. The impedance study again confirms that regardless of the large surface area compared to BNB, BNNP demonstrates sluggish sodium ion transport.

As evident from the electrochemical performance results, both morphologies of hexagonal boron nitride (i.e. bulk and nanoplatelets) perform very poorly in terms of charge capacity. The BNNP tends to exhibit favorable sodium-ion adsorption as suggested by the theoretical calculations. However, the charge/discharge for the 1^{st} and 3^{rd} cycle makes it apparent that the adsorption of sodium ions on both BNB and BNNP were irreversible. Therefore, building on the thorough electrochemical investigations, it can be concluded that although hBN nanostructures can interact favorably with Na^+, they are not conducive for hosting Na^+ with an efficient electrochemical charge storage mechanism. Nevertheless, there are still few innovative ways when implemented can improve hBN performance as SIB anode material. One way is by augmenting its interlayer spacing via metal ion insertion. Along with increasing sodium ion mobility in the lattice, it may also improve anode performance by enhancing its conductivity. Although, the stability of intercalation compounds needs to be investigated by computational studies. Fabricating hetero-structures with other layered materials is another possible method of improving hBN performance.

4.3 Conclusion

The theoretical predictions regarding hexagonal boron nitride use as the anode in SIBs boosted it to be a potential candidate that could lead to SIB's realization. With this motivation, we carried out a series of experimental testing via the galvanostatic charge-discharge technique. However, the outcome of our research suggests that the hexagonal boron nitride (bulk as well as nanoplatelets form) is ineffective in storing sodium ions thus rendering it incompetent for use in SIBs. To conclude, hBN in its pristine form is not suitable for SIB anode material, but that said hBN has been pronounced as the most versatile 2D material to date. Its superb properties such as good thermal conductivity, ultra-high mechanical strength, chemical stability, and monolayer structure may possibly be utilized in conjugation with other 2D materials forming novel hetero-structures that can tailor the interlayer spacing and tune the availability of adsorption sites to make the intercalation process a primary storage mechanism.