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Enhancing the thermal and electrochemical properties of 18650 type Li-ion batteries via boron nitride coating

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ABSTRACT

Lithium-ion batteries have a significant safety concern since they are prone to thermal runaway as the battery technology advances with high energy density and fast charge requirements. New material solutions are emerging that provide better heat dissipation to address this issue. Boron nitride is a promising candidate as a heat conductor material in thermal management systems because of its high thermal conductivity. Therefore, this material allows effective heat dissipation and reduces the risk of thermal runaway issues. To this end, hexagonal boron nitride (hBN) was coated onto the outer cases of 18650-type batteries to dissipate the generated heat inside the battery. In addition, a cyclic charge-discharge test was performed on the hBN-coated battery sample at 10C to compare the results with a reference sample with only a polymer insulator. The findings revealed that the hBN coating on the insulator-free battery case offered efficient heat dissipation, improved capacity retention, and less change in internal resistance. Thus, the hBN coating has the potential as a solution for the efficient thermal management of Li-ion battery cases.

1. Introduction

Electric vehicles (EVs) are becoming widespread thanks to their less greenhouse gas emissions than their gasoline counterparts. Besides, they offer several advantages, such as high energy efficiency, reduced dependence on oil, lower operating costs, and a more enjoyable driving experience. Parallel to the development of EVs, battery technologies are also advancing rapidly. As the world continues to face pressing environmental and energy security challenges, the vast growth of the electric vehicle industry will be inevitable [1]. Li-ion batteries play a critical role in developing long-range driving EV technology thanks to their high energy density and low self-discharge rate [2]. These batteries are practical for daily use because of being highly efficient and charging quickly [3]. They are also becoming greener thanks to developments in new material technologies [4]. With the growing EV market, the demand for Li-ion batteries is increasing daily for cleaner and more sustainable transportation. Therefore, developing high-performance and cost-effective electric vehicles is directly related to the development and innovation in Li-ion battery technology.

Although Li-ion batteries have several advantages, they also have some drawbacks, such as a high cost due to the expensive materials used in their construction [5]. Besides, the temperature sensitivity of Li-ion batteries can cause capacity and lifespan reduction [6] as well as thermal runaway issues such as explosions or fires. Internal short circuits, overcharging, physical damage, and manufacturing defects cause thermal runaway. The risk of thermal runaway increases with the increasing energy density of the battery because of the battery chemistry, which is more susceptible to electrode and liquid electrolyte reactions. Once the thermal runaway starts in the battery, it can be challenging to stop it due to the chain of exothermic reactions, which entirely results in the car's burning. Therefore, addressing the thermal runaway issue is critical for the safety and performance of Li-ion batteries for electric vehicle applications [7].

Battery management systems (BMS) are critical for the performance and safety of EV batteries, which help monitor the battery's properties, such as the state of charge, voltage, and temperature. Therefore, BMS can help extend battery lifespan by identifying and mitigating issues that could cause premature

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*Corresponding author: semihengun@beun.edu.tr aging or failure [8]. In addition, thermal management is essential to BMS since it helps regulate the battery's temperature and ensures it works within a safe and optimal temperature range [9]. This system keeps the temperature consistent by avoiding overheating and helps optimize the charge and discharge cycles of the battery throughout the process [10]. Therefore, the battery degradation is delayed, and the lifespan is extended.

BMS's typically consist of several parts that work together to keep the battery's optimal temperature based on transferring the heat away from the battery. Therefore, the material choice for battery cases is essential for efficient heat dissipation to operate the system in the desired temperature range. Several materials, like copper and aluminum, can better conduct heat in batteries. Applying a coating layer can also improve the thermal properties of such metal surfaces. This coating layer must be an excellent thermal conductor and electric insulator [11].

Boron nitride (BN) has been becoming an increasingly used ceramic material in various fields thanks to its excellent thermal conductivity, which allows transferring heat away outside quickly. hBN is a polymorph of BN with the same crystal structure as graphite consisting of hexagonal layers separated by a distance of 0.33 nm [12]. The essential physical and chemical properties of hBN are high corrosion resistance, good lubrication behaviour, good thermal conductivity (250-600 W/mK), high-temperature stability, good electronic insulation, and low dielectric constant [13]. Having those unique properties, hBN has broad application areas such as coatings, electrical insulation, optical storage, optoelectronic devices, medical treatment, and lubricants [14,15].

Several attempts have been made to use hBN for battery thermal management systems. The studies used hBN with various materials, such as silicon wax, expanded graphite, and paraffin. Mortazavi et al. compared the effect of expanded graphite and hexagonal BN addition on the thermal conductivity of paraffin wax using molecular dynamics simulation. Their results show that BN is more effective in improving the thermal conductivity of paraffin wax [16]. Zhang et al. developed a new flexible phase change material that utilized silicone rubber as a polymer support material, with boron nitride as a thermal conductivity additive and expanded graphite to enhance the compatibility between silicone rubber and paraffin wax. Their research revealed that the phase change material they designed reduced the temperature from 60.3 to 45.7°C at 3C and 74.3 to 53.4°C at 4C [13]. Li et al. developed a composite material made of silicon sealant and boron nitride, which they used to cover the surroundings of a 18650 battery. They then tested the battery's performance at a 3C charge-discharge rate and found that the composite material effectively reduced temperature [17]. Lu et al. utilized ice-template freeze-drying to fill paraffin wax with hBN nanosheets that were both highly ordered and interconnected. This approach led to efficient heat dissipation in commercial 18650 batteries, resulting in excellent performance [18]. Saw et al. examined the effect of a boron nitride coating on 18650 battery cases. They used the Taguchi experimental design method to optimize the coating's effectiveness to identify the optimal surface roughness and thickness. Testing various coating thicknesses and surface roughness levels revealed that both factors significantly affect adhesion strength. In addition, they found that the BN-coated battery effectively dissipated heat, whereas a significant temperature gradient occurred in the polymer-insulated battery [11]. Although most studies have focused only on using hBN as a filler in different phase-change materials, few studies have investigated the coating of batteries with hBN systematically, to the best of our knowledge [13,19,20]. Therefore, there is limited data on temperature change, capacity retention, and internal resistance during the cyclic use of hBN-coated 18650-type batteries.

This paper aims to investigate the potential use of hBN as a coating material for the 18650-type battery case to effectively dissipate the formed heat by enhancing thermal conductivity.

2. Experimental Studies

The polymeric outer surface of the 18650VTC4 model cylindrical battery is peeled and cleaned to ensure proper adhesion of the boron nitride. The characteristics of the battery used in the tests are given in Table 1.

Table 1. The characteristics of the battery used in this study.

Brand	Sony/Murata
Chemical Specification	Li-ion
Cathode Chemistry	$LiNiMnCoO_2$
Nominal Voltage	3,7 V
Battery Capacity	2100 mAh
Battery Size	18 mm * 65 mm
Maximum Discharge Current	30 A
Cycle Life	500 cycle
Weight	41 g

Then, the battery is sprayed with a thin, uniform coating of Boron nitride spray (Bortek, Boron Technologies, and Mechatronic Inc, >99.99% purity and D50: 120 nm) and left to dry for 24 hours. A comprehensive examination of the physical characteristics of hBN has been provided in the previous research [21]. The thickness of the coating was measured with a digital calliper as 200 µm. The coated battery is then placed in a battery test system (Battterymeter Gw Instek-Gmb3300) and charged and discharged using the constant current (CC) and constant voltage (CV) methods at different current rates. At the same time, temperature measurements were recorded using a thermal camera (Optris 500) throughout each test. The thermal camera was calibrated before making any measurements by considering the material found on the surface of the battery to ensure optimal accuracy and precision of readings. The ambient temperature was kept constant in the climatic test cabinet. The ambient temperature is between 25-28°C. The applied current densities during testing are varied to investigate the effect of current on battery performance and temperature. The schematic view of the experimental setup is given in Figure 1. The test results are analyzed to determine the effect of the hBN coating on the battery's thermal and electrochemical properties.

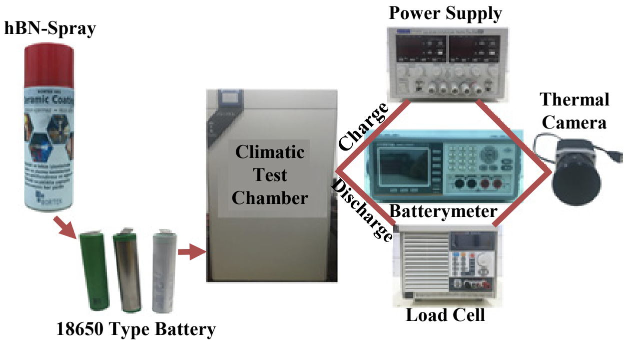

Figure 1. Schematic view of the experimental setup.

3. Results and Discussions

Three 18650-type batteries having similar properties are tested with three different configurations. In the first configuration, the battery with a polymer insulator, PI, was not processed as received. In the second configuration, an hBN is sprayed onto the battery surface with a polymer insulator, PI+hBN. Lastly, in the third configuration, after removing the polymer insulator, the hBN is sprayed on the battery, namely hBN, by masking the pole heads to prevent contact problems.

Temperature changes during cyclic were recorded to understand the heat dissipation behavior of noncoated and hBN-coated batteries during charge and discharge, and the results are given in Figure 2. At the beginning of the charge step, all three batteries have similar temperatures of around 25-26°C (Figure 2a). The maximum temperature is observed around the 14th and 16th minutes when the battery reaches the maximum voltage. After getting the maximum voltage value, the current value decreases over time due to the CC-CV charging method [22]. Therefore, the maximum temperature is not exceeded. Due to the decrease in the current value, the power value given to the battery decreases, so the temperature drops. While the highest temperature was recorded for the hBN coated battery, which was 41.9°C, the battery with only polymer insulator (PI) had the lowest temperature of 34°C and the battery with polymer insulator and hBN coating (PI+hBN) had a slightly higher temperature of 37.4°C.

During the discharge step, the battery with only a polymer insulator (PI) recorded the lowest temperature of 55.7°C at the maximum voltage. The battery with polymer insulator and hBN coating (PI+hBN) recorded a slightly higher temperature of 56.4°C, and the battery with only hBN coating (hBN) recorded the highest temperature of 58.5°C (Figure 2b). These findings align with those reported by Li et al., supporting that the faster increase in temperature can be attributed to the higher degree of thermal conductivity [19]. It is important to note that the temperature measurements were taken using a thermal camera from the entire battery's outer surface rather than an interior thermocouple [13]. The temperature differences among these batteries suggest that the thermal behaviour of the batteries changes with the presence of a polymer case and hBN coating. Therefore, the higher measured temperature values of hBN-coated samples indicate the amount of heat removed from the inside of the battery. Although the hBN coating helps dissipate the battery's heat having a polymer shield, the heat is still trapped between the polymer and the metal case. As the polymer case is completely removed and coated with hBN, it is seen that the heat produced inside the battery can be quickly dissipated on the surface of the battery and transferred to the cooling system. Another important finding is that, after reaching the maximum voltage value, the measured temperature starts to drop with decreasing current.

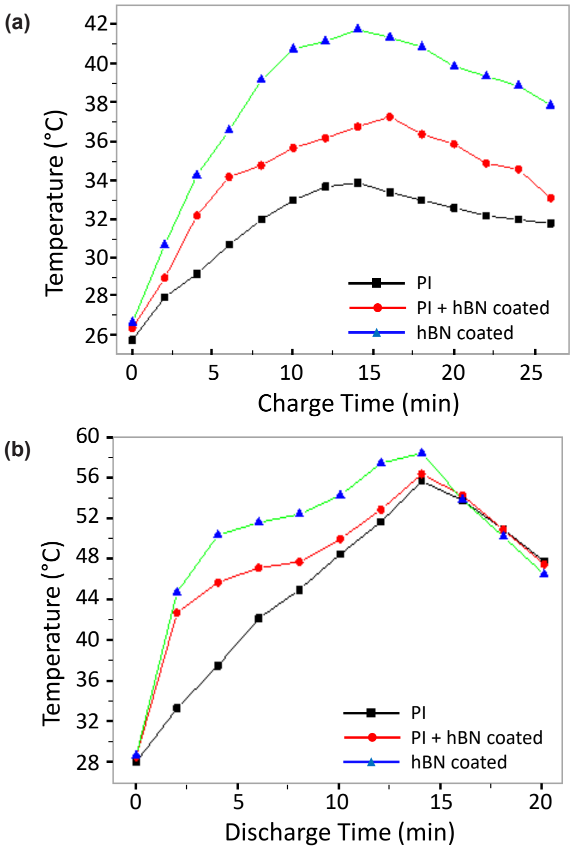

Figure 2. Temperature change with a) charge and b) discharge time.

Notably, this temperature drop is sharper in hBN-coated batteries, indicating that the hBN coating helps with heat dissipation of the battery.

Coatings were tested for uniformity and thickness using a digital caliper measuring each battery's top, middle, and bottom sides without any coating, with a polymer insulator (PI), and with only hBN coating. The results showed that the battery without any coating had a thickness of 18.0 mm, while the battery with PI had a slightly thicker coating with a thickness of 18.1 mm. The battery with only the hBN coating was found to be the thickest of all, measuring 18.2 mm. Therefore, it can be inferred that the thickness of the hBN coating is uniform, measuring approximately 200 μm. During the charge and discharge states, heat is primarily generated at the pole heads, which then progresses to the middle of the battery. Therefore, the temperature gradient on the battery surface is crucial for battery operation. An excessive temperature gradient due to the varying thickness of the coating can cause severe damage to the battery. In this regard, temperature differences between the battery surfaces were determined using thermal imaging analysis to investigate this issue. The results showed a temperature difference of 0.3°C between the pole heads and the center of the battery, which is not potentially dangerous to the battery.

Life-cycle charge-discharge tests at a 10 C rate for 100 cycles were carried out to investigate the effect of heat dissipation on capacity retention, as depicted in Figure 3. In the first cycle, the PI battery has a discharge capacity of 2068 mAh, while the hBN battery has a capacity of 2033 mAh. The difference in initial capacity between the two batteries was attributed to differences in their internal resistance, which may be related to the battery fabrication processes. After 100 cycles, the discharge capacity of the PI battery decreased to 1676 mAh, while the hBN battery decreased to 1726 mAh. Notably, the hBN battery retained 84% of its initial capacity, compared to the polymer-insulated battery, which kept only 81% of its initial discharge capacity. The decreased capacity retention of the battery at higher temperatures is attributed to the worsening Li-ion intercalation properties due to the increased tendency of chemical reactions and material migration [23]. It is seen that the hBN coating enhanced the capacity retention of the 18650-type battery. The improved capacity retention of the hBN battery can be attributed to the higher thermal conductivity of the hBN coating, which acted as a heat sink, helped dissipate the heat, and consequently maintained the battery performance. On the other hand, the polymer insulation did not provide effective heat dissipation, which could explain the lower capacity retention observed in this configuration.

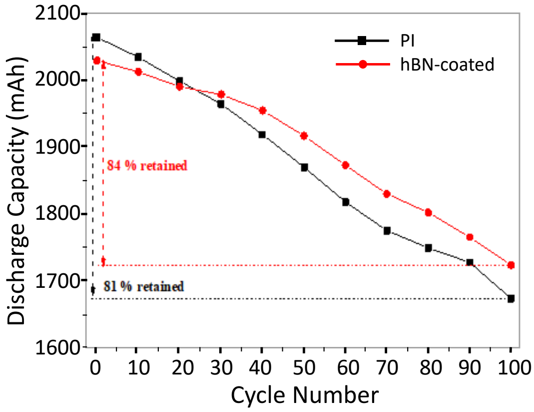

Figure 3. Discharge capacity change with cycle number.

Figure 4 displays the variation of the internal resistance during the cyclic charge and discharge tests. At the start of the test, the PI battery exhibited an internal resistance of 13Ω, while the hBN battery had an internal resistance of 14Ω. The difference in the internal resistance of the two batteries confirms the capacity difference observed at the end of the discharge cycle, as shown in Figure 3. During the discharge test, both batteries experienced an increase in internal resistance, which can be attributed to the degradation of active materials due to the liquid electrolyte reactions [24]. After 80 cycles, the internal resistance of both batteries had increased to 17Ω, and they were equal. At the end of the 100-cycle test, the internal resistances of the polymer-insulated and insulator-free and hBN-coated batteries were 17.6Ω and 17.2Ω, respectively. Therefore, the internal resistance of the PI battery increased more rapidly than that of the hBN-coated battery. The lower internal resistance observed in the insulator-free and hBN-coated battery can be attributed to the more efficient heat dissipation, resulting in less thermal degradation of the cathode active material within the battery.

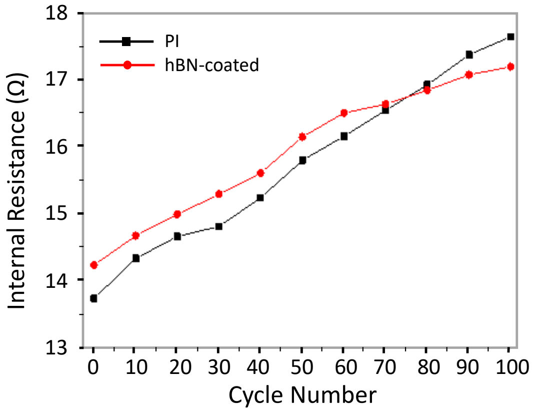

Figure 4. The change in internal resistance with cycle number.

4. Conclusions

18650-type Li-ion batteries were coated with hBN powder to dissipate the generated heat to the outside and to improve the battery's cyclic performance. The galvanostatic charge/discharge tests were conducted at a 10C current rate. During the cyclic test, heat variations were recorded using a thermal camera. Thermal measurements showed that the insulator-free and hBN-coated battery sample had the highest temperature at its surface, indicating efficient heat dissipation. In addition, galvanostatic test results showed that an hBN-coated sample exhibited a better cycle life. It was also observed that the internal resistance of hBN-coated batteries is lower. These findings suggest that effective heat dissipation is crucial in achieving optimal battery performance and capacity retention. Therefore, using hBN coating can potentially improve the safety and reliability of batteries, especially in high-temperature applications.

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