doi:10.20944/preprints202205.0303.v1

Review

Review of Boron Compounds in Lithium Batteries: Electrolyte, Anode, Cathode, Separator, and Battery Thermal Management System (BTMS)

Changlin (Allen) Zheng

U.S. Borax Inc., Rio Tinto. 12 Marina Boulevard, #20-01 Marina Bay Financial Centre Tower 3,
Singapore 018982, Singapore; allen.zheng@riotinto.com; Tel.: +65-9062-8520

Abstract: Lithium batteries and an increasing focus on CO_2 reduction have become an integral part of daily life and business for many people. Boron and boron compounds have been widely studied together in the history and development of lithium batteries. With a broad examination of battery components and systems but a boron-centric approach to raw materials, this review seeks to summarize past and recent studies on the following: which boron compounds are studied in lithium battery, in which parts of lithium batteries, what improvements are offered for battery performance, and what improvement mechanisms can be explained. The uniqueness of boron and its extensive application beyond batteries contextualizes the interesting similarity with studies on batteries. The paper predominantly focuses on lithium-ion batteries (LIBs) but also mentions other lithium batteries. At the end, the article aims to predict prospective trends for future studies that may lead to the successful and extensive use of boron compounds on a commercial scale.

Keywords: boron; lithium battery; lithium-ion batteries; cathode; anode; electrolyte; battery thermal management system (BTMS); battery performance

1. Introduction to Boron and Lithium

In the course of fighting climate change, the trend of electrification continues to intensify and will drive the demand for batteries, especially for electric vehicles (EVs), where lithium plays a critical role. The challenge to improve battery performance has made boron, in various forms of compounds, a research topic in relation to lithium-ion batteries (LIBs) for decades.

Boron and lithium are similar elements in some ways. They are both considered less abundant than other elements in present crustal concentrations and, indeed, in the Universe. Their formation requires a further enrichment process that involves continental crust growth [1,2]. Furthermore, extraction of lithium and boron together is common in existing mining operations and some prospective greenfield projects.

Why is boron used in batteries? Boron is a unique element in many respects. Firstly, its applications in urbanization are extremely diverse: glass and ceramics, oil and gases, polymer fire retardants, wood preservatives, fertilizers in agriculture, and many more. Secondly, the benefit of using boron is often multifaceted. For instance, when sodium borate pentahydrate is used in fiberglass, it brings a unique combination of benefits to both the melting process and fiber properties; when disodium octaborate tetrahydrate (DOT) is used as an indoor wood preservative, it offers deep penetration in wood and residential benefits (such as low mammal toxicity). Thirdly, boron is situated in the part of the periodic table that separates metals and non-metals, hence its classification of “metalloid”. In the table, boron is also the lightest element of the metalloids. Finally, the fact that many boron compounds are electron deficient means that they have Lewis acidic characteristics.

The four covalent bonds and variety in the molecular structure of its compounds result in a wide range of chemical properties [3].

2. Boron Used in Electrolytes

Battery mainly consists of four major components which are cathodes, anodes, electrolyte, and separators. Figure 1 shows the schematics of these components in conventional Li ion batteries (LIBs) and the movement of electrons, ions and current flow under charging and discharging condition.

2.1. Electrolyte Additives—LiBOB

As early as the year 2000, lithium bis(oxalato)borate, also known as LiBOB, was first reported for synthesis and use in electrolytes of LIBs [4]. The presence of bis(oxalate)borate (BOB) anions helps the formation of a solid electrolyte interface (SEI), Figure 1c, which is critical for stability and long-term cyclability of graphitic anodes [5]. Because of the merits of being halide-free and more thermally stable than $LiPF_6$, LiBOB has been proven beneficial either as a direct replacement for $LiPF_6$ or as an electrolyte additive (2 wt%) in a nickel cobalt aluminum (NCA)—graphite system [4][6]. Moreover, it was once considered the only known electrolyte salt that enables the use of propylene carbonate (PC) as a solvent [6]. Although it was beneficial to the NCA cathode system, research revealed that Co could play a role in catalyzing the decompositions of BOB anions on cathode surfaces, which explained the inferior performance of LiBOB in lithium cobalt oxide (LCO) cathodes and nickel manganese cobalt (NMC) cathodes. Research found that the disadvantage of using LiBOB was that SEI could become too resistive to perform well at sub-zero temperatures [7].

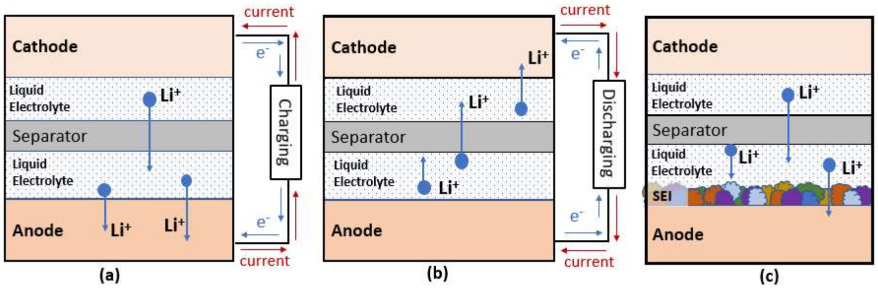

Figure 1. Schematic diagram of LIBs for (a) charging (b) discharging and (c) formation of SEI.

2.2. Electrolyte Additives—TPFPB and TB

Regarding the interface on the cathode side, tris(pentafluorophenyl)borane (TPFPB) can be added as an electrolyte additive to help stabilize the film on the cathode, which improves power capability in lithium manganese nickel (LMN), NMC333, and $LiFePO_4$ (LFP) cathodes [8–10]. Similarly, adding <0.1 M of trimethyl borate (TB) or 0.1 M TPFPB to $LiPF_6$ was found to be effective at suppressing the thermal decomposition of electrolytes and promoting the formation of a protective film on LFP, hence improving the cyclic stability at 55–60 °C [11,12]. TB with 10 wt% was also found to be beneficial to cyclic stability and coulombic efficiency in NMC333 [13].

2.3. Electrolyte Additives—$LiBF_4$

Around the time of the first report of LiBOB, $LiBF_4$ was found to have lower conductivity but better low-temperature performance than $LiPF_6$ [14]. Later in LIB development, $LiBF_4$ salt in carbonate electrolytes was tested as a direct replacement for $LiPF_6$, which improved capacity retention in NMC622 and NMC442 systems due to a more stable B-F bond compared to the P-F bond [15–17]. When only used as an additive to $LiPF_6$, 1 to 2 wt% of

$LiBF_4$ significantly enhanced capacity retention in the NMC532 system, suggesting the likely mechanism that $LiBF_4$ contributed to the formation of SEI on both electrodes [18]. Another study further explained that the mechanism that the decomposed products from $LiBF_4$ was boron trifluoride (BF_3) which was a typical Lewis acid and helped dissolve the decomposition product from $LiPF_6$ [19]. Harnessing the BF_3 functionality mechanism, pyridine-boron trifluoride (PBF) was tested as an additive. A 3 wt% dosage was found to improve capacity retention and maintain low impedance in high-voltage/high-temperature NMC/graphite systems such as NMC111 and NMC442 [19]. Similar effectiveness was also found in a pouch cell experiment on NMC532 and NMC622 [20]. A combination of using PBF as additives and $LiBF_4$ as electrolytes for NMC442 provided incremental benefits compared to using $LiBF_4$ as electrolytes [15]. Figure 2 shows the molecular structure of the abovementioned boron compounds.

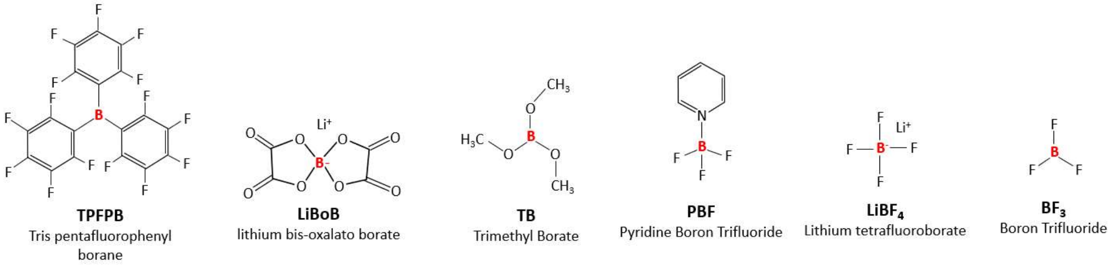

Figure 2. Molecular structure of boron compounds studied in LiB electrolytes.

2.4. Solid-State Electrolyte—Boron Nitride

To improve the safety performance of lithium batteries, solid electrolytes were also extensively studied for their mechanical stability and characteristic of lower flammability. Several combinations for solid electrolytes exist, but they usually contain inorganic and polymer materials. The typical challenge of using solid electrolytes, however, relates to the relatively inferior ionic conductivity and high interface resistance with electrodes [21]. Boron nitride has been commonly studied because of its physical, thermal, and electrical properties [22].

Studies revealed that boron nitride (BN) could be made into a sheet-form hosting structure for ionic liquids (ILs) containing solid electrolytes; as a result, low-temperature conductivity was increased [21]. Other studies showed that adding 1% BN as additives could improve the cycling performance in polymer/salt hybrid electrolytes [23]. Hexagonal boron nitride (h-BN) was also studied to improve cycling performance at a temperature of up to 175 °C [24]. It is also worth noting that, even in non-solid-state electrolytes, adding h-BN was proven to be effective at improving thermal stability and cycling performance [25].

Li metal batteries (LMBs), which utilize Li metal as anodes, have the advantage of higher energy density. Their use has been commonly studied together with solid-state electrolytes. The challenges of using Li metal concern Li reactivity and the formation of Li dendrites [26]. A study showed that BN could be used as a coating on solid-state electrolytes of LMBs to stabilize the electrolyte–anode interface and hence improve cycling performance in LFP systems [27]. Other studies showed that cycling performance could be improved by adding 1% BN to ceramic electrolytes [28]; adding hexagonal boron nitride (h-BN) to polymer composite electrolytes of LFP [29]; adding amine-functionalized boron nitride nanosheets to gel polymer electrolytes of LFP and LCO [26]; or adding hexagonal boron nitride nanosheets (h-BNNS) to a composite polymer on LFP [30]. An alternative route to electrolyte additives was found to use boric acid treatment on a Li anode to form a lithium borate layer that suppressed dendrite growth and enhanced cycling performance in LMO/Li systems [31].

3. Boron Used in Anodes

3.1. Graphite Anode—SEI

Notwithstanding extensive and intensive research and development (R&D) efforts for alternative materials, graphite, a key component of LIBs, has been successfully used for over three decades on a commercial scale in the LIB industry. Like typical cathodes in LIBs, graphite functions by acting as an intercalation compound, which means inserting Li^+ into the crystal structure to store energy [32].

Due to the active nature of graphite in LIBs and the issue around exfoliation because of solvent interaction and repeated volume change during the discharge/charge cycle, SEI continues to play a critical role in maintaining the performance of graphite anodes. The boron surface coating on graphite was found to benefit the formation and stability of SEI by contributing to formation chemistry or morphology changes [33–35]. The essential mechanism of which was identical to some boron-based electrolyte additives. When the surface of graphite was treated with borate acid, results showed improved rate capability, life cycle, and capacity [36–39]. U.S. Borax Inc. led similar in-house research projects and found a similar outcome to these findings in the literature.

3.2. Graphite Anode—Graphitization

As well as graphite coating, borate addition during the high-temperature treatment process of synthetic graphite (SG) could lower the required temperature for graphitization [40]. When placing boron in a lattice structure, it was found to act as an electron acceptor; hence, it increased the specific capacity to 437 mAh/g, a level higher than the theoretical maximum of pure graphite at 372 mAh/g [41]. Regarding improved graphitization, the degree of graphitization was increased with boron substitution which was found to exist in the form of B_4C [42]. As B_2O_3 can be decomposed from boric acid at pitch synthesis temperature, adding either B_2O_3 or boric acid will form B_4C during graphitization process by the reaction of carbon and B_2O_3 [40]. A study in 2001 used boric acid, boron oxide, and B_4C as the graphitization catalyst, suggesting that 1–2 wt% boron atoms enhanced anode performance [43]. A recent study (2021) also found that preparation of pitch and boric acid (max. 5 wt%) to make SG resulted in enhanced graphitization and a higher C-rate, the speed at which a battery can be fully charged or discharged. It was further reported that excessive boric acid dosage (7 wt%) was however detrimental to graphitization and capacity [40]. Hence optimization was required for the use of boric acid.

3.3. Graphite Anode—Upcycling

While recycling of LIBs is becoming increasingly topical, the industry does not practice graphite recycling, presumably due to a relatively lower value of recycling anodes compared to recycling cathodes.

A recent study (2020) by the University of California, San Diego, revealed that using boric acid solution was considered a green and upcycling approach to rejuvenate spent graphite anodes, providing significant advantages over the use of HCl and H_2SO_4. Firstly, the process of boric acid solution treatment and a short annealing afterward at a moderate temperature was considered relatively simple and low-cost compared to high-temperature sintering. Secondly, using boric acid alleviated concerns over secondary pollution caused by using volatile and corrosive acids. Thirdly, using boric acid completely recovered Li^+ trapped not only in SEI but also in graphite bulk. Finally, the boric acid treatment modified the graphite surface with functional B-doping afterward. The outcome was that the rejuvenated graphite anodes were found to have improved electrochemical activity and excellent cycling stability [44].

3.4. Graphene Anode—Li Adsorption

Graphene is a two-dimensional monolayer structure that was first studied and obtained in 2004 by mechanical exfoliation from graphite materials [45]. Due to its larger specific area and physical strength, graphene was studied as an alternative anode material to improve the capacity retention and cycling performance of graphite [46,47]. Graphene anodes could help to overcome the challenge of LIBs, that is, having the advantage of high power density (energy discharge rate) but the relative disadvantage of low energy density (amount of energy stored) [48]. A lithium iron phosphate (LFP) system could be a classic example of that.

Boron doping in graphene could provide higher capacity because introducing lattice defects allows more active sites for Li^+ intercalation [49]. It could increase capacity and suppress the decomposition of electrode materials to some degree [50]. It was later discovered that a green, large-scale synthesis was successful by using boric acid as a boron precursor to make boron-doped graphene. This method was reported to achieve a doping level of 5.93% and improve the discharge capacity by 66% from pristine graphene [51].

3.5. Other Anodes—Miscellaneous

While there is also extensive R&D for other anode materials, boron has commonly been studied jointly. For example, boric acid was studied as a catalyst to synthesize hard carbon microfiber for LIB anodes from cotton [52].

Another example is a silicon anode, which was revealed to have a significantly larger specific capacity [53], with a theoretical value of approximately 3580 mAh/g. To optimize the binder system for silicon-based anodes, boric acid was studied as an effective chemical to crosslink polyvinyl alcohol (PVA) and chemically connect binders with the Si surface. Furthermore, elemental boron was also found to promote the formation of SEI, which resulted in improving initial coulombic efficiency (ICE) [54]. This application draws comparison with the current commercial use of boric acid to crosslink PVA polarizer film in the liquid crystal display industry. Boric acid was also evaluated in carbon-coated porous silica macroparticles ($SiO_2@C$). The formation of a borosilicate (Si-O-B) phase and B-O bonding helped to improve charge capacity and stability [55]. However, a large volume change during the intercalation process is one of the main challenges for silicon-based anodes in LIBs [56].

TiO_2 have been studied as anodes in LIBs due to their outstanding merits of low volume change during the Li^+ intercalation process, a faster diffusion rate, and more lithium hosting channels [57]. By applying boron doping (up to 10.4 wt%) to the TiO_2 anodes, the results demonstrated that TiO_2 lattices were enlarged, and the specific surface area was increased. The further increased Li^+ diffusion rate therefore improved the cycle capacity of TiO_2 [58].

4. Boron Used in Cathodes

The appearance and dominance of LIBs has originated from the nature of high energy density [59]. The design and development of cathode materials are critical and remain a key focus of LIBs because cathode materials not only dictate energy density but also represent the bulk of battery costs [60]. Boron, like its applications in other parts of LIBs, has been studied throughout the development history of cathode materials mainly through either doping or coating.

4.1. LCO, LNO, and LMO

Since the first commercialization of LIBs by Sony in 1991 [61], lithium cobalt oxide or $LiCoO_2$ (LCO) has been used widely in portable consumer electronics due to high volumetric energy densities. However, the irreversible and significant structural changes during the charge/discharge cycle resulted in rapid capacity fading [62]. To improve cycling performance, lithium metaborate $LiBO_2$ was studied to modify cathode composition to form $LiCo_{0.85}B_{0.15}O_2$ (2011) [63]. Another cycling performance improvement strategy involved modifying the cathode surface. For example, $LiBO_2$ was used to form a layer over LCO in all-solid-state LIBs, enhancing cycling performance [64]; the use of boric acid to form a glassy B_2O_3 coating on the interface with LCO helped to suppress electrolyte decompositions [65]. A recent study (2021) demonstrated the value of using a lithium borohydride (LiBH4)-modified LCO surface to increase cycling stability [66].

Later in the development, lithium nickel oxide (LNO) was studied as an alternative to LCO because (1) they have similar specific capacities of 274 and 275 mAh/g, respectively; (2) nickel was more abundant than cobalt, hence more cost effective; and (3) LNO had a similar lattice structure, allowing Li^+ intercalation [60]. A study showed that using 2 wt% lithium difluoro(oxalato)borate (LIODFB) was effective to improve cycling performance. Although application was through the route of an electrolyte additive rather than direction application on the cathode, the mechanism was essentially about forming a boron-rich layer on the cathode [67].

Further to LNO, lithium manganese oxide (LMO) was considered as an alternative material given its merits of low cost, greater natural abundance, and low toxicity. However, LMO also faced similar issues of capacity fading [68]. Single-crystal boron-doped $LiMn_{1.96}B_{0.04}O_4$ could be synthesized by a facile approach with no changes to the spinel structure. The result exhibited high initial discharge and improved cycling performance [69]. A glassy coating of lithium boron oxide (LBO) $Li_2O–2B_2O_3$, which was a commonly studied boron compound, was another strategy to improve LMO cyclability. Compared to uncoated LMO, a number of studies examined how beneficial impacts varied by different application methods of LBO and by various particle sizes of LMO such as powder or nanoparticles [70–74]. The reasons for extensive studies of glassy LBO as a surface treatment were as follows: (1) good ionic conductivity; (2) good wetting properties; and (3) low viscosity in a molten state for easy processing [75,76]. It is interesting to note that other boron-in-glass applications such as enamel glaze coating and insulation fiberglass have similar benefits for the use of boron compounds.

4.2. LFP

Lithium iron phosphate (LFP) or $LiFePO_4$ is one of the most widely used mainstream battery systems in EVs and even utility-scale stationary applications. LFP is widely used and produced in China [77]. As LFP cathodes do not contain nickel or cobalt, both of which are considered to be in short supply and have high price volatility. Therefore, cost is the first key advantage of LFP. The second advantage is safety because LFP is non-toxic and more thermally stable than other LiB cathode systems [78], and hence less susceptible to fire or explosion. The disadvantage of LFP is that it has lower energy density and lower operating voltage because of the inferior electronic conductivity and diffusion rate of Li^+ through the $LiFePO_4/FePO_4$ interface [79,80].

To overcome this challenge, direct substitution of $(PO4)^{3-}$ in $LiFePO_4$ in the form of $(BO_3)^{3-}$ at 6 mol% could improve the rate performance of LFP cathodes [81]. Another similar B-doping experiment used 3–9 wt% of BPO_4 as a precursor and reported that the rate capability was enhanced due to the improved diffusivity of Li^+ [82]. In addition to direct doping, B-doped carbon coating was adopted to improve rate performance. The doping on the carbon layer could be achieved either by boron alone [83] or jointly with other elements such as N or P [84,85]. The rate performance was enhanced due to improved conductivity.

4.3. NMC

The development history of LCO, LNO, and subsequent LMO led to studying a combination of the three, commonly named nickel manganese cobalt (NMC). Apart from LFP, NMC is currently the most used category of battery cathode for EVs. By forming a tertiary system, the individual benefits of LCO, LNO, and LMO (capacity, rate performance, and safety, respectively) can be combined. Accordingly, the overall performance can be tailored by relative composition. Figure 3 shows in a ternary plot the location of relative NMC compositions and the part of the battery in which boron's study have been mentioned in this paper. As battery capacity remains the focus of development for EVs due to so-called range anxiety, the clusters of commercially used systems are currently situated toward the vertex of $LiNiO_2$, with NMC333 having the lowest LNO ratio. The major challenge of high nickel was that it was believed to have low thermal stability due to the high reactivity of Ni^{4+} [60].

NMC811 is currently (2022) the highest commercial NMC cathode in terms of LNO ratio. A 2020 study showed that using boric acid through a wet-chemical coating treatment followed by a sintering process was able to improve the cycling stability and high-temperature performance of NMC811. The formed glassy borate lithium film successfully prevented microcracks [86]. Apart from wet-chemical treatment, solid boric acid could also be mixed dry with an NMC811 cathode followed by 300 °C heat treatment to form a lithium borate coating on the NMC cathode. This coating improved cycling performance of the NMC811/sulfide-based solid electrolyte system [87].

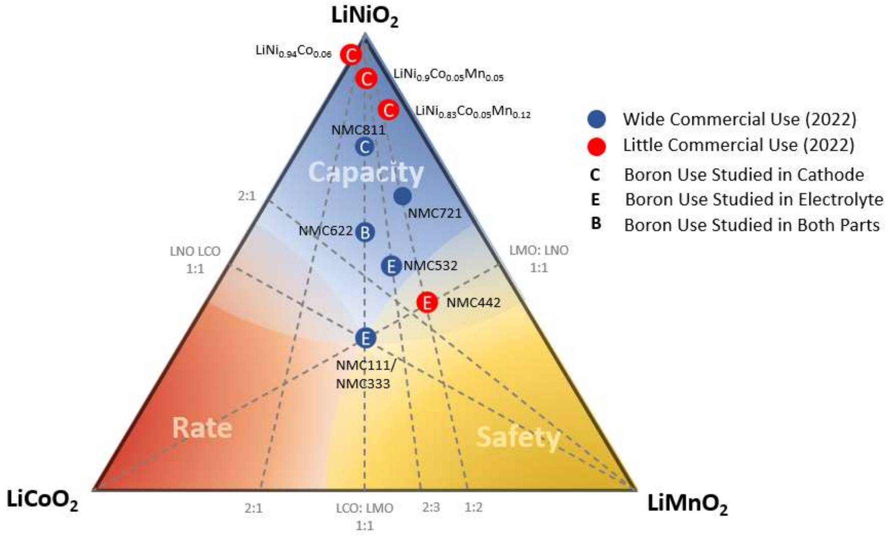

Figure 3. Ternary plot of NMC systems.

Regarding B-doping, a 2021 study utilized boric acid as a co-sintering agent to achieve boron doping (3 at%). This not only improved rate performance and cyclability but also improved structural stability [88]. The mechanism behind the B-doping benefit is not fully understood, but one study suggested that B-doping affected crystal structure and cation disorder [89]. In NMC622, B-doping was found to change the microstructure of primary particles significantly and doping alone provided a marginal benefit to structural and electrochemical stability. When 0.5% B was co-doped with 1% Mg, there was a synergistic effect that improved the capacity retention noticeably due to a reduction in impedance growth and cation mixing [90].

Other high-nickel NMC, such as $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ and $LiNi_{0.83}Co_{0.05}Mn_{0.12}O_2$, despite having little commercial use currently (2022), could increase their capacity retention and cycling performance with 1 mol% and 0.6 mol% B-doping, respectively. The mechanism was believed to be related to a stronger B-O bond and the release of the internal lattice strain [91,92]. The research of $LiNi_{0.83}Co_{0.05}Mn_{0.12}O_2$ was also demonstrated on pouch cells [92]. A similar beneficial impact and mechanism were also found in high-nickel systems such as $LiNi_{0.9}Co_{0.05}Ti_{0.05}O_2$ and $LiNi_{0.94}Co_{0.06}O_2$ [93,94]. Another less common approach was adding bi-boron additive to electrolytes, which could improve the interfacial stability of $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ and hence the cycling life [95].

Li-rich layer oxides (LLOs) could be considered a variant of NMC since NMC can turn into LLO, with Li ions partially replacing Ni, Co, and Mn in NMC. LLO has the advantage of high capacity but the disadvantage of capacity fading [96]. One example of LLO is $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$. A study in 2015 showed that B-doping improved rate capability and cycling performance [97]. Another example of LLO is $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ [98]. Studies showed B-doping improved cycling performance in both half cells and pouch cell experiments. The abovementioned advantageous mechanism of B-doping was very similar to that in NMC systems [98,99].

4.4. NCA and NCMA

The focus on capacity increases the LNO content but at the expense of safety. This is because, as the LNO ratio increases, the structural and thermal stability decrease, thus also decreasing cycling ability [100]. The role of aluminum substitution for nickel is to provide thermal stability and safety owing to the inertness of Al [101]. Aluminum can be found in lithium nickel cobalt aluminum (NCA) and NCMA (nickel, cobalt, manganese, aluminum), both of which have wide commercial use in cathode systems of EVs (2022).

In NCA of $LiNi_{0.885}Co_{0.1}Al_{0.015}O_2$, using B-doping enabled the modification of the microstructure and helped alleviate internal strains, which then enhanced cycling performance [102]. A gradient B-doping method, which allowed the concentration to change with depth, was applied to $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. Even at high temperature, the research demonstrated that structural stability and cycling performance were improved because doping could encumber impedance increase during cycling [103]. In relation to coating on NCA, an ultrathin LBO layer was constructed on the interface that enhanced structural stability and cycling performance of $LiNi_{0.87}Co_{0.10}Al_{0.03}O_2$ [104].

In the NMCA system of $LiNi_{0.88}Co_{0.06}Mn_{0.03}Al_{0.03}O_2$, an LBO coating was applied for chemical stability and structural stability during the charge/discharge cycle, which in turn improved cycling performance significantly [105].

5. Boron Used to Assist Manufacturing

Beyond batteries, boron compounds are often used in manufacturing and chemical processes. For instance, borates have been used as glass melting flux since the 17th century. Sodium borates are also widely used in various metal cleaning processes. The cleaning application is attributed to the known capability of degreasing and the pH stability at various concentrations and temperatures. Again, it is interesting to observe similarities in how boron could help with the manufacturing process of LIBs.

In relation to the abovementioned NCMA cathode, one study showed boron could assist fluxing agents and to make uniform single crystals of $LiNi_{0.92}Co_{0.06}Mn_{0.01}Al_{0.01}O_2$, which exhibited outstanding rate capacity and thermal stability [106].

Regarding cleaning, there has been increasing focus recently (2020–2022) on studying boric acid as a washing agent for residual lithium compounds (RLCs). Ni-rich cathodes are prone to reacting with H_2O and CO_2 in the air, forming RLCs such as LiOH and Li_2CO_3. RLCs are highly undesirable because they (1) deteriorate cathode performance as well as creating (2) manufacturing challenges and (3) potential safety hazards [107].

The efficacy has been demonstrated on Ni-rich cathode systems such as NCM811 [108] and NCMA system of $LiNi_{0.8}Co_{0.1}Mn_{0.09}Al_{0.01}O_2$ [109] and $LiNi_{0.90}Co_{0.06}Mn_{0.04}O_2$ [110]. In an NCM811 study, boric acid was used not only to clean surfaces but also to transform RLCs into uniform boron-containing lithium coatings, resulting in high discharge capacity and better cycling performance compared to pristine NCM811 and ethanol-washed samples [108]. This dual benefit was also tested in a study of NCMA, simultaneously improving structural stability and electrochemical performance [109]. When using a system of $LiNi_{0.90}Co_{0.06}Mn_{0.04}O_2$, optimal parameters were established at a boric acid concentration of 1 g/L; wash time of 5 min; and solid–liquid ratio of 1 g/mL. The benefits found in the study included effective washing and suppressing formation of RLCs during storage [110].

doi:10.20944/preprints202205.0303.v1

6. Boron Used in Separators

In internal combustion engine (ICE) vehicles, lead-acid start-stop batteries commonly use borosilicate glass microfiber as absorbent glass mat (AGM) that not only functions as separators but also as electrolyte absorbents. For LIBs in electric vehicles (EVs), a battery separator is a critical and complex component. On the one hand, it functions like a physical barrier to separate the anode and cathode, preventing short circuiting. On the other hand, it also acts as a channel to allow for the passage of ions during charging/discharging cycles. Therefore, proper functioning demands a complex suite of parameters. Table 1 lists typical required parameters for separators used in LIBs [111,112]. The current conventional commercial mainstream materials are polyolefin-based, such as polypropylene (PP) and polyethylene (PE), although other fibers such as polyester, cotton, and glass are also available in the nonwoven type of separators.

Table 1. Parameters and requirements for separators [111,112].

Parameters	Requirement
Chemical and Electrochemical Stability	Yes. Long Duration
Wettability	Quick and Complete Wetting
Mechanical Property	>100 kg/cm
Thickness	20–25 μm
Permeability	<0.025 s/μm
Porosity	40–60%
Pore Size	<1 μm
Dimensional Stability	Yes
Thermal Stability	<5% shrinkage after 60 min at 90 °C

The typical challenge of using polymer-based separators was believed to be limited thermal stability, which could potentially result in thermal runaway (an uncontrolled and exothermal chain reaction) and subsequent catastrophic failure [113]. Extensive studies were carried out on the synergetic benefit of boron nitride (BN). BN has a unique combination of high thermal conductivity and high electrical insulation and, as mentioned in Section 2.3, has been commonly studied as an additive for solid-state electrolytes.

A 2019 paper studied the use of boron nitride nanotubes (BNNTs). When synthetic long and fine BNNTs were incorporated into polyolefin separators, thermal stability was improved by up to 150 °C. The incorporation assisted heat absorption and distribution during the cycling process [114].

There are also studies on the applications of hexagonal boron nitride (h-BN), which was mentioned in Section 2.3, being studied as an electrolyte additive. A composite material made of carbon-coated hexagonal boron nitride (h-BN) and polyvinylidene fluoride (PDVF) exhibited superior electrochemical performance compared to polyolefin, allowing safe operation of LIBs up to 120 °C [113]. Another study showed coating conventional PP with a layer made by h-BN and polyimide helped effectively suppress Li dendrite growth and consequentially improved NCM811 performance compared to PP separators without coating [115].

For separators used in Li metal batteries (LMBs), there was a study on using a layer of boron nitride graphene coating on one side of a PP membrane to improve the stability of the LFP/Li system [116].

7. Boron Used in BTMS

When LIBs or other high-energy-intensity batteries operate, there are different types of heat generated in various parts of the battery pack, such as reaction heat, entropy-change heat, and electrical resistance heat. The battery temperature can then affect both kinetic and thermodynamics aspects of battery, including the power rate and capacity

doi:10.20944/preprints202205.0303.v1

fading [117]. A battery thermal management system (BTMS) is therefore required to provide an optimal working temperature range for batteries. If the BTMS fails to provide timely heat distribution and dissipation, localized acute heat generation could lead to thermal runaway [118].

Among conventional BTMSs, such as water-cooled or phase-change material cooling, thermal interface materials (TIMs) play a critical role in establishing seamless physical contact on a microlevel between heat source and dissipation media because of surface roughness (Figure 4). Boron nitride, which has a unique combination of high heat conductivity and high electrical insulation, is often used in experiments as a filler in TIMs. One experiment showed that using surface-modified spherical boron nitrides (SBNs) reduced maximum temperature [119]. The silicone rubber matrix was also studied to incorporate hexagonal boron nitride (h-BN) as a filler to increase thermal conductivity. One paper concluded that 30 wt% of h-BN made the thermal conductivity 3.4 times higher than that of pristine silicone rubber [120]. Another paper showed that the thermal conductivity would be four times higher if using hybrid fillers of h-BN carbon fillers [121].

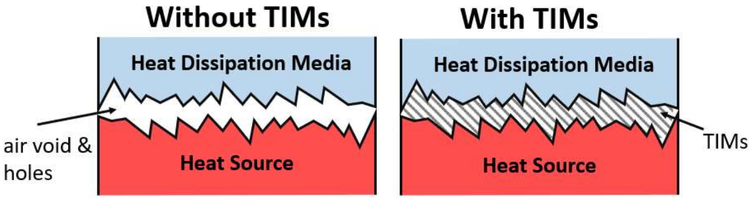

Figure 4. Schematics of thermal interface materials.

Apart from conventional systems, there are also studies on using non-conventional systems along with BN. For example, using a silicone sealant as an immersion medium with 10 wt% BN loading reduced the maximum temperature compared to an air-cool module or a silicone sealant module [122]. There was also a study on solid cooling media by using h-BN together with paraffin wax, which has a high heat capacity and good electrical insulation. The results show that, with 20 wt% loading, an orderly interconnected h-BN frame inside a paraffin wax exhibited eight times more thermal conductivity than pristine paraffin wax and four times more than random dispersed h-BN [123]. Finally, BN was also studied for use as a coating on the external casing of LIBs. With the Taguchi method, the parameters of coating thickness and casing surface roughness were optimized with the use of BN to improve thermal performance [124].

8. Boron Used in Lithium Sulfur Batteries

This paper has so far predominately focused on a category of LIBs that have been proven successful in commercialization. Lithium sulfur batteries (LSBs), although not yet commercially available, have attracted great research interest due to the merits of low material costs (i.e., free of cobalt and nickel) and higher energy density. In terms of mechanism, LSBs differ remarkably from LIBs in the following areas. Firstly, LSBs utilize lithium metal as an anode, which is similar to lithium metal batteries (LMBs). Secondly, the charge-holding mechanism of LSBs is based on Li^+ reactions on the electrodes rather than Li^+ intercalation [125,126]. As shown on Figure 5. these reactions during the charge/discharge cycle are part of a complex multi-step process with lithium polysulfides that range from solid to liquid [127]. Thirdly, with some soluble polysulfides, LSBs pose a major challenge that LIBs do not; that is, the “shuttle effect”, a mechanism related to diffusion of soluble polysulfide through separators and subsequent undesired reactions with the lithium anode surface. The shuttle effect directly results in self-discharging [126]. The combined effects with anode corrosion and dendrite growth lead to impaired cycling stability and capacity [128,129].

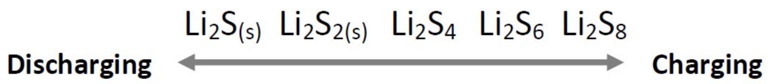

Figure 5. Lithium polysulfides in LSBs during charge/discharge cycle

To alleviate the shuttle effect, one research direction of interest was to make separators hinder the passage of polysulfides. Hexagonal-boron nitride (h-BN) and BNNT separators were reported to lessen the shuttle effect preventing polysulfide passage [129–131]. These reports further suggested the mechanism was owing to the presence of boron atoms and availability of a vacant p-orbital, which enabled the Lewis-acid characteristics of boron nitride [129,130]. A similar research direction was pursued by studying boron-doped functional layer on separators to improve cycling stability, such as using B-doped graphene oxide [132,133] or B-doped anatase TiO_2 [134].

Another research direction of interest to alleviate the shuttle effect was to better trap polyamide on cathodes. Using the nanostructure of B_4C inside the cathode of LSBs was reported to increase cycling performance [135–137]. The improvement was due to the following: (1) B_4C improved the kinetics of polysulfide conversion; and (2) nano B_4C structures provided entrapment for polysulfides [135].

9. Summary and Prospect

This paper has extensively reviewed literatures on testing boron compounds in various parts of lithium batteries. Herein, conclusions and additional reflections are offered to assist discussion for future study that might lead to commercialization.

9.1. Summary

- Various boron lithium compounds were studied and proven effective in assisting the formation and stability of SEI. These can be introduced through electrolyte additives or through direct application to the anode.
- For direct application of boron compounds to the anode, using boric acid was reported to provide diverse benefits.
- In the cathode, boron doping and forming an LBO layer were of particular interest. Cathode doping and cathode coating are the two conventional approaches to improving the cycling performance.
- The use of boron compounds has been widely employed in experiments on those cathode systems that currently have wide commercial applications in EVs, such as NCMA, NMC, NCA, and LFP.
- Using boron compounds to assist manufacturing and recycling could be a way of achieving the “one stone, two birds” outcome. Using boron compounds to achieve multifaced benefits is common beyond batteries.
- For applications in separators and BTMS, boron nitride and its derivatives have been the primary focus of research, given their unique electrical insulation and thermal conductivity.
- For novel lithium systems such as LSBs, boron nitride in separators and boron carbide in cathodes were reported to be effective at alleviating shuttle effects through different mechanisms.

9.2. Prospect

- Boron compounds will continue to be of interest in battery research and development, in lithium batteries and others. This can be evidenced by the boron studies on other novel battery systems such as sodium-ion batteries and magnesium rechargeable batteries.

- While there are extensive studies on coin cells, more research on pouch cells is required to narrow the significant gap towards commercialization. Gaps include but are not limited to processing difficulty and raw material costs.
- In particular, the study of using more commercially available boron sources as precursors, such as boric acid and boron oxide, will be useful to achieve a fine balance between cost and efficacy.
- With a closer link to commercialization, studies on the use of boron compounds (e.g., boric acid) to assist the actual production environment will likely attract more interest.
- The topic of battery recycling is important and currently topical in the industry. Therefore, more studies on recycling or upcycling batteries with the use of boron will be likely.
- Given the diversity of available boron compounds, using a machine learning approach and leveraging existing extensive studies on boron compound might be of interest in guiding research.
- Leveraging machine learning may also help with the growing need for performance benchmarking among various types of battery system.

Acknowledgments: I greatly appreciate the opportunity to work for U.S. Borax Inc.-Rio Tinto, who supported my time and provided me with access to the company's privileged knowledge in borate chemistry and boron applications.

Conflicts of Interest: The author declares no conflicts of interest.

Reference

1. Grew, E.S.; Hystad, G.; Toapanta, M.P.C.; Eleish, A.; Ostroverkhova, A.; Golden, J.; Hazen, R.M. Lithium mineral evolution and ecology: Comparison with boron and beryllium. *Eur. J. Miner.* **2019**, *31*, 755–774. https://doi.org/10.1127/ejm/2019/0031-2862.
2. Vangioni-Flam, E.; Cassé, M.; Audouze, J. Lithium–beryllium–boron: Origin and evolution. *Phys. Rep.* **2000**, *333*, 365–387.
3. Huang, Z.; Wang, S.; Dewhurst, R.D.; Ignat'Ev, N.V.; Finze, M.; Braunschweig, H. Boron: Its Role in Energy-Related Processes and Applications. *Angew. Chem. Int. Ed.* **2019**, *59*, 8800–8816. https://doi.org/10.1002/anie.201911108.
4. Xu, W.; Angell, C.A. LiBOB and Its Derivatives. *Electrochem. Solid-State Lett.* **2001**, *4*, E1–E4.
5. Xu, K.; Lee, U.; Zhang, S.; Wood, M.; Jow, T.R. Chemical analysis of graphite/electrolyte interface formed in LiBOB-based electrolytes. *Electrochem. Solid-State Lett.* **2003**, *6*, A144.
6. Täubert, C.; Fleischhammer, M.; Wohlfahrt-Mehrens, M.; Wietelmann, U.; Buhrmester, T. LiBOB as electrolyte salt or additive for lithium-ion batteries based on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite. *J. Electrochem. Soc.* **2010**, *157*, A721.
7. Xu, K. Tailoring Electrolyte Composition for LiBOB. *J. Electrochem. Soc.* **2008**, *155*, A733–A738. https://doi.org/10.1149/1.2961055.
8. Chen, Z.; Amine, K. Tris (pentafluorophenyl) borane as an additive to improve the power capabilities of lithium-ion batteries. *J. Electrochem. Soc.* **2006**, *153*, A1221.
9. Chang, C.-C.; Chen, T.-K. Tris (pentafluorophenyl) borane as an electrolyte additive for LiFePO4 battery. *J. Power Sources* **2009**, *193*, 834–840.
10. Rong, H.; Xu, M.; Xie, B.; Liao, X.; Huang, W.; Xing, L.; Li, W. Tris (trimethylsilyl) borate (TMSB) as a cathode surface film forming additive for 5 V Li/LiNi0. 5Mn1. 5O4 Li-ion cells. *Electrochim. Acta* **2014**, *147*, 31–39.
11. Chang, C.-C.; Lee, K.-Y.; Lee, H.-Y.; Su, Y.-H.; Her, L.-J. Trimethyl borate and triphenyl borate as electrolyte additives for $LiFePO_4$ cathode with enhanced high temperature performance. *J. Power Sources* **2012**, *217*, 524–529. https://doi.org/10.1016/j.jpowsour.2012.05.083.
12. Sun, X.; Lee, H.S.; Yang, X.-Q.; McBreen, J. Using a boron-based anion receptor additive to improve the thermal stability of LiPF6-based electrolyte for lithium batteries. *Electrochem. Solid-State Lett.* **2002**, *5*, A248.
13. Wang, Z.; Xing, L.; Li, J.; Li, B.; Xu, M.; Liao, Y.; Li, W. Trimethyl borate as an electrolyte additive for high potential layered cathode with concurrent improvement of rate capability and cyclic stability. *Electrochim. Acta* **2015**, *184*, 40–46.
14. Zhang, S.; Xu, K.; Jow, T. Low-temperature performance of Li-ion cells with a LiBF4-based electrolyte. *J. Solid State Electrochem.* **2003**, *7*, 147–151. https://doi.org/10.1007/s10008-002-0300-9.
15. Shen, C.; Xiong, D.; Ellis, L.D.; Gering, K.L.; Huang, L.; Dahn, J.R. Using the charge-discharge cycling of positive electrode symmetric cells to find electrolyte/electrode combinations with minimum reactivity. *J. Electrochem. Soc.* **2017**, *164*, A3349.
16. Ellis, L.D.; Xia, J.; Louli, A.J.; Dahn, J.R. Effect of substituting $LiBF_4$ for $LiPF_6$ in high voltage lithium-ion cells containing electrolyte additives. *J. Electrochem. Soc.* **2016**, *163*, A1686.
17. Jow, T.; Ding, M.; Xu, K.; Zhang, S.; Allen, J.; Amine, K.; Henriksen, G. Nonaqueous electrolytes for wide-temperature-range operation of Li-ion cells. *J. Power Sources* **2003**, *119*, 343–348. https://doi.org/10.1016/s0378-7753(03)00153-8.

18. Zuo, X.; Fan, C.; Liu, J.; Xiao, X.; Wu, J.; Nan, J. Lithium tetrafluoroborate as an electrolyte additive to improve the high voltage performance of lithium-ion battery. *J. Electrochem. Soc.* **2013**, *160*, A1199.
19. Nie, M.; Xia, J.; Dahn, J.R. Development of pyridine-boron trifluoride electrolyte additives for lithium-ion batteries. *J. Electrochem. Soc.* **2015**, *162*, A1186.
20. Ma, L.; Self, J.; Nie, M.; Glazier, S.; Wang, D.Y.; Lin, Y.S.; Dahn, J.R. A systematic study of some promising electrolyte additives in $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$/graphite, Li $[Ni_{0.5}Mn_{0.3}Co_{0.2}]$/graphite and Li $[Ni_{0.6}Mn_{0.2}Co_{0.2}]$/graphite pouch cells. *J. Power Sources* **2015**, *299*, 130–138.
21. Li, M.; Zhu, W.; Zhang, P.; Yang, B.; Li, H.; He, Q.; Borisevich, A.Y.; Dai, S. Graphene-analogues Boron Nitride nanosheets with ultrahigh ionic liquid uptake capacity as quasi-solid electrolytes. *Mater. Sci.* **2017**. https://orca.cardiff.ac.uk/92038/3/BN%2020150904.pdf
22. Jiang, H.; Wang, Z.; Ma, L.; Yang, Q.; Tang, Z.; Song, X.; Zeng, H.; Zhi, C. Boron ink assisted in situ boron nitride coatings for anti-oxidation and anti-corrosion applications. *Nanotechnology* **2019**, *30*, 335704. https://doi.org/10.1088/1361-6528/ab193c.
23. Zhang, Z.; Antonio, R.G.; Choy, K.L. Boron nitride enhanced polymer/salt hybrid electrolytes for all-solid-state lithium ion batteries. *J. Power Sources* **2019**, *435*, 226736.
24. Hyun, W.J.; de Moraes, A.C.M.; Lim, J.-M.; Downing, J.R.; Park, K.-Y.; Tan, M.T.Z.; Hersam, M.C. High-Modulus Hexagonal Boron Nitride Nanoplatelet Gel Electrolytes for Solid-State Rechargeable Lithium-Ion Batteries. *ACS Nano* **2019**, *13*, 9664–9672. https://doi.org/10.1021/acsnano.9b04989.
25. Rodrigues, M.-T.F.; Kalaga, K.; Gullapalli, H.; Babu, G.; Reddy, A.L.M.; Ajayan, P.M. Hexagonal Boron Nitride-Based Electrolyte Composite for Li-Ion Battery Operation from Room Temperature to 150 °C. *Adv. Energy Mater.* **2016**, *6*, 1600218. https://doi.org/10.1002/aenm.201600218.
26. Kim, D.; Liu, X.; Yu, B.; Mateti, S.; O'Dell, L.A.; Rong, Q.; Chen, Y. Amine-functionalized boron nitride nanosheets: A new functional additive for robust, flexible ion gel electrolyte with high lithium-ion transference number. *Adv. Funct. Mater.* **2020**, *30*, 1910813.
27. Cheng, Q.; Li, A.; Li, N.; Li, S.; Zangiabadi, A.; Huang, W.; Li, A.C.; Jin, T.; Song, Q.; Xu, W.; et al. Stabilizing solid electrolyte-anode interface in Li-metal batteries by boron nitride-based nanocomposite coating. *Joule* **2019**, *3*, 1510–1522.
28. Zhang, Z.; Gonzalez, A.R.; Choy, K.L. Boron Nitride Enhanced Garnet-Type ($Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$) Ceramic Electrolyte for an All-Solid-State Lithium-Ion Battery. *ACS Appl. Energy Mater.* **2019**, *2*, 7438–7448. https://doi.org/10.1021/acsaem.9b01431.
29. Li, Y.; Zhang, L.; Sun, Z.; Gao, G.; Lu, S.; Zhu, M.; Zhang, Y.; Jia, Z.; Xiao, C.; Bu, H.; et al. Hexagonal boron nitride induces anion trapping in a polyethylene oxide based solid polymer electrolyte for lithium dendrite inhibition. *J. Mater. Chem. A* **2020**, *8*, 9579–9589.
30. Zhang, X.; Guo, W.; Zhou, L.; Xu, Q.; Min, Y. Surface-modified boron nitride as a filler to achieve high thermal stability of polymer solid-state lithium-metal batteries. *J. Mater. Chem. A* **2021**, *9*, 20530–20543. https://doi.org/10.1039/d1ta05410d.
31. Kang, H.; Song, M.; Yang, M.; Lee, J.W. Lithium metal anode with lithium borate layer for enhanced cycling stability of lithium metal batteries. *J. Power Sources* **2021**, *485*, 229286.
32. Asenbauer, J.; Eisenmann, T.; Kuenzel, M.; Kazzazi, A.; Chen, Z.; Bresser, D. The success story of graphite as a lithium-ion anode material–fundamentals, remaining challenges, and recent developments including silicon (oxide) composites. *Sustain. Energy Fuels* **2020**, *4*, 5387–5416.
33. Kurita, Noriyuki. "Molecular orbital calculations on lithium absorption in boron-or nitrogen-substituted disordered carbon." Carbon 38, no. 1 (2000): 65-75.
34. Nie, M.; Lucht, B.L. Role of lithium salt on solid electrolyte interface (SEI) formation and structure in lithium ion batteries. *J. Electrochem. Soc.* **2014**, *161*, A1001.
35. Arai, J.; Matsuo, A.; Fujisaki, T.; Ozawa, K. A novel high temperature stable lithium salt ($Li_2B_{12}F_{12}$) for lithium ion batteries. *J. Power Sources* **2009**, *193*, 851–854. https://doi.org/10.1016/j.jpowsour.2009.04.001.
36. Yeo, J.S.; Park, T.H.; Seo, M.H.; Miyawaki, J.; Mochida, I.; Yoon, S.H. Enhancement of the rate capability of graphite via the introduction of boron-oxygen functional groups. *Int. J. Electrochem. Sci.* **2013**, *8*, 1308–1315.
37. Park, M.-S.; Lee, J.; Lee, J.-W.; Kim, K.-J.; Jo, Y.-N.; Woo, S.-G.; Kim, Y.-J. Tuning the surface chemistry of natural graphite anode by H_3PO_4 and H_3BO_3 treatments for improving electrochemical and thermal properties. *Carbon* **2013**, *62*, 278–287.
38. Fu, L.J.; Liu, H.; Li, C.; Wu, Y.P.; Rahm, E.; Holze, R.; Wu, H.Q. Surface modifications of electrode materials for lithium ion batteries. *Solid State Sci.* **2006**, *8*, 113–128. https://doi.org/10.1016/j.solidstatesciences.2005.10.019.
39. Zhang, S.S.; Xu, K.; Jow, T.R. Enhanced performance of natural graphite in Li-ion battery by oxalatoborate coating. *J. Power Sources* **2004**, *129*, 275–279. https://doi.org/10.1016/j.jpowsour.2003.10.012.
40. Hwang, J.U.; Ahn, W.J.; Im, J.S.; Lee, J.D. Properties of synthetic graphite from boric acid-added pitch: Performance as anode in lithium-ion batteries. *SN Appl. Sci.* **2021**, *3*, 1–14. https://doi.org/10.1007/s42452-021-04566-9.
41. Way, B.M.; Dahn, J.R. The Effect of Boron Substitution in Carbon on the Intercalation of Lithium in $Li_x(B_zC_{1-z})$ 6. *J. Electrochem. Soc.* **1994**, *141*, 907–912. https://doi.org/10.1149/1.2054856.
42. Liu, Tao, Ruiying Luo, Seong-Ho Yoon, and Isao Mochida. "Anode performance of boron-doped graphites prepared from shot and sponge cokes." Journal of power sources 195, no. 6 (2010): 1714-1719.
43. Fujimoto, H.; Mabuchi, A.; Natarajan, C.; Kasuh, T. Properties of graphite prepared from boron-doped pitch as an anode for a rechargeable Li ion battery. *Carbon* **2002**, *40*, 567–574. https://doi.org/10.1016/s0008-6223(01)00152-x.

44. Markey, B.; Zhang, M.; Robb, I.; Xu, P.; Gao, H.; Zhang, D.; Holoubek, J.; Xia, D.; Zhao, Y.; Guo, J.; et al. Effective Upcycling of Graphite Anode: Healing and Doping Enabled Direct Regeneration. *J. Electrochem. Soc.* **2020**, *167*, 160511. https://doi.org/10.1149/1945-7111/abcc2f.
45. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306*, 666–669. https://doi.org/10.1126/science.1102896.
46. Hou, J.; Shao, Y.; Ellis, M.W.; Moore, R.B.; Yi, B. Graphene-based electrochemical energy conversion and storage: Fuel cells, supercapacitors and lithium ion batteries. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15384–15402.
47. Luo, R.-P.; Lyu, W.-Q.; Wen, K.-C.; He, W.-D. Overview of graphene as anode in lithium-ion batteries. *J. Electron. Sci. Technol.* **2018**, *16*, 57–68.
48. Sui, D.; Si, L.; Li, C.; Yang, Y.; Zhang, Y.; Yan, W. A Comprehensive Review of Graphene-Based Anode Materials for Lithium-ion Capacitors. *Chemistry* **2021**, *3*, 1215–1246.
49. Ayala, P.; Reppert, J.; Grobosch, M.; Knupfer, M.; Pichler, T.; Rao, A.M. Evidence for substitutional boron in doped single-walled carbon nanotubes. *Appl. Phys. Lett.* **2010**, *96*, 183110.
50. Wu, Z.-S.; Ren, W.; Xu, L.; Li, F.; Cheng, H.-M. Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries. *ACS Nano* **2011**, *5*, 5463–5471.
51. Sahoo, M.; Sreena, K.P.; Vinayan, B.P.; Ramaprabhu, S. Green synthesis of boron doped graphene and its application as high performance anode material in Li ion battery. *Mater. Res. Bull.* **2015**, *61*, 383–390.
52. Tan, M.; Zhang, W.; Fan, C.; Li, L.; Chen, H.; Li, R.; Luo, T.; Han, S. Boric Acid–Catalyzed Hard Carbon Microfiber Derived from Cotton as a High-Performance Anode for Lithium-Ion Batteries. *Energy Technol.* **2019**, *7*, 1801164.
53. Zuo, X.; Zhu, J.; Müller-Buschbaum, P.; Cheng, Y.-J. Silicon based lithium-ion battery anodes: A chronicle perspective review. *Nano Energy* **2017**, *31*, 113–143.
54. Cao, Z.; Zheng, X.; Huang, W.; Wang, Y.; Qu, Q.; Zheng, H. Dynamic bonded supramolecular binder enables high-performance silicon anodes in lithium-ion batteries. *J. Power Sources* **2020**, *463*, 228208.
55. Kim, Y.-K.; Moon, J.-W.; Lee, J.-G.; Baek, Y.-K.; Hong, S.-H. Porous carbon-coated silica macroparticles as anode materials for lithium ion batteries: Effect of boric acid. *J. Power Sources* **2014**, *272*, 689–695. https://doi.org/10.1016/j.jpowsour.2014.08.128.
56. Mukhopadhyay, A.; Sheldon, B.W. Deformation and stress in electrode materials for Li-ion batteries. *Prog. Mater. Sci.* **2014**, *63*, 58–116. https://doi.org/10.1016/j.pmatsci.2014.02.001.
57. Liu, Y.; Yang, Y. Recent Progress of TiO2-Based Anodes for Li Ion Batteries. *J. Nanomater.* **2016**, *2016*, 1–15. https://doi.org/10.1155/2016/8123652.
58. Jeong, J.-H.; Jung, D.-W.; Shin, E.W.; Oh, E.-S. Boron-doped TiO_2 anode materials for high-rate lithium ion batteries. *J. Alloys Compd.* **2014**, *604*, 226–232.
59. Manthiram, A. A reflection on lithium-ion battery cathode chemistry. *Nat. Commun.* **2020**, *11*, 1–9. https://doi.org/10.1038/s41467-020-15355-0.
60. Schipper, F.; Erickson, E.M.; Erk, C.; Shin, J.-Y.; Chesneau, F.F.; Aurbach, D. Recent advances and remaining challenges for lithium ion battery cathodes. *J. Electrochem. Soc.* **2016**, *164*, A6220.
61. Nishi, Y. The development of lithium ion secondary batteries. *Chem. Rec.* **2001**, *1*, 406–413.
62. Cho, J.; Kim, Y.J.; Kim, T.-J.; Park, B. Zero-Strain Intercalation Cathode for Rechargeable Li-Ion Cell. *Angew. Chem.* **2001**, *113*, 3471–3473. https://doi.org/10.1002/1521-3757(20010917)113:18<3471::aid-ange3471>3.0.co;2-y.
63. Mauger, A.; Zhang, X.; Groult, H.; Julien, C.M. Boron Doped $LiCoO_2$ as Cathode Materials for Rechargeable Lithium Batteries. In *ECS Meeting Abstracts*; IOP Publishing: Bristol, UK, 2011; p. 583.
64. Ramkumara, B.; So-Younga, K.; Chan-Wooa, N.; Aravindanb, V.; Sunga, L.Y. $LiBO_2$-modified $LiCoO_2$ as an efficient cathode with garnet framework $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ electrolyte toward building all-solid-state lithium battery for high-temperature operation. *Electrochim. Acta* **2020**, *359*, 136955. https://doi.org/10.1016/j.electacta.2020.136955.
65. Zhou, A.; Wang, W.; Liu, Q.; Wang, Y.; Yao, X.; Qing, F.; Li, E.; Yang, T.; Zhang, L.; Li, J. Stable, fast and high-energy-density LiCoO2 cathode at high operation voltage enabled by glassy B_2O_3 modification. *J. Power Sources* **2017**, *362*, 131–139. https://doi.org/10.1016/j.jpowsour.2017.06.050.
66. Pu, W.; Meng, Y.; Wang, Y.; Ge, Y.; Li, X.; Wang, P.; Zhang, Z.; Guo, Y.; Xiao, D. Investigation of the LiBH4 Modification Effect on Cycling Stability and High-Rate Capacity of $LiCoO_2$ Cathodes. *ACS Appl. Energy Mater.* **2021**, *4*, 6933–6941.
67. Deng, T.; Fan, X.; Cao, L.; Chen, J.; Hou, S.; Ji, X.; Chen, L.; Li, S.; Zhou, X.; Hu, E.; et al. Designing in-situ-formed interphases enables highly reversible cobalt-free $LiNiO_2$ cathode for Li-ion and Li-metal batteries. *Joule* **2019**, *3*, 2550–2564.
68. Eriksson, T. LiMn2O4 as a Li-Ion Battery Cathode. From Bulk to Electrolyte Interface. Ph.D. Thesis, Acta Universitatis Upsaliensis, Uppsala, Sweden, 2001.
69. Liu, Q.; Zhong, L.; Guo, Y.; Xiang, M.; Su, C.; Ning, P.; Guo, J. Facile flameless combustion synthesis of high-performance boron-doped LiMn2O4 cathode with a truncated octahedra. *J. Alloys Compd.* **2021**, *874*, 159912.
70. Chan, H.-W.; Duh, J.-G.; Sheen, S.-R. Electrochemical performance of LBO-coated spinel lithium manganese oxide as cathode material for Li-ion battery. *Surf. Coatings Technol.* **2004**, *188–189*, 116–119. https://doi.org/10.1016/j.surfcoat.2004.08.065.
71. Choi, S.H.; Kim, J.H.; Na Ko, Y.; Hong, Y.J.; Kang, Y.C. Electrochemical properties of $Li_2O–2B_2O_3$ glass-modified $LiMn_2O_4$ powders prepared by spray pyrolysis process. *J. Power Sources* **2012**, *210*, 110–115. https://doi.org/10.1016/j.jpowsour.2012.03.016.
72. Chan, H.W.; Duh, J.G.; Sheen, S.R. Surface treatment of the lithium boron oxide coated $LiMn_2O_4$ cathode material in Li-ion battery. *Key Eng. Mater.* **2005**, *280*, 671–676.

73. Choi, S.H.; Kim, J.H.; Ko, Y.N.; Kang, Y.C. Electrochemical properties of boron-doped $LiMn_2O_4$ nanoparticles covered with glass material prepared by high-temperature flame spray pyrolysis. *Int. J. Electrochem. Sci.* **2013**, *8*, 1146–1162.
74. Şahan, H.; Göktepe, H.; Patat, Ş.; Ülgen, A. The effect of LBO coating method on electrochemical performance of $LiMn_2O_4$ cathode material. *Solid State Ion.* **2008**, *178*, 1837–1842.
75. Eddrief, M.; Dzwonkowski, P.; Julien, C.; Balkanski, M. The ac conductivity in B_2O_3-Li_2O films. *Solid State Ion.* **1991**, *45*, 77–82.
76. Soppe, W.; Aldenkamp, F.; Den Hartog, H.W. The structure and conductivity of binary and ternary glasses $(B_2O_3)_{1-xy}(Li_2O)x(Li_2Cl_2)_y$. *J. Non-Cryst. Solids* **1987**, *91*, 351–374.
77. Li, J.; Ma, Z.-F. Past and Present of LiFePO4: From Fundamental Research to Industrial Applications. *Chem* **2019**, *5*, 3–6. https://doi.org/10.1016/j.chempr.2018.12.012.
78. Wu, B.; Ren, Y.; Li, N. $LiFePO_4$ cathode material. In *Electric Vehicles—The Benefits and Barriers*; BoD: Norderstedt, Germany, 2011; pp. 199–216.
79. Padhi, A.K.; Nanjundaswamy, K.S.; Goodenough, J.B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.* **1997**, *144*, 1188.
80. Prosini, P.P. Determination of the Diffusion Coefficient of $LiFePO_4$. In *Iron Phosphate Materials as Cathodes for Lithium Batteries*; Springer: London, UK, 2011; pp. 21–27.
81. Wang, F.; Zhang, Y.; Chen, C. Research on high rate capabilities B-substituted LiFePO4. *J. Nanosci. Nanotechnol.* **2013**, *13*, 1535–1538. https://doi.org/10.1166/jnn.2013.5981.
82. Trócoli, R.; Franger, S.; Cruz, M.; Morales, J.; Santos-Peña, J. Improving the electrochemical properties of nanosized LiFePO4-based electrode by boron doping. *Electrochim. Acta* **2014**, *135*, 558–567.
83. Feng, J.; Wang, Y. High-rate and ultralong cycle-life LiFePO4 nanocrystals coated by boron-doped carbon as positive electrode for lithium-ion batteries. *Appl. Surf. Sci.* **2016**, *390*, 481–488. https://doi.org/10.1016/j.apsusc.2016.08.066.
84. Zhang, J.; Nie, N.; Liu, Y.; Wang, J.; Yu, F.; Gu, J.; Li, W. Boron and Nitrogen Codoped Carbon Layers of $LiFePO_4$ Improve the High-Rate Electrochemical Performance for Lithium Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 20134–20143. https://doi.org/10.1021/acsami.5b05398.
85. Tuo, K.; Mao, L.; Ding, H.; Dong, H.; Zhang, N.; Fu, X.; Huang, J.; Liang, W.; Li, S.; Li, C. Boron and Phosphorus Dual-Doped Carbon Coating Improves Electrochemical Performances of $LiFe_{0.8}Mn_{0.2}PO_4$ Cathode Materials. *ACS Appl. Energy Mater.* **2021**, *4*, 8003–8015.
86. Mo, W.; Wang, Z.; Wang, J.; Li, X.; Guo, H.; Peng, W.; Yan, G. Tuning the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ primary particle with lithium boron oxide toward stable cycling. *Chem. Eng. J.* **2020**, *400*, 125820. https://doi.org/10.1016/j.cej.2020.125820.
87. Wu, E.A.; Jo, C.; Tan, D.H.S.; Zhang, M.; Doux, J.-M.; Chen, Y.-T.; Deysher, G.; Meng, Y.S. A facile, dry-processed lithium borate-based cathode coating for improved all-solid-state battery performance. *J. Electrochem. Soc.* **2020**, *167*, 130516.
88. Wu, C.-Y.; Bao, Q.; Tsai, Y.-T.; Duh, J.-G. Tuning (003) interplanar space by boric acid co-sintering to enhance Li+ storage and transfer in $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ cathode. *J. Alloys Compd.* **2021**, *865*, 158806.
89. Roitzheim, C.; Kuo, L.-Y.; Sohn, Y.J.; Finsterbusch, M.; Möller, S.; Sebold, D.; Valencia, H.; Meledina, M.; Mayer, J.; Breuer, U.; et al. Boron in Ni-Rich NCM811 Cathode Material: Impact on Atomic and Microscale Properties. *ACS Appl. Energy Mater.* **2021**, *5*, 524–538. https://doi.org/10.1021/acsaem.1c03000.
90. Zhang, N.; Li, Y.; Qiao, Y. Boosting the electrochemical performance of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ through a trace amount of Mg-B co-doping. *J. Mater. Sci. Technol.* **2021**, *89*, 167–178.
91. Park, K.-J.; Jung, H.-G.; Kuo, L.-Y.; Kaghazchi, P.; Yoon, C.S.; Sun, Y.-K. Improved cycling stability of $Li[Ni_{0.90}Co_{0.05}Mn_{0.05}]O_2$ through microstructure modification by boron doping for Li-ion batteries. *Adv. Energy Mater.* **2018**, *8*, 1801202.
92. Liu, Y.; Fan, X.; Luo, B.; Zhao, Z.; Shen, J.; Liu, Z.; Xiao, Z.; Zhang, B.; Zhang, J.; Ming, L.; et al. Understanding the enhancement effect of boron doping on the electrochemical performance of single-crystalline Ni-rich cathode materials. *J. Colloid Interface Sci.* **2021**, *604*, 776–784. https://doi.org/10.1016/j.jcis.2021.07.027.
93. Kim, G.J.; Park, H.W.; Lee, J.D. Electrochemical Properties of Boron-doped Cathode Materials ($LiNi_{0.90}Co_{0.05}Ti_{0.05}O_2$) for Lithium-ion Batteries. *Korean Chem. Eng. Res.* **2019**, *57*, 832–840.
94. Xie, Q.; Li, W.; Dolocan, A.; Manthiram, A. Insights into Boron-Based Polyanion-Tuned High-Nickel Cathodes for High-Energy-Density Lithium-Ion Batteries. *Chem. Mater.* **2019**, *31*, 8886–8897. https://doi.org/10.1021/acs.chemmater.9b02916.
95. Zou, Y.; Liu, G.; Zhou, K.; Zhang, J.; Jiao, T.; Zhang, X.; Yang, Y.; Zheng, J. Enhanced Interfacial Stability of a $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ Cathode by a Diboron Additive. *ACS Appl. Energy Mater.* **2021**, *4*, 11051–11061.
96. Xie, Y.; Jin, Y.; Xiang, L. Li-rich layered oxides: Structure, capacity and voltage fading mechanisms and solving strategies. *Particuology* **2021**, *61*, 1–10. https://doi.org/10.1016/j.partic.2021.05.011.
97. Uzun, D. Boron-doped $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ as a cathode active material for lithium ion battery. *Solid State Ionics* **2015**, *281*, 73–81. https://doi.org/10.1016/j.ssi.2015.09.008.
98. Pan, L.; Xia, Y.; Qiu, B.; Zhao, H.; Guo, H.; Jia, K.; Gu, Q.; Liu, Z. Structure and electrochemistry of B doped Li $(Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54})_{1-x}B_xO_2$ as cathode materials for lithium-ion batteries. *J. Power Sources* **2016**, *327*, 273–280.
99. Sun, Z.; Xu, L.; Dong, C.; Zhang, H.; Zhang, M.; Liu, Y.; Zhou, Y.; Han, Y.; Chen, Y. Enhanced cycling stability of boron-doped lithium-rich layered oxide cathode materials by suppressing transition metal migration. *J. Mater. Chem. A* **2019**, *7*, 3375–3383. https://doi.org/10.1039/c8ta10786f.
100. Julien, C.M.; Mauger, A. NCA, NCM811, and the Route to Ni-Richer Lithium-Ion Batteries. *Energies* **2020**, *13*, 6363. https://doi.org/10.3390/en13236363.

101. Guilmard, M.; Croguennec, L.; Denux, D.; Delmas, C. Thermal Stability of Lithium Nickel Oxide Derivatives. Part I: $Li_xNi_{1.02}O_2$ and $Li_xNi_{0.89}Al_{0.16}O_2$ (x = 0.50 and 0.30). *Chem. Mater.* **2003**, *15*, 4476–4483.
102. Ryu, H.-H.; Park, N.-Y.; Seo, J.H.; Yu, Y.-S.; Sharma, M.; Mücke, R.; Kaghazchi, P.; Yoon, C.S.; Sun, Y.-K. A highly stabilized Ni-rich NCA cathode for high-energy lithium-ion batteries. *Mater. Today* **2020**, *36*, 73–82. https://doi.org/10.1016/j.mattod.2020.01.019.
103. Chen, T.; Li, X.; Wang, H.; Yan, X.; Wang, L.; Deng, B.; Ge, W.; Qu, M. The effect of gradient boracic polyanion-doping on structure, morphology, and cycling performance of Ni-rich $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode material. *J. Power Sources* **2018**, *374*, 1–11.
104. Yang, W.; Xiang, W.; Chen, Y.-X.; Wu, Z.-G.; Hua, W.-B.; Qiu, L.; He, F.-R.; Zhang, J.; Zhong, B.-H.; Guo, X.-D. Interfacial regulation of Ni-rich cathode materials with an ion-conductive and pillaring layer by infusing gradient boron for improved cycle stability. *ACS Appl. Mater. Interfaces* **2020**, *12*, 10240–10251.
105. Zhao, Z.; Zhang, B.; Cheng, L.; Liu, Z.; Liu, Y.; Su, S.; Ming, L.; Zhang, J.; Ou, X. Enhanced electrochemical and structural stability of Ni-Rich cathode materials by lithium metaborate coating for lithium-ion batteries. *ChemElectroChem* **2022**, *9*, e202101395.
106. Yan, W.; Jia, X.; Yang, S.; Huang, Y.; Yang, P.Y.; Yuan, P.G. Synthesis of Single Crystal $LiNi_{0.92}Co_{0.06}Mn_{0.01}Al_{0.01}O_2$ Cathode Materials with Superior Electrochemical Performance for Lithium Ion Batteries. *J. Electrochem. Soc.* **2020**, *167*, 120514. https://doi.org/10.1149/1945-7111/abacea.
107. Su, Y.; Li, L.; Chen, G.; Chen, L.; Li, N.; Lu, Y.; Bao, L.; Chen, S.; Wu, F. Strategies of Removing Residual Lithium Compounds on the Surface of Ni-Rich Cathode Materials. *Chin. J. Chem.* **2021**, *39*, 189–198.
108. You, L.; Chu, B.; Li, G.; Huang, T.; Yu, A. H_3BO_3 washed $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ with enhanced electrochemical performance and storage characteristics. *J. Power Sources* **2021**, *482*, 228940.
109. Li, X.; Zhao, C.; He, J.; Li, Y.; Wang, Y.; Liu, L.; Huang, J.; Li, C.; Wang, D.; Duan, J.; et al. Removing lithium residues via H_3BO_3 washing and concurrent in-situ formation of a lithium reactive coating on Ni-rich cathode materials toward enhanced electrochemical performance. *Electrochim. Acta* **2022**, *406*, 139879.
110. Su, Y.; Chen, G.; Chen, L.; Li, L.; Li, C.; Ding, R.; Liu, J.; Lv, Z.; Lu, Y.; Bao, L.; et al. Clean the Ni-rich cathode material surface with boric acid to improve its storage performance. *Front. Chem.* **2020**, *8*, 573. https://doi.org/10.3389/fchem.2020.00573.
111. Li, Ao, Anthony Chun Yin Yuen, Wei Wang, Ivan Miguel De Cachinho Cordeiro, Cheng Wang, Timothy Bo Yuan Chen, Jin Zhang, Qing Nian Chan, and Guan Heng Yeoh. "A review on lithium-ion battery separators towards enhanced safety performances and modelling approaches." Molecules 26, no. 2 (2021): 478.
112. Lee, H.; Yanilmaz, M.; Toprakçi, O.; Fu, K.; Zhang, X. A review of recent developments in membrane separators for rechargeable lithium-ion batteries. *Energy Environ. Sci.* **2014**, *7*, 3857–3886. https://doi.org/10.1039/c4ee01432d.
113. De Moraes, A.C.M.; Hyun, W.J.; Luu, N.S.; Lim, L.-M.; Park, K.-Y.; Hersam, M.C. Phase-inversion polymer composite separators based on hexagonal boron nitride nanosheets for high-temperature lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2020**, *12*, 8107–8114.
114. Rahman, M.M.; Mateti, S.; Cai, Q.; Sultana, I.; Fan, Y.; Wang, X.; Hou, C.; Chen, Y. High temperature and high rate lithium-ion batteries with boron nitride nanotubes coated polypropylene separators. *Energy Storage Mater.* **2019**, *19*, 352–359. https://doi.org/10.1016/j.ensm.2019.03.027.
115. Sheng, J.; Zhang, Q.; Liu, M.; Han, Z.; Li, C.; Sun, C.; Chen, B.; Zhong, X.; Qiu, L.; Zhou, G. Stabilized Solid Electrolyte Interphase Induced by Ultrathin Boron Nitride Membranes for Safe Lithium Metal Batteries. *Nano Lett.* **2021**, *21*, 8447–8454. https://doi.org/10.1021/acs.nanolett.1c03106.
116. Rodriguez, J.R.; Kim, P.J.; Kim, K.; Qi, Z.; Wang, H.; Pol, V.G. Engineered heat dissipation and current distribution boron nitride-graphene layer coated on polypropylene separator for high performance lithium metal battery. *J. Colloid Interface Sci.* **2021**, *583*, 362–370.
117. Kim, J.; Oh, J.; Lee, H. Review on battery thermal management system for electric vehicles. *J. Appl. Therm. Eng.* **2019**, *149*, 192–212. https://doi.org/10.1016/j.applthermaleng.2018.12.020.
118. Pesaran, A.A. Battery thermal management in EV and HEVs: Issues and solutions. *Battery Man* **2001**, *43*, 34–49.
119. Ge, X.; Chen, Y.; Liu, W.; Zhang, G.; Li, X.; Ge, J.; Li, C. Liquid cooling system for battery modules with boron nitride based thermal conductivity silicone grease. *RSC Adv.* **2022**, *12*, 4311–4321. https://doi.org/10.1039/d1ra08929c.
120. Zhang, Y.; Huang, J.; Cao, M.; Du, G.; Liu, Z.; Li, W. Preparation of Boron Nitride and Silicone Rubber Composite Material for Application in Lithium Batteries. *Energies* **2021**, *14*, 999.
121. Meng, Z.; Dai, Z.; Chen, K.; Wang, S. Investigation on preparation, thermal, and mechanical properties of carbon fiber decorated with hexagonal boron nitride/silicone rubber composites for battery thermal management. *Int. J. Energy Res.* **2021**, *45*, 4396–4409.
122. Li, X.; Huang, Q.; Deng, J.; Zhang, G.; Zhong, Z.; He, F. Evaluation of lithium battery thermal management using sealant made of boron nitride and silicone. *J. Power Sources* **2020**, *451*, 227820.
123. Wang, Z.; Zhang, K.; Zhang, B.; Tong, Z.; Mao, S.; Bai, H.; Lu, Y. Ultrafast battery heat dissipation enabled by highly ordered and interconnected hexagonal boron nitride thermal conductive composites. *Green Energy Environ.* **2022**. https://doi.org/10.1016/j.gee.2022.02.007.
124. Saw, L.H.; Ye, Y.; Tay, A.A.O. Feasibility study of Boron Nitride coating on Lithium-ion battery casing. *Appl. Therm. Eng.* **2014**, *73*, 154–161.
125. Evers, S.; Nazar, L.F. New Approaches for High Energy Density Lithium–Sulfur Battery Cathodes. *Accounts Chem. Res.* **2012**, *46*, 1135–1143. https://doi.org/10.1021/ar3001348.

doi:10.20944/preprints202205.0303.v1

126. Seh, Z.W.; Sun, Y.; Zhang, Q.; Cui, Y. Designing high-energy lithium–sulfur batteries. *Chem. Soc. Rev.* **2016**, *45*, 5605–5634.
127. Cheng, Q.; Xu, W.; Qin, S.; Das, S.; Jin, T.; Li, A.; Li, A.C.; Qie, B.; Yao, P.; Zhai, H.; et al. Full Dissolution of the Whole Lithium Sulfide Family (Li_2S_8 to Li_2S) in a Safe Eutectic Solvent for Rechargeable Lithium–Sulfur Batteries. *Angew. Chem.* **2019**, *131*, 5613–5617. https://doi.org/10.1002/ange.201812611.
128. Wang, Q.; Jin, J.; Wu, X.; Ma, G.; Yang, J.; Wen, Z. A shuttle effect free lithium sulfur battery based on a hybrid electrolyte. *Phys. Chem. Chem. Phys.* **2014**, *16*, 21225–21229. https://doi.org/10.1039/c4cp03694h.
129. Kim, H.-S.; Kang, H.-J.; Lim, H.; Hwang, H.J.; Park, J.-W.; Lee, T.-G.; Cho, S.Y.; Jang, S.G.; Jun, Y.-S. Boron Nitride Nanotube-Based Separator for High-Performance Lithium-Sulfur Batteries. *Nanomaterials* **2021**, *12*, 11. https://doi.org/10.3390/nano12010011.
130. Babu, G.; Sawas, A.; Thangavel, N.K.; Arava, L.M.R. Two-dimensional material-reinforced separator for Li–sulfur battery. *J. Phys. Chem. C* **2018**, *122*, 10765–10772.
131. Fan, Y.; Liu, D.; Rahman, M.; Tao, T.; Lei, W.; Mateti, S.; Yu, B.; Wang, J.; Yang, C.; Chen, Y. Repelling Polysulfide Ions by Boron Nitride Nanosheet Coated Separators in Lithium–Sulfur Batteries. *ACS Appl. Energy Mater.* **2019**, *2*, 2620–2628. https://doi.org/10.1021/acsaem.8b02205.
132. Han, P.; Manthiram, A. Boron- and nitrogen-doped reduced graphene oxide coated separators for high-performance Li-S batteries. *J. Power Sources* **2017**, *369*, 87–94. https://doi.org/10.1016/j.jpowsour.2017.10.005.
133. Li, B.; Sun, Z.; Zhao, Y.; Tian, Y.; Tan, T.; Gao, F.; Li, J. Functional separator for Li/S batteries based on boron-doped graphene and activated carbon. *J. Nanoparticle Res.* **2018**, *21*, 7. https://doi.org/10.1007/s11051-018-4451-8.
134. Eroglu, O.; Kiai, M.S.; Kizil, H. Glass fiber separator coated by boron doped anatase TiO_2 for high-rate Li–S battery. *Mater. Res. Bull.* **2020**, *129*, 110917. https://doi.org/10.1016/j.materresbull.2020.110917.
135. Luo, L.; Chung, S.; Asl, H.Y.; Manthiram, A. Long-Life Lithium–Sulfur Batteries with a Bifunctional Cathode Substrate Configured with Boron Carbide Nanowires. *Adv. Mater.* **2018**, *30*, e1804149. https://doi.org/10.1002/adma.201804149.
136. Song, N.; Gao, Z.; Zhang, Y.; Li, X. B4C nanoskeleton enabled, flexible lithium-sulfur batteries. *Nano Energy* **2019**, *58*, 30–39. https://doi.org/10.1016/j.nanoen.2019.01.018.
137. Zhang, R.; Chi, C.; Wu, M.; Liu, K.; Zhao, T. A long-life Li–S battery enabled by a cathode made of well-distributed B4C nanoparticles decorated activated cotton fibers. *J. Power Sources* **2020**, *451*, 227751. https://doi.org/10.1016/j.jpowsour.2020.227751.