Pilot Scale Hybrid Organic/Inorganic Coatings on a Polyolefin Separator to Enhance Dimensional Stability for Thermally Stable Long-Life Rechargeable Batteries

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Abstract: The electric vehicle and energy storage markets have grown rapidly in recent years. Thermal runaway caused by malfunctioning Li-ion batteries is an urgent issue with many causes (e.g., mechanical, electrical, and thermal abuse). The most common cause of thermal runaway is the formation of an internal short circuit because of damage to the separator. There has been significant effort to improve the design of separators, but to our knowledge, only inorganic nanoparticle coatings are used in commercial Li-ion batteries. Here, hybrid organic/inorganic coating layers are synthesized in a pilot-scale process that was developed from a crosslinkable polyamide-imide synthesis technique. The fabrication process is optimized to achieve reproducible hybrid organic/inorganic coating layers that are thin ($\leq 4 \, \mu m$), permeable ($\leq 250 \, s/100 \, cc$), and thermally stable beyond 150 $^\circ C$. The hybrid coating layer is applied to mini-18650 Li-ion cells to show that the discharge capacity did not change at low discharge rates, and the retention capacity after 500 cycles was better than that of the reference cells used for comparison. This work demonstrates that a novel hybrid coating layer has the potential to improve the stability of commercial Li-ion batteries.

Keywords: crosslinkable polyamide-imide; hybrid organic/inorganic coating; pilot-scale; mini-18650 Li-ion cell; thermal stability

1. Introduction

Li-ion batteries play a crucial role in modern daily life as a robust portable power source with high energy density [1], small memory effect [2], and long lifespan [3]. Consumer use of “smart” devices has increased substantially as battery energy density increases, at a rate of 5.5 Wh kg$^{-1}$ per year [4], and the availability of large batteries capable of storing 60 kWh has contributed to the growth of environmentally friendly electric vehicles [5]. Furthermore, smart grids reduce carbon emissions by generating electricity from solar, wind, geothermal, and tidal energy sources and storing it in and supplying it from energy storage systems [6]. Development of the next generation rechargeable batteries, such as Zn based batteries [7–9], has been raising expectations for far safer and much more advanced energy storage devices that contribute to smarter and cleaner lives.

Li-ion batteries are an integrated component in a wide range of technologies; however, malfunctioning batteries are susceptible to thermal runaway, which presents a significant risk to users and their property. Thermal runaway can be caused by mechanical, electrical, and thermal abuse [10]. Mechanical abuse typically results in deformation, while electrical abuse encourages the growth of dendrites and elevated temperatures, which can cause thermal damage. Any damage to the battery separators can result in electrical short circuits, which are the most direct cause of thermal runaway [11]. Once an internal short circuit is formed, exothermic reactions, such as solid electrolyte interface decomposition, separator disintegration, and redox reactions between the cathode and anode are initiated, the battery...
temperature increases rapidly [12,13]. Therefore, it is important that improvements be made to separator designs to prevent or delay damage and improve the safety of Li-ion batteries. Research efforts have been focused on the development of advanced separators that address the aforementioned issues. These include: separators fabricated from phase-changing thermoregulating coaxial fibers [14], flame-retardant coaxial fibers [15], and an electrochemically active silica sandwich [16]. Among the technologies that have been explored, separators coated with inorganic nanoparticles are of particular interest as they are low-cost and simple to process, both of which are attractive properties for commercial production. Electrochemically inactive inorganic materials, such as SiO$_2$ [17–19], Al$_2$O$_3$ [20–22], and AlOOH [23–25], have been used to improve the thermal and mechanical performance of separators, and increase their wettability at the interface with the electrolyte. Polyvinyl alcohol [24], polyvinylidene hexafluoropropylene [21], and polyurethane acrylate [26] have been used as binders. Most studies concluded that inorganic nanoparticle-coated separators have superior electrolyte wettability [20], thermally stability [17], and improved electrochemical performances [18], but research has focused on their use in single coin cells and small pouch cells. Therefore, there is a need to develop inorganic nanoparticle separators suitable for the fabrication of large-scale Li-ion batteries. Furthermore, the inorganic nanoparticles and organic components must be thermally stable. In this work, we design a thermally stable organic crosslinked polyamide-imide component and optimize a pilot-scale process to apply a hybrid organic/inorganic coating to a polyolefin separator. The consequences of applying the hybrid layer are thoroughly evaluated by testing its electrochemical performance in mini-18650 Li-ion cells.

2. Experimental

2.1. Crosslinkable Polyamide-Imide Preparation

Hexafluoroisopropylidene-bis-phthalic anhydride (6-FDA; Sigma-Aldrich, Burlington, MA, USA), toluene diisocyanate (TDI; Sigma-Aldrich, Burlington, MA, USA), fumaric acid (FA; Sigma-Aldrich, Burlington, MA, USA), and pentaerythritol triacrylate (PETA; Sigma-Aldrich, Burlington, MA, USA) were used as monomers to design a crosslinkable polyamide-imide (PAI). 6-FDA, FA, and TDI were polymerized at a monomer ratio of 0.9:0.1:1.1 in dimethylacetamide (DMAc; Sigma-Aldrich, Burlington, MA, USA) 100 °C for 1 h. The monomer content in DMAc was 60 wt %. 6-FDA was used to ensure solubility in acetone, and FA and TDI were selected to promote dimensional stability in the electrolyte solution and crosslinking. To improve crosslinking, the residual-NCO group was capped with PETA at a monomer ratio of 6-FDA + FA + TDI:PETA of 1:1, at 70 °C for 1 h. The PAI was characterized using gel permeation chromatography (GPC; Waters Co., Ltd., Milford, MA, USA) and thermogravimetric analysis (TGA; Discovery TGA; TA Instruments, New Castle, DE, USA).

2.2. Polyethylene Separator Coating

A 12-µm-thick polyethylene separator was used as a substrate, with a Gurley number of 120 s/100 cc. The following hybrid organic/inorganic layers with various compositions were deposited on the substrate to determine the adhesion and permeability (Gurley number): polyurethane acrylate, polyvinylidene fluoride (PVdF), Al$_2$O$_3$ nanoparticles = 0.8, 0.2, 2.0; PAI, PVdF, Al$_2$O$_3$ nanoparticles = 1.0, 0, 2.0; PAI, PVdF, Al$_2$O$_3$ nanoparticles = 0.9, 0.1, 2.0; PAI, PVdF, Al$_2$O$_3$ nanoparticles = 0.8, 0.2, 2.0; PAI, PVdF, Al$_2$O$_3$ nanoparticles = 0.7, 0.3, 2.0; PAI, PVdF, Al$_2$O$_3$ nanoparticles = 0.8, 0.2, 3.0; and PAI, PVdF, Al$_2$O$_3$ nanoparticles = 0.7, 0.3, 3.0. The adhesion strengths of the hybrid coating layers were evaluated by the 180° peel test between the hybrid coating layer and the 3 M adhesive tape (Scotch Magic tape, 18 mm. 3 M) adhered to their surface using a Universal Testing Machine (Instron 3343, Instron, Norwood, MA, USA). Changes in permeability as a result of humidity and nonsolvent effects were examined. Gurley numbers were measured by the JIS P8117 method (Testing Method for Air Permeability of Paper and Paperboard [27]) using a Digital
Oken Type Air-Permeability tester (EGO-1-55-1MR, Asahi Seiko Co., Ltd., Osaka, Japan). All coatings were applied and tested using pilot-scale techniques.

2.3. Thermal and Electrochemical Characterization

The thermal characteristics of separators coated with ceramic or hybrid organic/inorganic layers were tested by heating the separators at 200 °C for 10 min. Coated separators were then assembled into a cylindrical battery pack filled with electrolyte and heated to 150 °C for 1 h to further evaluate their thermal behavior. Cylindrical mini-18650 cells were assembled in a dry-room, and the rate and cycling performance of the hybrid coated separators were examined. A Li(Ni, Co, Al)O₂ (NCA) and Li(Ni, Co, Mn)O₂ (NCM) mixed cathode (NCA/NCM/carbon black/PVdF = 96/1.8/2.2 by weight, loading level = 40.73 mg cm⁻²) and graphite anode (graphite/styrene-butadiene rubber (SBR)/carboxymethylcellulose (CMC) = 97.5/1.5/1.0 by weight, loading level = 20.50 mg cm⁻²), provided by Samsung SDI (South Korea) were used in the electrochemical performance tests. The cathode and anode were cut into 54 mm × 130 mm and 58 mm × 160 mm pieces, respectively. The separator was 60 mm wide. The liquid electrolyte comprised 1.15 M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (EC/EMC/DMC 2/4/4 by volume; PANAX ETEC Co., Busan, Korea) with 1% lithium difluorophosphate (MP1), and 1.5% vinyl chloride (VC) additives. Galvanostatic rate and cycling tests were conducted in the range 3.0–4.25 V under constant current-constant voltage charging and constant current discharging modes (WonATech, Seoul, Korea). The direct current internal resistance (DCIR) of as-assembled cells and cells that had been cycled 100 times was measured. Charge and discharge rates were tested at current density C-rates between 0.1 and 5C. In the cycling tests, the cells were charged to 4.25 V at 1C with a 0.2C current cut-off, and then discharged to 3.0 V at 1C. The cells were left to stabilize for 10 min after charging and 15 min after discharging.

3. Results and Discussion

A separator coated with a hybrid organic/inorganic layer was placed between an NCA cathode and graphite anode; the hybrid layer was in contact with the cathode, as shown in Figure 1. The hybrid layer comprised inorganic Al₂O₃ nanoparticles, organic PAIX, and a PVdF binder. The inorganic-coated polyolefin is inexpensive (<$1 m⁻²), dimensionally stable, and highly wettable in carbonate electrolyte, whereas the polymer-coated separator is flexible, forms intimate contact with the electrode, and has better electrolyte uptake [28–32]. However, the inorganic-coated polyolefin is brittle after thermal treatment, and the polymer coating is less robust against mechanical failure modes. Therefore, the hybrid organic/inorganic coating was designed to exploit the advantages and compensate for the disadvantages of each layer component.

A schematic of the PAIX synthesis process is presented in Figure 2. First, 6-FDA, TDI, and FA monomers were polymerized in DMAc at 100 °C for 1 h; then, PETA was added as a multifunctional crosslinker [33,34]. It is important that the components are soluble to ensure processibility; 6-FDA was crosslinked with the TDI using an isocyanate-anhydride reaction [35] so that it was soluble in acetone. The acrylamides, formed from the addition of isocyanate and alcohol [35], were crosslinked with acrylates so that the product was stable in the carbonate electrolyte. After the hybrid organic/inorganic layer was cast on the polyolefin separator, a crosslinking process was initiated using benzoyl peroxide (BPO; 10 wt % with respect to the PAIX content) and left to react overnight at 100 °C.
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Figure 1. Schematic of a Li rechargeable battery in which the separator is coated with a hybrid organic/inorganic layer.

Figure 2. Schematic of PAIX synthesis. 6-FDA, FA, and TDI monomers were polymerized in DMAc at 100 °C for 1 h, and PETA was used as a multifunctional terminal.

The pilot-scale PAIX synthesis process was repeated three times to determine the reproducibility, and its macromolecular properties were studied using GPC and TGA as shown in Figure 3. The PAIX was dissolved in DMF in preparation for GPC testing. As shown in Figure 3a, the number (M_n) and weight (M_w) of the average molecular weights were approximately 19,325 and 34,940, respectively. The inter-sample molecular weights

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differed by <1.1%. The polydispersity index (PDI), defined as $M_w/M_n$, was approximately 1.8, which agrees with the PDI of previous polyamide-imide synthesis works [36]. Therefore, we concluded that the pilot-scale polymerization produced a product of reasonable quality.

TGA was used to assess the thermal stability, as shown in Figure 3b. The TGA tests were conducted under a nitrogen blanket between 25 and 700 °C at a ramp rate of 5 °C per minute. Significant weight loss was observed above 400 °C, which coincides with the polyamide-imide decomposition temperature [37]. These results show that the pilot-scale PAIX synthesis was reproducible and thermally stable, and suitable for use as the organic component of the hybrid organic/inorganic coating.

The optimal hybrid coating recipe was analyzed, and the results are presented in Table 1. ASTM test D726 [38,39] was used to measure the permeability of a 12-µm-thick polyethylene separator, which yielded a Gurley number of 120 s/100 cc. The polyethylene separator was coated with a range of test slurries. A mixture of polyurethane acrylate and PVdF was applied to produce an organic reference coating, which is referred to as acrylate in Table 1. The Gurley number of the acrylate sample was 1,770 s/100 cc, which is more than 14 times greater than that of the untreated separator material. PAIX 100% was used to create a second organic reference coating, referred to as PAIX12 in Table 1. The Gurley number of the PAIX12 sample was 226 s/100 cc, which is less than twice that of the untreated separator material. The PAIX-polyethylene and acrylate-polyethylene adhesion forces were 49.2 and 193.2 gf cm–1, respectively. Commercial cell standards require that the adhesion force between the coating layer and substrate exceed 100 gf cm–1; thus, a PVdF binder was used to increase the PAIX coating adhesion without significantly increasing the permeability.

PVdF binder was added to PAIX to produce PAIX1291 and PAIX1282 with adhesion forces of 206.1 and 226.4 gf cm–1, respectively, but the Gurley numbers increased to 582 and 820 s/100 cc, respectively. The Gurley number was reduced by decreasing the organic:Al2O3 ratio from 1/2 to 1/3. Consequently, the Gurley number of PAIX1382 was 326 s/100 cc with an adhesion force of 104.8 gf cm–1. Finally, the recipe was tuned by adding more PVdF binder and increasing the solid content to 12 wt %, to produce PAIX1373–12 with a Gurley number of 278 s/100 cc.

Table 1. Coating recipes tested and corresponding Gurley numbers.

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| Sample Code   | Solid Content (wt %) | Organic to Al$_2$O$_3$ Ratio | Organic Content (wt %) | PAIX Polyurethane Acrylate PVdF | Gurley Number (s/100 cc) |
|---------------|----------------------|------------------------------|------------------------|-------------------------------|--------------------------|
| Acrylate      | 10                   | 1/2                          | 0                      | 80                            | 20                       |
| PAIX12        | 10                   | 1/2                          | 100                    | 0                             | 0                        |
| PAIX1291      | 10                   | 1/2                          | 90                     | 0                             | 10                       |
| PAIX1282      | 10                   | 1/2                          | 80                     | 0                             | 20                       |
| PAIX1382      | 10                   | 1/3                          | 80                     | 0                             | 20                       |
| PAIX1373-12   | 12                   | 1/3                          | 70                     | 0                             | 30                       |

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Nonsolvent additives were introduced into the optimized PAIX1373-12 recipe to increase the permeability, as shown in Table 2. The coating thickness and density, and the organic:Al$_2$O$_3$ and PAIX:PVdF ratios, were precisely controlled, and the phase separation effect was used to decrease the coating density by adding distilled water at concentrations of 1 and 2 wt % to produce PAIX_D11 and PAIX_D12, respectively. Although PAIX_D11 and PAIX_D12 were thicker coatings, the Gurley number decreased to 260 and 245 s/100 cc, respectively. The density was decreased further (2.04 g cc$^{-1}$) by adding ethylene glycol at a concentration of 3 wt % to produce PAIX_EG3 with a Gurley number of 207 s/100 cc, which also mitigated the phase separation and improved the coating uniformity. The morphologies of PAIX_D11 and PAIX_EG3 are given in Figure 4. Low-magnification SEM images of PAIX_D11 and PAIX_EG3 suggest that the coating surfaces are uniform, but high-magnification images reveal the surface roughness that is introduced by phase separation. The surface of PAIX_D11, shown in Figure 4b, was significantly rougher than the surface of PAIX_EG3, shown in Figure 4d. As presented in Figure 4e, the PAIX_D11 and PAIX_EG3 surfaces featured an average of 2.27 and 3.00 peaks per unit micrometer, respectively. Therefore, we concluded that ethylene glycol was the best nonsolvent to form a highly permeable hybrid organic/inorganic coating layer.

Table 2. Summary of the hybrid coating layer properties with the addition of nonsolvents.

| Sample Code | Solid Content (wt %) | Organic to Al$_2$O$_3$ Ratio | PAIX to PVdF Ratio | Density (g cc$^{-1}$) | Thickness (µm) | Gurley Number (s/100 cc) |
|-------------|----------------------|------------------------------|--------------------|-----------------------|----------------|--------------------------|
| PAIX1373-12 | 12                   | 1/3                          | 7/3                | 2.15                  | 2.500          | 278                      |
| PAIX_D11    | 12                   | 1/3                          | 7/3                | 1.84                  | 3.000          | 260                      |
| PAIX_D12    | 12                   | 1/3                          | 7/3                | 1.46                  | 3.875          | 245                      |
| PAIX_EG3    | 12                   | 1/3                          | 7/3                | 2.04                  | 4.000          | 207                      |
Figure 4. Hybrid organic/inorganic coating morphologies. (a) Low- and (b) high-magnification SEM images of a PAIX-PVdF-Al$_2$O$_3$ layer with a 1 wt % distilled water additive (PAIX_DI1). (c) Low- and (d) high-magnification SEM images of a PAIX-PVdF-Al$_2$O$_3$ layer with a 3 wt % ethylene glycol additive (PAIX_EG3). (e) Surface roughness of the PAIX_DI1 and PAIX_EG3 samples.

Polyolefin becomes deformable below 180 °C [40–42] so it is important that the hybrid coating protects the separator. The thermal durability of the PAIX coating was tested using dry and wet thermal exposure tests, as shown in Figure 5. The hybrid polyurethane acrylate/Al$_2$O$_3$ (organic:Al$_2$O$_3$ ratio of 1/8 and Gurley number of 145 s/100 cc)—coated reference separator was severely damaged by the dry exposure test, as shown in Figure 5a, and the separator coated with PAIX/Al$_2$O$_3$ was preserved without shrinkage after the same test, as shown in Figure 5b. The yellow color visible in the images was a result of imidization during thermal exposure. Separator samples were immersed in an electrolyte solution at 150 °C for 1 h and then disassembled and photographed, as shown in Figure 5c.
The separator coated with polyurethane acrylate/Al₂O₃ shrank significantly during the test, whereas the hybrid PAIX/Al₂O₃ coating resisted deformation during exposure to the same conditions. The enhanced thermal properties of the hybrid PAIX/Al₂O₃ layer were clearly demonstrated by these tests, which show that the hybrid coating was more thermally robust than the untreated and acrylate-coated separators.

Figure 5. Photographs of separator samples following dry and wet thermal tests. (a) Acrylate- and (b) hybrid PAIX/AL₂O₃-coated separators after dry thermal treatment at 200 °C for 10 min, and (c) disassembled acrylate- (top) and hybrid PAIX/Al₂O₃-coated (second to fifth) separators after immersion in an electrolyte solution at 150 °C for 1 h.

The electrochemical performance of the separator with a hybrid organic/inorganic layer was tested by incorporating it into cylindrical mini-18650 cell assemblies. As shown in Figure 6a, the average DCIR of the as-assembled reference cell with an acrylate-coated separator was 117.6 mΩ and the DCIR of the separator with a hybrid PAIX coating was 128.6 mΩ. The impedance of the PAIX-based cell was greater than that of the reference cell because of its relatively low permeability. However, the structural stability of the PAIX-based separator meant that the DCIR value increased by < 1.7 mΩ after 100 charge cycles, whereas the reference cell DCIR increased by 4 mΩ. Figure 6b shows that the discharge capacity of the cells was similar at lower rates (≤ 0.5C), but the capacity of the PAIX cell was lower than that of the reference cell at higher discharge rates. At 1.0, 3.0, and 5.0C, the PAIX cell discharge capacity was 94.9%, 89.0%, and 81.5% of the reference cell capacity, respectively. This is because of the higher DCIR of the PAIX cells. Figure 6c,d present the cycling performance of the reference and PAIX cells, respectively. The cells were cycled 500 times each at 1.0C, after which the better cyclability of the PAIX cell was clear. The discharge capacities of the reference and PAIX cells after 500 cycles were 416.3 and 425.5 mAh, respectively, which were 77.0% and 78.6% of the initial discharge capacities, respectively. These tests suggest that although the hybrid PAIX/Al₂O₃ coating
worsens electrolyte permeability, the negative effects are less significant at low current densities, and the performance improves over many cycles. Based on the material properties and electrochemical performances, it was summarized as follows: i) the electrochemical performances of the PAIX cells at low rates (≤ 0.5C) were comparable to the that of the reference cell, ii) the discharge capacities of the PAIX cells at high rates were inferior to the reference cells due to the lower permeability, and iii) the discharge capacities of the PAIX cells after 500 cycles were higher than that of the reference cells owing to the improved structural stability. Therefore, we conclude that a separator coated with a hybrid PAIX/Al2O3 layer has a minor negative impact on the cell rate performance, but improves the thermal stability at high temperatures even when the cell is filled with electrolyte.

Figure 6. Electrochemical performance tests. (a) The DCIR increase of the cells, as-assembled and after 100 cycles. (b) The rate performance, (c) cycling discharge capacity, and (d) cycle retention ratio at 1.0C for each cell design.

4. Conclusions

A pilot-scale method for synthesizing a hybrid organic/inorganic coating was developed from a crosslinkable polymer synthesis technique and optimized. Multistep polymerization was used to successfully synthesize a reproducible, thermally stable PAIX with high thermal decomposition temperatures. The PAIX and PVdF ratio, organic to Al2O3 ratio, solid content, and nonsolvent additive concentration were controlled and optimized to produce a thin (≤4 µm), permeable (≤250 s/100 cc), and thermally stable (>150 °C) hybrid coating. The reduced permeability owing to the hybrid coating layer caused the DCIR to increase, and the discharge capacity to decrease at high rates (>1.0 C). However, in comparison with reference cells, mini-18560 cells that incorporated the hybrid separator coating showed the same discharge capacity at low rates and better cycling retention after 500 charge cycles. Therefore, we conclude that a polyolefin separator coated with a hybrid organic PAIX and inorganic Al2O3 layer provides a pathway to more thermally stable commercial Li-ion batteries with few electrochemical performance sacrifices.

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References

1. Cao, W.; Zhang, J.; Li, H. Batteries with high theoretical energy densities. Energy Stor. Mater. 2020, 26, 46–55. [CrossRef]
2. Madani, S.S.; Schaltz, E.; Knudsen Kær, S. Review of Parameter Determination for Thermal Modeling of Lithium Ion Batteries. Batteries 2018, 4, 20. [CrossRef]
3. Qi, W.; Shapter, J.G.; Wu, Q.; Yin, T.; Gao, G.; Cui, D. Nanostructured anode materials for lithium-ion batteries: Principle, recent progress and future perspectives. J. Mater. Chem. A 2017, 5, 19521–19540. [CrossRef]
4. Lee, B.-S.; Wu, Z.; Petrova, V.; Xing, X.; Lim, H.-D.; Liu, H.; Liu, P. Analysis of Rate-Limiting Factors in Thick Electrodes for Electric Vehicle Applications. J. Electrochem. Soc. 2018, 165, A525–A533. [CrossRef]
5. Mehrjerdi, H.; Hemmati, R. Stochastic model for electric vehicle charging station integrated with wind energy. Sustain. Energy Technol. Assess. 2020, 37, 100577. [CrossRef]
6. Ahmad, A.; Khan, A.; Javaid, N.; Hussain, H.M.; Abdul, W.; Almogren, A.; Alamri, A.; Azim Niaz, I. An Optimized Home Energy Management System with Integrated Renewable Energy and Storage Resources. Energies 2017, 10, 549. [CrossRef]
7. Rao, P.; Wu, D.; Luo, J.; Li, J.; Deng, P.; Shen, Y.; Tian, X. A plasma bombing strategy to synthesize high-loading single-atom catalysts for oxygen reduction reaction. Cell. Phys. Sci. 2022, 3, 100880. [CrossRef]
8. Rao, P.; Wu, D.; Wang, T.-J.; Li, J.; Deng, P.; Chen, Q.; Shen, Y.; Chen, Y.; Tian, X. Single atomic cobalt electrocatalyst for efficient oxygen reduction reaction. eScience 2022, 2, 399–404. [CrossRef]
9. Rao, P.; Wang, T.-J.; Li, J.; Deng, P.-L.; Shen, Y.-J.; Chen, Y.; Tian, X.-L. Plasma induced Fe-NX active sites to improve the oxygen reduction reaction performance. Adv. Energy Mater. 2022, 1, 100005. [CrossRef]
10. Ghiji, M.; Novozhilov, V.; Moinuddin, K.; Joseph, P.; Burch, I.; Suedermann, B.; Gamble, G. A Review of Lithium-Ion Battery Fire Suppression. Energies 2020, 13, 5117. [CrossRef]
11. Ren, D.; Feng, X.; Liu, L.; Hsu, H.; Lu, L.; Wang, L.; He, X.; Ouyang, M. Investigating the relationship between internal short circuit and thermal runaway of lithium-ion batteries under thermal abuse condition. Energy Stor. Mater. 2021, 34, 563–573. [CrossRef]
12. Zhang, G.; Wei, X.; Tang, X.; Zhu, J.; Chen, S.; Dai, H. Internal short circuit mechanisms, experimental approaches and detection methods of lithium-ion batteries for electric vehicles: A review. Renew. Susst. Energy. Rev. 2021, 141, 110790. [CrossRef]
13. Kumaravel, V.; Bartlett, J.; Pillai, S.C. Solid Electrolytes for High-Temperature Stable Batteries and Supercapacitors. Adv. Energy Mater. 2021, 11, 2002869. [CrossRef]
14. Liu, Z.; Hu, Q.; Guo, S.; Yu, L.; Hu, X. Thermoregulating Separators Based on Phase-Change Materials for Safe Lithium-Ion Batteries. Adv. Mater. 2021, 33, 2008088. [CrossRef]
15. Liu, K.; Liu, W.; Qiu, Y.; Kong, B.; Sun, Y.; Chen, Z.; Zhuo, D.; Lin, D.; Cui, Y. Electrosynp core-shell microfiber separator with thermal-triggered flame-retardant properties for lithium-ion batteries. Sci. Adv. 2017, 3, e1601978. [CrossRef]
16. Liu, K.; Zhuo, D.; Lee, H.-W.; Liu, W.; Lin, D.; Lu, Y.; Cui, Y. Extending the Life of Lithium-Based Rechargeable Batteries by Reaction of Lithium Dendrites with a Novel Silica Nanoparticle Sandwiched Separator. Adv. Mater. 2017, 29, 1603987. [CrossRef]
17. Prasanna, K.; Kim, C.-S.; Lee, C.W. Effect of SiO2 coating on polyethylene separator with different stretching ratios for application in lithium ion batteries. Mater. Chem. Phys. 2014, 146, 545–550. [CrossRef]
18. Shin, W.-K.; Kim, D.-W. High performance ceramic-coated separators prepared with lithium ion-containing SiO2 particles for lithium-ion batteries. J. Power Sources 2013, 226, 54–60. [CrossRef]
19. Cho, J.; Jung, Y.-C.; Lee, Y.S.; Kim, D.-W. High performance separator coated with amino-functionalized SiO2 particles for safety enhanced lithium-ion batteries. J. Membr. Sci. 2017, 535, 151–157. [CrossRef]
20. Ding, L.; Yan, N.; Zhang, S.; Xu, R.; Wu, T.; Yang, F.; Cao, Y.; Xiang, M. Low-Cost Mass Manufacturing Technique for the Shutdown-Functionalized Lithium-Ion Battery Separator Based on Al2O3 Coating Online Construction during the β-ilP Cavitation Process. ACS Appl. Mater. Interfaces 2022, 14, 6714–6728. [CrossRef]
21. Lee, D.-W.; Lee, S.-H.; Kim, Y.-N.; Oh, J.-M. Preparation of a high-purity ultrafine α-Al2O3 powder and characterization of an Al2O3-coated PE separator for lithium-ion batteries. Powder Technol. 2017, 320, 125–132. [CrossRef]
22. Zhang, H.; Sheng, L.; Bai, Y.; Song, S.; Liu, G.; Xue, H.; Wang, T.; Huang, X.; He, J. Amino-Functionalized Al2O3 Particles Coating Separator with Excellent Lithium-Ion Transport Properties for High-Power Density Lithium-Ion Batteries. Adv. Eng. Mater. 2020, 22, 1901545. [CrossRef]
23. Zhong, G.; Wang, Y.; Wang, C.; Wang, Z.; Guo, S.; Wang, L.; Liang, X.; Xiang, H. An AlOOH-coated polyimide electrospun fibrous membrane as a high-safety lithium-ion battery separator. *Ionics* 2019, 25, 2677–2684. [CrossRef]

24. Yang, C.; Tong, H.; Luo, C.; Yuan, S.; Chen, G.; Yang, Y. Boehmite particle coating modified microporous polyethylene membrane: A promising separator for lithium-ion batteries. *J. Power Sources* 2017, 348, 80–86. [CrossRef]

25. Wang, Y.; Wang, Q.; Lan, Y.; Song, Z.; Luo, J.; Wei, X.; Sun, F.; Yue, Z.; Yin, C.; Zhou, L.; et al. Aqueous aluminate ceramic coating polyethylene separators for lithium-ion batteries. *Solid State Ion.* 2020, 345, 115188. [CrossRef]

26. Zhi, Y.; Sun, X.; Li, N.; Yuan, S.; Wang, Z.; Jin, L.; Hang, J.; Shi, L. UV curable organic-inorganic hybrid coatings on microporous polyethylene separator for enhancing mechanical and electrochemical performance. *J. Alloys Compd.* 2018, 743, 756–762. [CrossRef]

27. Mizutani, Y.; Matsuda, H.; Ishiji, T.; Furuya, N.; Takahashi, K. Improvement of electrochemical NO2 sensor by use of carbon-fluorocarbon gas permeable electrode. *Sens. Actuators B Chem.* 2005, 108, 815–819. [CrossRef]

28. Wang, Y.; Travas-Sejdic, J.; Steiner, R. Polymer gel electrolyte supported with microporous polyolefin membranes for lithium ion polymer battery. *Solid State Ion.* 2002, 148, 443–449. [CrossRef]

29. Xie, Y.; Zou, H.; Xiang, H.; Xia, R.; Liang, D.; Shi, P.; Dai, S.; Wang, H. Enhancement on the wettability of lithium battery separator toward nonaqueous electrolytes. *J. Membr. Sci.* 2016, 503, 25–30. [CrossRef]

30. Xu, R.; Huang, X.; Lin, X.; Cao, J.; Yang, J.; Lei, C. The functional aqueous slurry coated separator using polyvinylidene fluoride powder particles for Lithium-ion batteries. *J. Electroanal. Chem.* 2017, 786, 77–85. [CrossRef]

31. Xue, C.; Jin, D.; Nan, H.; Wei, H.; Chen, H.; Zhang, C.; Xu, S. A novel polymer-modified separator for high-performance lithium-ion batteries. *J. Power Sources* 2020, 449, 227548. [CrossRef]

32. Zhao, J.; Hu, Q.; Wang, J.; Zhang, P.; Zhu, Y.; Wu, G.; Lv, Y.; Lv, L.; Zhao, Y.; Yang, M. Effects of Island-Coated PVdF-HFP Composite Separator on the Performance of Commercial Lithium-ion Batteries. *Coatings* 2018, 8, 437. [CrossRef]

33. Erkoc, P.; Odeh, Y.N.; Alrifai, N.; Zirhli, O.; Gunduz Akdogan, N.; Yildiz, B.; Misirlioglu, I.B.; Akdogan, O. Photocurable pentaerythritol triacrylate/lithium phenyl-2,4,6-trimethylbenzoylphosphinate-based ink for extrusion-based 3D printing of magneto-responsive materials. *J. Appl. Polym. Sci.* 2020, 137, 49043. [CrossRef]

34. Jung, B.; Lee, B.; Jeong, Y.-C.; Lee, J.; Yang, S.R.; Kim, H.; Park, M. Thermally stable non-aqueous ceramic-coated separators with enhanced nail penetration performance. *J. Power Sources* 2019, 427, 271–282. [CrossRef]

35. Delebecq, E.; Pascault, J.-P.; Boutevin, B.; Ganachaud, F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethanes. *Chem. Rev.* 2013, 113, 80–118. [CrossRef]

36. Liaw, D.-J.; Chen, W.-H. High glass transitions of novel organosoluble polyamide-imides based on noncoplanar and rigid diimide-dicarboxylic acid. *Polym. Degrad. Stab.* 2006, 91, 1731–1739. [CrossRef]

37. Gong, W.; Gu, J.; Ruan, S.; Shen, C. A high-strength electrospun PPEKS fibrous membrane for lithium-ion battery separator. *Polym. Bull.* 2019, 76, 5451–5462. [CrossRef]

38. Venugopal, G.; Moore, J.; Howard, J.; Pendalwar, S. Characterization of microporous separators for lithium-ion batteries. *J. Power Sources* 1999, 77, 34–41. [CrossRef]

39. Ooms, F.G.B.; Kelder, E.M.; Schoonman, J.; Gerrits, N.; Smedinga, J.; Calis, G. Performance of Solupor® separator materials in lithium ion batteries. *J. Power Sources.* 2001, 97–98, 598–601. [CrossRef]

40. Gong, W.; Gu, J.; Ruan, S.; Shen, C. A high-strength electrospun PPEKS fibrous membrane for lithium-ion battery separator. *Polym. Bull.* 2019, 76, 5451–5462. [CrossRef]

41. Li, Y.; Wang, X.; Liang, J.; Wu, K.; Xu, L.; Wang, J. Design of A High Performance Zeolite/Polyimide Composite Separator for Lithium-Ion Batteries. *Polymers* 2020, 12, 764. [CrossRef] [PubMed]

42. Tian, Y.; Lin, C.; Wang, Z.; Jin, J. Polymer of intrinsic microporosity-based macroporous membrane with high thermal stability as a Li-ion battery separator. *RSC Adv.* 2019, 9, 21539–21543. [CrossRef] [PubMed]