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Editorial

Advances in Surface Functionalization of Lithium Battery Separators and Their In-Service Process Damage Behavior

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In recent years, with the rapid development of the lithium battery and energy storage industry, lithium-ion/lithium batteries have received extensive attention and have applications in high-power, portable household and power energy storage. Although the separator does not participate in any electrode reaction, its structure and performance greatly affect the performance of the entire battery in different working conditions, including safety performance, cycle life, capacity retention, energy density, etc. In the working environment of the battery, many of its own properties need to be considered, including electrochemical stability, high-temperature structural stability, mechanical properties, electrolyte wettability, porosity, pore size distribution, ion conductivity, etc.

This Special Issue aims to provide a forum for researchers to share their current research results and to promote further research on the structure and properties of lithium-ion/lithium battery separators, modification methods, and failure behavior analysis, including experimental modeling, theoretical calculations, and interesting mechanical behavior. This Special Issue is a collection of 15 original research articles on new studies.

At present, in order to improve the performance of commercially prepared polyolefin microporous separators prepared by dry or wet processes, inorganic ceramic powders are commonly used in the industry for single-sided or double-sided coatings. However, this inorganic ceramic coating can only meet the needs of conventional batteries. Many researchers have proposed modified process design methods for separators with the following high-performance requirements, including process improvement for high-temperature structure stability, process improvement to enhance electrolyte absorption capacity, and process improvement to ensure a high voltage cycle rate.

Chen et al. [1] proposed that the zeolitic imidazolate framework-67 (ZIF-67) could be employed as a separator via direct coating onto the surface of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ electrodes through a facile blade-coating technique. Compared with the conventionally used polypropylene (PP) separator, the new ZIF-67-based separator features superior electrolyte uptake, higher ionic conductivity and thermal stability. Notably, at a high temperature of 55 °C, the cell with a ZIF-67-based separator exhibits nearly 2 times higher capacity retention than the PP separator. Liu et al. [2] proposed a fiber-supported alumina separator with better flexibility and thermal stability, due to the introduction of a flexible silicon carbide fiber network skeleton. This film has excellent high-temperature stability compared to ordinary polyolefin separators, with a conductivity of 5.12 mS cm^{-1} at 120 °C, three times its room-temperature conductivity. These works improve the stability of the high-temperature structure to a certain extent due to the introduction of the porous skeleton, and further improve the cycle performance of the battery.

Polymer powders can also be used as functional coatings to improve the surface properties of common polyolefin separators. Xu et al. [3] proposed the use of polyvinylidene fluoride (PVDF) powder instead of ceramic particles such as alumina as a functional coating for lithium battery separators. The results show that PVDF powder particles can accumulate and be scattered on the surface of PP membranes, which greatly improves their porosity and allows them to obtain a more uniform pore size distribution. At the same time, due to the strong affinity of PVDF components in polar solvents, it improves the electrolyte absorption rate, reduces the interface resistance, and improves the cycle rate performance. Fu et al. [4] also prepared composite separators by synthesizing silica-poly(cyclotriphosphatenitrile-co-4,40-sulfonyldiphenol) nanoparticles with a core-shell structure, and coating both sides of a polyethylene (PE) microporous membrane with these nanoparticles. Compared to pure SiO_2-coated separators and PE films, they showed higher ionic conductivity, while their discharge capacity at a rate of 8C reached 115 mA h/g. Both of these works used the method of direct coating or modification of inorganic nanoparticles, which not only stabilizes the performance of the high-temperature structure of the separator, but also improves the rate performance of the battery. However, it is worth noting that the choice of dispersant, binder and surfactant should be taken into account when configuring the coating slurry. The choice of these solvents affects the surface uniformity of the separator and water absorption. In the work of Xu et al. [5], β-cyclodextrin is chosen as the binder, and its hydrophilicity is regulated by chemical oxidation, while titanium dioxide (TiO_2) is used as the ceramic component. It was found that the water absorption rate of the coated separator using modified β cyclodextrin was lower than that of commercial aqueous binders, such as PVA. In addition, the Li-ion battery assembled with the coated separator showed better discharge capacity retention. This work provides a new method to modify water-based coated separators with reduced water absorption in the storage stage.

In the research work of Cai et al. [6], a novel PVDF-HFP/PI parallel two-component cross-linked electrospinning separator was prepared. The two-component composite fiber has excellent mechanical strength, thermal dimensional stability (up to 200 °C) and good interfacial structure. At the same time, three-dimensional simulations further confirmed that PVDF-HFP/PI nonwoven materials used as LIB separators are conducive to the uniform transmission of lithium ions. The non-woven fabric obtained using the electrospinning method has a porous structure similar to that of polyolefin battery separators, and functionalized lithium battery separators based on the new material can be developed in the future through electrostatic spinning macroscopic manufacturing.

In recent years, as high-voltage lithium-ion batteries have become a development trend, researchers have also begun to pay attention to the structural design of high-voltage resistant lithium battery separators. Zuo et al. [7] developed a poly (vinylidene fluoride)/ethyl cellulose and amino-functionalized nano-SiO_2 (PVDF-EC-(A-SiO_2)) composite coated with polyethylene (PE). It can be used as a functional separator for 5 V high-voltage lithium-ion batteries. Compared with PE separators, composite membranes have a uniform interconnection structure, in which their contact angle is significantly reduced, and their ionic conductivity is also improved. In particular, the electrochemical window rises to 5.3 V. N. Xue et al. [8] prepared a porous polymer membrane that contained polar B phases by solution casting phase separation, and then swelled and activated in the electrolyte solution to obtain the PVDF-PU composite GPE, which also has a high oxidation limit. Shi et al. [9] studied lithium-ion conductive glass-ceramic $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ and prepared polypropylene-based inorganic–organic back separators. $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ provides a diffusion channel for lithium ions compared to common ceramic powders such as alumina, resulting in the superior C-rate capacity, and cycling capability of the lithium batteries using this separator. The design of the gelatinous flexible coating and the corresponding application of the organic–inorganic-coated separator form part of the modification process of high-voltage cycle batteries.

In order to improve the high-temperature dimensional stability and electrolyte wettability of polyolefin microporous separators, many researchers have studied a variety of inorganic ceramic powders as potential types of coatings on polypropylene microporous separators, but these coatings will be subjected to various compressive stresses during the actual use of the battery, resulting in the peeling and shedding phenomenon, which will affect its cycle stability to a certain extent. Therefore, some researchers have carried out corresponding design studies on gelatinous flexible coatings. Some researchers have also selected cellulose membranes and nonwoven materials instead of polyolefin separators or used electrospinning and other technologies when working with battery separators. The several works mentioned above provide reliable methods for the design of high-temperature-resistant and high-voltage-resistant battery separators.

With the widespread use of lithium batteries, the structural changes, ageing and failure behavior of separators in service have become a new research hotspot, in the industrial and scientific circles, and many excellent reviews and research articles cover related fields, such as microstructure analysis and mechanical modeling of separators, separator failure behavior analysis, and separator modification process design for various high-performance separators. Researchers expect this to provide fundamental research data for the optimization of lithium battery separators.

In the work of Xu et al. [10], a statistical representation and random reconstruction method based on two-dimensional microscopic images was established, and three-dimensional microstructure modeling was realized to predict the mechanical behavior of anisotropic battery separators. The researchers obtained key data on the microstructure of the separator by counting the pore size and shape on the SEM images. In addition, a stochastic reconstruction algorithm was proposed to generate random, but statistically equivalent, three-dimensional microstructure models for mechanical performance analysis and uncertainty quantification. However, this work has certain limitations, as coated and polymer electrolyte films gradually became suitable for commercial use, and the model does not include equivalent standards for polymer phases. In the work of Finegan et al. [11], the microstructure of a battery polymer separator was captured with a phase-contrast X-ray microscope. Through the application of 3D quantification technology and stereoscopic science, the spatial variation in the key structural parameters was determined, and the anisotropy of porosity, bending coefficient and average pore size of various commercial battery separators was revealed. The detailed structural characteristics were then linked to their impact on battery safety and rate capability. This technique can be extended to the changes in separator pore structure at high temperatures and with applied strain, leading to a better understanding of failure mechanisms.

Failure due to ruptures or thermal runaway caused by the breakdown of the separator by lithium dendrites and expansion of the electrodes is a major problem in lithium battery systems. In the work of Sarkar et al. [12], they modeled the mechanical behavior and ionic conductance of a separator membrane under compression and its influence on lithium cell thermal performance. In the simulation experiments, the separator was modelled as an open-cell foam and the relationship between mechanical deformation and ionic conductivity under different compressive loads was compared. The predicted correlation between mechanical deformation and ionic conductivity was compared with experimental reports of membrane performance. Next, the validated model was used to simulate the thermal performance of lithium-ion pouch cells. A design diagram of the maximum battery temperature over the applied load range under different charging rates and cooling conditions was drawn and used to determine the design conditions that led to the melting of the separator and thermal runaway.

In the work of Zhang et al. [13], four types of commonly used battery separators were characterized and their mechanical performance, strength, and failure were compared. This included two dry-processed polyethylene (PE) and tri-layer separators, a wet-processed ceramic-coated separator, and a nonwoven separator. In detail, uniaxial tensile tests were performed along the machine direction (MD), transverse direction (TD) and diagonal direction (DD). In addition to uniaxial tensile tests, four separators were also subjected to compression and bi-directional tensile tests. Comprehensive mechanical tests revealed interesting deformation and failure patterns under extreme mechanical loads. Finally, a finite element model of a PE separator was developed in LSDYNA based on the uniaxial tensile and thickness compression test data. The model succeeded in predicting the response of PE separators under punch tests with different sizes of punch heads.

In the work of Kalnauset al. [14], the anisotropic mechanical properties of three commercial lithium-ion battery separators were measured and compared. A large number of performance anisotropies, in addition to Young's modulus and ultimate strength values between orthogonal directions within the polymer separation layer were determined, and the strain rate strengthening coefficients of the elastic modulus and yield stress were determined. In the research work of Yuan et al. [15], a device that can simulate the environment of the separator in the battery was designed to track the structural evolution of the separator during periodic deformation, so that the polypropylene separator can be cyclically compressed with different electrolytes under different compression strains. The connection between the evolution of separator structures and the restriction of lithium-ion transport was preliminarily established. The failure modes of the above-mentioned work for battery separator failures, as well as the factors considered and the methods used to characterize them, are significantly different, which adds additional variables to the safety design of lithium-ion batteries to prevent internal short circuits.

In the future, as the international energy situation changes and the requirements of green development, new energy devices represented by lithium-ion batteries will play an increasingly important role in the development of society. High-performance lithium battery separator structure design will become an important part of the new energy industry. separator as the weakest device in lithium batteries, its structural damage will directly affect the safety, so the study of structural changes and performance degradation of the separator during service is of great significance to improve battery safety, and related research will help the design and development of high-safety lithium batteries.

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