

Application of Graphene Separator in Different Battery Systems

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Abstract. The rapid development of the new energy industry has raised higher demands on battery safety and energy density. As a physical barrier between the positive and negative electrodes, the diaphragm's performance directly determines the batteries' cyclic lifespan and safety margins. The current commercial diaphragms have obvious deficiencies in thermal stability, electrolyte wettability, and mechanical strength. Graphene, with its two-dimensional layered structure, high mechanical strength, and excellent thermal stability, has become a research hotspot for modified membranes. This article outlines the mechanism of action and application progress of graphene-modified separators in different battery systems. In lithium-ion batteries, a graphene coating can enhance the thermal stability and ion conductivity of the separator, thereby improving the battery's cycling performance and safety. In lithium metal batteries, using heteroatom-doped or surface-functionalized graphene separators can effectively inhibit lithium dendrite growth and improve coulombic efficiency. In lithium-sulfur batteries, the graphene functional layer effectively alleviates capacity degradation caused by the shuttle effect through the synergistic action of physical sieving, chemical adsorption, and catalytic transformation. The article finally points out the main bottlenecks currently faced in this field and the directions for future research.

Keywords: Graphene, Lithium-ion battery, Lithium metal battery, Lithium-sulfur battery, Diaphragm.

1. Introduction

A separator is a physical barrier between the positive and negative electrodes in a battery, avoiding direct contact between them and short circuits caused by lithium dendrite penetration. The widely used polyolefin membranes currently have problems such as insufficient thermal stability, poor electrolyte wettability, and relatively low ionic conductivity. Dendrite penetration is particularly prone to occur in lithium metal batteries [1]. Graphene and graphene oxide (GO) have a single-atom thickness and high mechanical strength and have been widely used in membrane modification research [1].

This article focuses on the research progress of graphene-based membrane modification in different battery systems, sorts out their application strategies and mechanisms in lithium-ion batteries (LIBs), lithium metal batteries (LMBs), and lithium sulfur batteries (LSBs), respectively, analyzes the current technological bottlenecks, and discusses future improvement directions. Intended to provide a scientific basis for the design and application of high-energy density and high-safety batteries.

2. The Mechanism of Graphene Modified Separators in Different Battery Systems

2.1. Application in LIBs

The main function of the LIB separator is to isolate the positive and negative electrodes, prevent internal short circuits of the battery, and ensure the free passage of lithium ions during the charging and discharging processes. The most widely used polypropylene/polyethylene (PP/PE) separator currently has problems such as poor electrolyte infiltration and easy shrinkage when exposed to heat, which can easily cause internal short circuits in batteries. Graphene, with its excellent conductivity,

mechanical strength, and two-dimensional layered structure, has shown great potential in the field of membrane modification, effectively enhancing thermal stability and improving ionic conductivity.

2.1.1. Graphene/polymer composite diaphragm

A composite of graphene and polymer matrix is an effective strategy to enhance the comprehensive performance of membranes. Peter et al. prepared polyvinylidene fluoride/graphene (PVDF/graphene) composite membranes by the solution casting method. Research has found that adding only 0.05 wt% graphene nanosheets increases the beta phase content of PVDF from 52% to 74%. The porosity of the composite membrane has been increased to 38% (26% for pure PVDF), and the ion conductivity has reached 0.34 mS·cm⁻¹, the capacity retention rate of the assembled graphite//PVDF/graphene/LCO full cell after 50 cycles is 88%, much higher than the 38% of pure PVDF separator, and there is almost no thermal shrinkage at 140 °C [2]. The above research indicates that the addition of trace amounts of graphene can regulate the polymer crystalline phase, enhance porosity and surface energy, simultaneously optimizing the electrolyte wettability and ion transport efficiency of the separator, enhancing the cycling stability.

2.1.2. Graphene/inorganic nanoparticle composite diaphragm

Combining graphene with inorganic nanoparticles can synergistically enhance the conductivity of graphene and the mechanical support and thermal stability of inorganic particles. Rodriguez's team designed a boron nitride graphene (BNxGy) bilayer coating modified PP membrane, which utilized the synergistic effect of graphene reducing local current density and boron nitride dissipating local heat, significantly improving the polarization and impedance of the membrane. The Li/LiFePO₄ full battery with BN50Gr50/PP separator achieved 1000 stable charge and discharge cycles at 1C rate, maintaining a specific capacity of 114 mAh g⁻¹ [3]. This work indicates that graphene and boron nitride have different roles in membrane coatings. Graphene is mainly used for uniform current distribution to avoid excessive local current from inducing lithium dendrites. The addition of boron nitride helps to quickly dissipate local heat and prevent thermal shrinkage of diaphragm due to temperature rise. When the two are combined in a 1:1 ratio, the polarization and interface impedance of the battery are significantly improved, further boosting the overall performance of the separator.

2.2. Application in LMBs

LMBs, because of their high theoretical specific capacity (3860 mAh g⁻¹) and lowest reduction potential (-3.04 V vs SHE), are considered a strong candidate for next-generation high-energy-density storage systems. However, lithium metal negative electrodes are prone to forming lithium dendrites during cycling, leading to a decrease in coulombic efficiency (CE), shortened cycle life, and even causing safety hazards such as membrane puncture and battery short circuits. Unlike LIBs, the core requirement for separators in LMBs is to regulate the distribution of lithium -ion flux, induce uniform lithium deposition, and suppress dendrite growth. Graphene and its derivatives exhibit unique advantages in the design of functional separators for LMBs due to their excellent mechanical strength, two-dimensional layered structure, and adjustable lithium affinity.

2.2.1. Doping of heteroatoms to regulate lithium nucleation behavior

Regulating the affinity of graphene-coated separators for lithium through heteroatom doping engineering is an important strategy for optimizing the cycling reversibility of lithium metal negative electrodes. Son et al. systematically compared the effects of nitrogen (N) doping and boron (B) doping on the lithium nucleation behavior of graphene-coated membranes [4]. Research has found that N-G coatings show lower lithium nucleation overpotentials, while B-G coatings have better cyclic reversibility. The atomic simulation results indicate that the adsorption strength of lithium by lithium functional groups is a key factor affecting reversibility - moderate adsorption (B-based sites) is more conducive to improving cycling stability than strong adsorption (N-based sites) [4]. The Li | Cu battery using B-G coated separators exhibits higher average CE and superior cycling performance, with CE remaining above 98% after 150 cycles [4]. Therefore, it can be seen that the stronger the

lithium affinity of heteroatom doping, the better. Moderate adsorption strength (such as B doping) is more conducive to improving the cyclic reversibility of lithium metal negative electrodes.

2.2.2. Surface functionalization improves interface stability

Surface functionalization is an effective means to improve the compatibility between graphene membranes and electrolyte interfaces. Kwon et al. deposited two different functional graphene layers on the surface of membranes to prepare surface functional graphene membranes (SFGS) [5]. The membrane significantly improves the wettability of the electrolyte by introducing polar functional groups, which helps to increase Ionic conductivity and form a uniform lithium ion flux distribution [5]. The Li | Cu battery using SFGS achieved a high CE of 98% after 200 cycles, while the unmodified separator battery decreased to below 85% after 100 cycles, confirming the effectiveness of surface functionalization strategies in improving the electrochemical reversibility of lithium metal anodes [5]. This indicates that regulating the interface properties between the separator and electrolyte through surface functionalization modification is a feasible way to improve the cycling stability of lithium metal batteries.

2.2.3. Coating configuration optimization induces uniform lithium deposition

The spatial configuration of graphene coating on the membrane surface has a significant impact on lithium deposition behavior. Park et al. prepared graphene-enhanced membranes (GES) by modifying the surface of PP membranes with graphene coatings and systematically revealed the key regulatory mechanism of graphene coating configuration on lithium deposition behavior [6]. Research has found that GES can induce the formation of a dense lithium layer between graphene layers and copper current collectors, guiding lithium dendrites to grow from the membrane to the anode and effectively reducing the risk of membrane puncture [6]. The CE of Li | Cu batteries using GES reaches~99% at a high current density of 4 mA cm², which is significantly better than unmodified membrane batteries (about 90%) [6]. This study indicates that the spatial configuration of graphene coatings has a decisive impact on the direction of lithium deposition. By optimizing the spatial configuration of graphene coatings, the growth direction of lithium dendrites can be changed to move away from the separator and towards the current collector, thereby reducing the risk of separator puncture and improving the safety of batteries.

2.2.4. Lithium oxide graphene composite membrane inhibits the shuttle effect

By utilizing the electrostatic interaction between charged groups in lithiated polymers and lithiated graphene oxide (Li-GO), Redox molecules that shuttle between the positive and negative electrodes can be effectively suppressed, while ensuring excellent lithium ion conductivity of the membrane. Liang et al. obtained a composite membrane of lithium polystyrene sulfonate and Li-GO [7]. This separator exhibits excellent cycling stability in lithium metal batteries, providing new research ideas for lithium metal negative electrode protection [7]. Therefore, lithiation modification makes the membrane skeleton negatively charged, inhibits the shuttle of anionic redox molecules through electrostatic repulsion, and ensures the rapid transport of lithium ions, providing a new direction for functional membrane design based on the "ion selective permeation" mechanism.

2.3. Application in LSBs

LSBs have a high theoretical energy density (2600 Wh kg⁻¹), and sulfur cathodes are low cost, so they are considered one of the most promising next-generation energy storage systems. However, the commercialization process of LSBs is constrained by two core issues. One is the "shuttle effect"(SE) of intermediate product lithium polysulfides (LiPSs), which allows soluble polysulfides to diffuse through the separator to the lithium negative electrode side, resulting in loss of active material and rapid capacity decay. The second issue is the dendrite growth on the lithium negative electrode side. The modification strategy of graphene-based membranes can effectively inhibit the shuttle of polysulfides through multiple mechanisms, such as physical barrier, chemical adsorption, and catalytic conversion, while improving interfacial stability.

2.3.1. Size-selective screening of nanoporous graphene

The use of graphene's nanoporous structure to achieve size-selective separation of polysulfides and lithium ions is a direct strategy to suppress shuttle effects. Researchers have prepared nanoporous atomic-scale thin graphene films (NATMs) with pore sizes ranging from 0.7 to 1.0 nm and coated them on the surface of PP membranes [8]. This aperture design cleverly utilizes the size difference between lithium ions and polysulfide anions: lithium ions can freely pass through, while larger polysulfides are effectively blocked [8]. adopt NATM@PP The lithium sulfur battery with a separator showed almost no capacity loss in 150 cycles, fully demonstrating the effectiveness of the size-selective molecular sieving strategy [8].

2.3.2. Quantum dot/graphene composite functionalized membrane

By combining transition metal carbide quantum dots with graphene, efficient adsorption and catalytic conversion of polysulfides can be achieved. Yu et al. designed a Mo₂C quantum dot @ graphene functionalized membrane, which significantly suppressed the shuttle effect due to the strong chemical adsorption and catalytic conversion ability of Mo₂C quantum dots towards polysulfides, as well as the high conductivity of graphene [9]. The use of this separator in lithium sulfur batteries has achieved stable cycling at high current densities, providing new ideas for the functional design of lithium sulfur battery separators [9]. Therefore, the composite of Mo₂C quantum dots and graphene achieves an integrated synergy of "adsorption catalysis conduction" for polysulfides, significantly improving the cycling stability of lithium sulfur batteries.

2.3.3. Dual-function asymmetric diaphragm design

Researchers have proposed a dual-function asymmetric separator design strategy to address the challenges of positive electrode SE and negative electrode lithium dendrite coexistence in LSBs. Chen et al. developed a nitrogen doped reduced graphene oxide (N-rGO) and cellulose fiber (CF) dual coated asymmetric PP membrane: the N-rGO coating on the positive electrode side achieves physical/chemical dual adsorption of polysulfides and catalyzes their redox reaction kinetics through a porous structure and nitrogen doped active sites; the CF coating on the negative electrode side is rich in hydroxyl and carboxyl functional groups, which can reduce the overpotential of lithium nucleation, promote the uniform deposition of metallic lithium, and effectively inhibit the growth of lithium dendrites [10]. Adopt N-rGO@PP @The initial specific capacity of the CF diaphragm lithium sulfur battery reaches 1294 mAh g⁻¹ at a 1C rate, and the average capacity decay rate after 500 cycles is only 0.076% per cycle [10]. This work demonstrates that dual-function asymmetric separators can simultaneously inhibit polysulfide shuttle and lithium dendrite growth by setting functional coatings on the positive and negative electrode sides.

3. Challenges and Prospects

3.1. Current Limitations

The preparation of graphene-modified membranes currently mainly relies on methods such as scraping, vacuum filtration, or spin coating, which pose difficulties when scaled up to roll-to-roll continuous production. The reduction degree and batch stability of graphene oxide also fluctuate greatly, and the performance of membranes prepared from different batches often varies. Hossain et al. believe that the transition from laboratory coating to industrial-grade roll-to-roll processes is currently the main bottleneck facing industrialization [11]. The choice of coating thickness is also a dilemma. Increasing the thickness of the graphene coating is beneficial for improving mechanical strength and barrier ability, but at the same time, it will prolong the transmission path of lithium ions, leading to a decrease in ion conductivity. If the coating is thinned, it may weaken the inhibitory effect on dendrites and polysulfides. Gribble et al. attempted to avoid this contradiction by using atomically thin layers of nanoporous graphene films, but it is still not easy to maintain uniform pore channels under large-area preparation conditions. The research on long-term cycling stability is also

insufficient [8]. Most existing literature only achieves 500 cycles, and the testing conditions are biased towards idealization. There is currently a lack of systematic answers to the questions of whether the structure of graphene coatings will change after hundreds of cycles and whether the bonding between graphene coatings and substrate membranes is firm.

3.2. Future Development Direction

Continuous preparation technologies, such as roll-to-roll coating and spray printing, are the key research directions for the future. Hossain et al. suggested establishing a structure-activity relationship between materials, structures, and properties, and combining it with machine learning-assisted process optimization [11]. Using data-driven methods to predict the optimal membrane preparation parameters, it can accelerate process development and reduce costs. Density functional theory (DFT) calculations and finite element simulations can predict key performance parameters of graphene membranes before experiments. Gribble et al.'s research shows that theoretical simulations can effectively predict the relationship between the size of nanopores and ion sieving ability, which helps to reduce experimental trial and error costs [8]. Future research should conduct performance validation under conditions closer to practical applications, including high surface capacity ($>4 \text{ mAh cm}^{-2}$), low electrolyte usage ($\text{E/S ratio} < 3 \text{ } \mu\text{L mg}^{-1}$), and compatibility with high-voltage cathodes. Only by verifying the effectiveness of the diaphragm under harsh conditions can reliable evidence be provided for its commercialization.

4. Conclusion

Graphene-modified separators can improve electrochemical performance in LIBs, LMBs, and LSBs, but there are significant differences in the mechanisms of action among the three systems. In LIBs, polyolefin separators modified with graphene coating significantly reduce the contact angle of the electrolyte, effectively suppress thermal shrinkage, and improve the cycling stability and safety performance. In LMBs, graphene separators doped with heteroatoms or surface functionalized can regulate the nucleation overpotential of lithium ions, induce uniform deposition of metallic lithium on the negative electrode surface, thereby reducing dendrite growth and improving CE. The essence of this effect is that the functional groups on the graphene surface change the distribution of lithium ions at the separator/negative electrode interface, avoiding the risk of dendrite puncture caused by high local current density. In LSBs, the graphene functional layer limits soluble polysulfides to the positive electrode region through multiple synergistic effects of pore size screening, polar adsorption, and catalytic conversion, alleviating capacity degradation caused by shuttle effects. Among them, polar adsorption mainly relies on the chemical bonding between graphene oxygen-containing functional groups and polysulfides, while catalytic conversion accelerates the redox kinetics of polysulfides and reduces irreversible loss of active substances.

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