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High temperature stable Li-ion battery separators based on polyetherimides with improved electrolyte compatibility

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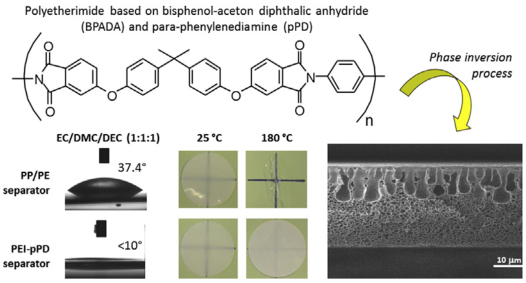
HIGHLIGHTS

- Li-ion battery separators based on electrolyte-compatible polyetherimides.
- Non-solvent induced phase inversion process to produce 15–25 µm thick separators.
- Such separators showing high dimensional stability (>200 °C) and fast wetting.
- Separator resistance can be tuned over broad range by process conditions.
- Graphite/NMC pouch cells show >89% capacity retention after 1000 1C/2C cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

We report (electro-)chemically stable, high temperature resistant and fast wetting Li-ion battery separators produced through a phase inversion process using novel polyetherimides (PEI) based on bisphenol-aceton diphthalic anhydride (BPADA) and *para*-phenylenediamine (pPD). In contrast to previous studies using PEI based on BPADA and *meta*-phenylenediamine (mPD), the separators reported herein show limited swelling in electrolytes and do not require fillers to render sufficient mechanical strength and ionic conductivity. In this work, the produced 15–25 µm thick PEI-pPD separators show excellent electrolyte compatibility, proven by low degrees of swelling in electrolyte solvents, low contact angles, fast electrolyte wicking and high electrolyte uptake. The separators cover a tunable range of morphologies and properties, leading to a wide range of ionic conductivities as studied by Electrochemical Impedance Spectroscopy (EIS). Dynamic Mechanical Analysis (DMA) demonstrated dimensional stability up to 220 °C. Finally, single layer graphite/lithium nickel manganese cobalt oxide (NMC) pouch cells were assembled using this novel PEI-pPD separator, showing an excellent capacity retention of 89.3% after 1000 1C/2C cycles, with a mean Coulombic efficiency of 99.77% and limited resistance build-up. We conclude that PEI-pPD is a promising new material candidate for high performance separators.

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1. Introduction

Li-ion batteries are widely adopted due to their favourable combination of energy density, power density, cost, safety and lifetime, where each of these performance characteristics can be tuned by selecting from a wide range of active material chemistries, electrolytes, separators, additives and cell geometries [1,2]. One of the most critically important cell components to ensure safety is the separator, since its role is to physically separate the anode from cathode, preventing electrical short-circuiting. The porous separator is therefore required to be an electrical insulator, yet permit ion conduction within its porous network. While the probability of a Li-ion battery catching fire is low, thermal runaway has led to many public examples of cells that have either caught fire or exploded, including those found in laptops, phones, electric vehicles and even airliners [3,4]. Although the mechanisms involved in thermal runaway are not fully understood, its onset may arise due to extreme events such as overcharging, internal or external short-circuits, or exposure to excessive temperature. The consequential temperature increase leads to breakdown of the solid-electrolyte interphase [5], resulting in exothermic reactions between the electrolyte and intercalated lithium [6]. At temperatures exceeding ~100 °C, the separator loses its mechanical integrity and melts (~130 °C), allowing internal short circuits to develop. If the cell temperature continues to rise, the cathode eventually breaks down in a rapid, exothermic event releasing oxygen, which may lead to a fire or explosion of the cell.

Most commercial separators are based on polyethylene (PE) and/or polypropylene (PP) and are made through a so-called dry process, where porosity is induced by (uniaxial) stretching and controlled crystallization of melt-extruded films [7,8]. Although dry-processed separators typically have high mechanical strength and a tortuous network of sub-micron pores, the stretching process intrinsically leads to anisotropic morphologies with residual stresses in the material. PE and PP have relatively low melting temperatures (T_m) of ~130 and ~160 °C, respectively, and softening typically sets in well before reaching T_m. The combination of low T_m and residual stresses may lead to significant separator deformation starting at temperatures as low as 120 °C for PP and 105 °C for PE-based separators, which imposes a significant safety risk [9]. Therefore, separators with a high temperature melt integrity (HTMI) are desirable, with minimal shrinkage or loss of mechanical integrity at temperatures exceeding 150 °C [10].

Recent efforts to overcome the lack of HTMI of polyolefin separators can be divided into two classes, namely non-woven fabrics and inorganic composite membranes [7,8]. Non-woven fabrics based on melt or solution-bond fibers based on natural and synthetic polymers have been widely studied. At the targeted separator thickness of $\leq$25 μm [7,10], however, such non-woven fabrics generally suffer from excessively large pore sizes (>1 μm), which is insufficient to ensure adequate electrode separation. The use of ultra-fine nanofibers can reduce the pore size to <1 μm, but such nanofibers are challenging to produce at commercially relevant throughput and quality. Inorganic composite membranes formed by introducing ceramic particles into the bulk of the membrane generally provide improved thermal stability and faster electrolyte wetting [8,11], however, the high concentration of inorganic particles deteriorates the mechanical strength and increases the basis weight, which can reduce the cell's overall energy density [7]. Potential risks with ceramic-coated separators are particle shedding due to insufficient binding, and the relatively low thermal transition temperature of the used binders. In addition, a secondary processing step is needed to apply the ceramic coating, adding complexity and cost.

Fast electrolyte wetting of the separator is required to facilitate cell filling and ensure electrolyte retention during cycling. The wettability of polyolefin separators is inherently poor due to the mismatch in polarity between polyolefins and polar carbonate solvents used in electrolyte solutions. Consequently, a period of 12–24 h under vacuum is typically required to achieve sufficient pore wetting during cell filling, which may still leave a substantial fraction of the smallest pores unwetted [12]. Since long wetting times extend the duration of cell assembly, and hence increase cost, replacing polyolefins with polar constituents may bring considerable advantage to the cell manufacturing process. In addition, should the replacement polymer also afford high temperature stability, separators based on such polymers may be attractive in terms of both safety and cost. While the application of thin ceramic coatings may enhance both the separator melt integrity and improve electrolyte wetting, the core of the separator is still based on an apolar polyolefin, hence the improved electrolyte wetting might be concentrated at the surface coating primarily.

In addition to the aforementioned dry-stretching and non-woven approaches, battery separators may be prepared through phase inversion [7,13–15]. Phase inversion is advantageous over dry-stretching methods, since the desired porosity is attained without the need for stretching, which results in minimal residual stress in the separator. In contrast to non-woven, fiber-based approaches, the phase inversion technique is also able to produce membranes having very fine pore structures that can be controlled by the tuning the respective process parameters. Phase inversion methods have widely been used to produce porous structures for a broad range of applications, where phase inversion can be induced by temperature, a non-solvent and/or a chemical reaction [16–20]. Non-solvent induced phase inversion typically consists of (1) dissolving the polymer in a good solvent, (2) casting a wet film of the polymer solution onto a substrate and (3) forming the porous membrane by immersing the wet film into a coagulation bath containing a non-solvent to the polymer. The solvent/non-solvent exchange drives the polymer solution into a thermodynamically metastable or unstable state, which results in phase separation of the polymer out of solution and the formation of the porous membrane. The application of phase inversion processes to the production of membranes for filtration, reverse osmosis and distillation applications has led to a thorough understanding of how process conditions may be tuned to control membrane structure and properties [21].

Usually, such membranes have an asymmetric pore structure, with a top surface comprising of small pores, a sponge-like inner structure, and a bottom surface with larger pores. The presence of a dense skin layer at either the top or the bottom surface may restrict electrolyte absorption and ion conduction through the membrane. To improve electrolyte wetting and ion conduction, the phase inversion approach has primarily been used to produce separators based on electrochemically stable polymers that swell significantly in the liquid electrolytes, such as polyvinylidene fluoride (PVdF) [22–24], polyacrylonitrile (PAN) [25] and polyetherimide (PEI) [26,27]. However, such membranes may be more accurately classified as porous gel electrolytes rather than true battery separators. Without the addition of a ceramic filler [26,28,29] and/or incorporation of specific co-monomers [29,30] and/or combining multiple polymers in a blend [14], such membranes typically have low ionic conductivities and insufficient mechanical stiffness, strength and dimensional stability, specifically in their swollen state [31]. The PEI used in such studies has always been based on bisphenol-aceton diphthalic anhydride (BPADA) and *meta*-phenylenediamine (mPD). This work presents the physical properties and electrochemical performance of battery separators made through a modified phase inversion process using a high glass transition temperature PEI (T_g 225 °C) having improved compatibility with