Novel Separator Materials for Lithium-Ion Batteries

Authors: David Hu, Sangyoon Shim, Mengjia Zhao

Summary

In the past few decades, Lithium-ion batterys (LIBs) have become an important power supply in portable electronic devices, electric vehicles, green grid energy storage, and other fields. These new technologies put forward higher requirements for the comprehensive performance and safety of LIBs, such as high current, high-rate discharge, long-time stable output, low thickness, high heat resistance, and low thermal shrinkage at high temperature. The battery separator is a porous, thin membrane soaked in the electrolyte to prevent the short circuit caused by the direct contact between the cathode and the anode. As the migration channel for lithium ions, it allows lithium ions in the electrolyte to pass freely during charging and discharging. It is closely related to the safety performance, cycle life, and lithium ion release rate of the battery.

Unfortunately, the traditional polyolefin membrane can no longer meet these requirements of new applications. Therefore, the development of a membrane that can meet the requirements of high-performance lithium-ion batteries has become an urgent demand in the lithium battery industry. This report's objective aims to develop internal safe separators to achieve flame retardant behavior, dimension stability, and interface compatibility.

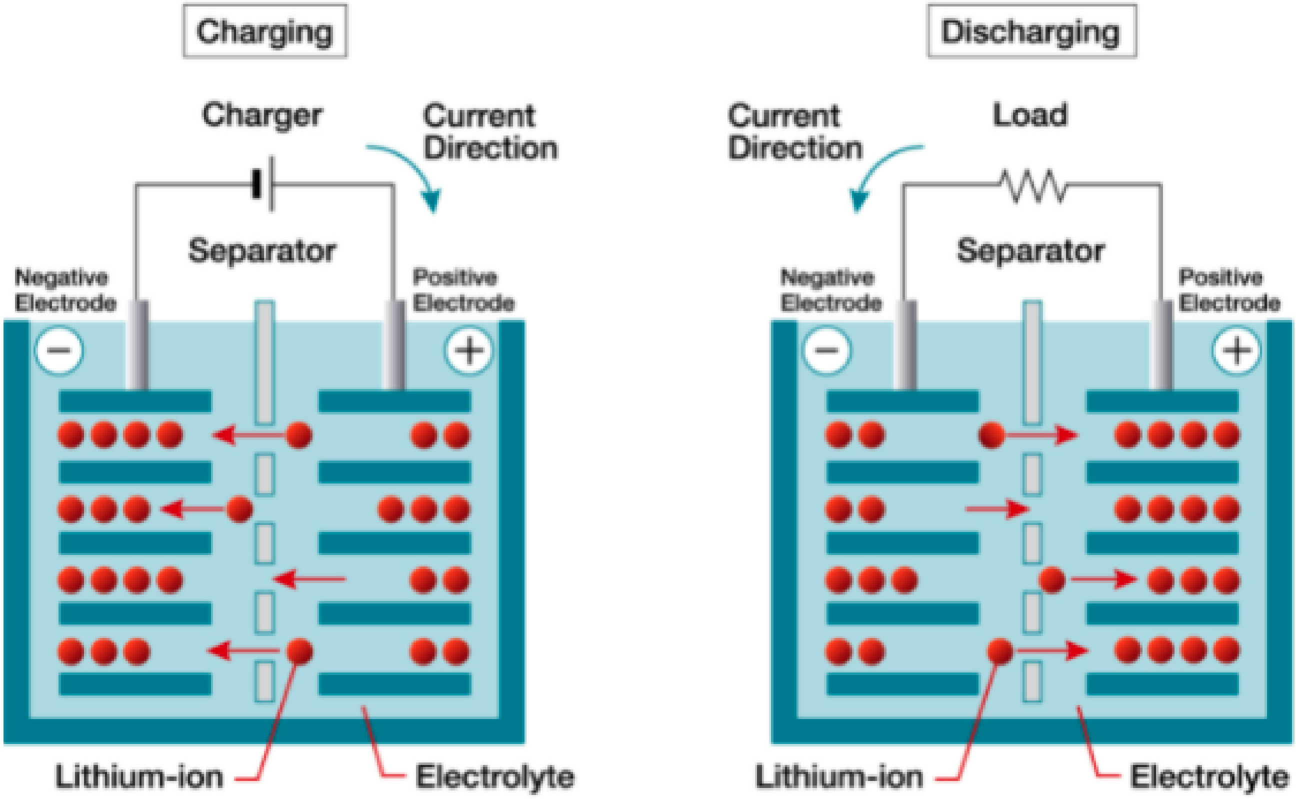


Figure 1: Structure of a Battery - Emphasizing Battery Separator Function

A good LIB separator should have good ionic conductivity, thermal stability, interface stability, and cycle performance, to meet the requirements of battery performance and safety. There are some additional parameters that are normally used to quantitative describe properties and morphologies of battery separators, and these will be discussed firstly here.

1) Porosity (P)

Porosity is a parameter which affects several properties of interest, such as ionic conductivity, and is thereby desirable. Porosity can be identified through a variety of means including pycnometry and the equation $Porosity = \frac{W_w - W_d}{\rho V}$, where W_w and W_d are the weights of wet and dry separator, and rho and V are the density of the formula unit and separator volume. [1]

2) Tortuosity(t)

Tortuosity is a property of a curve being tortuous (i.e. being twisted, having many turns). It is defined as the ratio of the lengths, L_t and L, of the preferential tortuous fluid pathways and the porous media: t= $\frac{L_t}{L}$

3) Electrolyte uptake (EU)

EU is measured as $\frac{(W_1 - W_0)}{W_0}$, for W_0 being the pristine separator weight and W_1 being the separator weight after being soaked in electrolyte for 1 hr [1].

4) Ionic conductivity (k)

Ionic conductivity will show the film's electrochemical impedance, and controls waste heat and power capability, and is related to the conductivity of the separator. It can be measured using typical impedance measurements and higher conductivity is desired [2].

System Design Chart

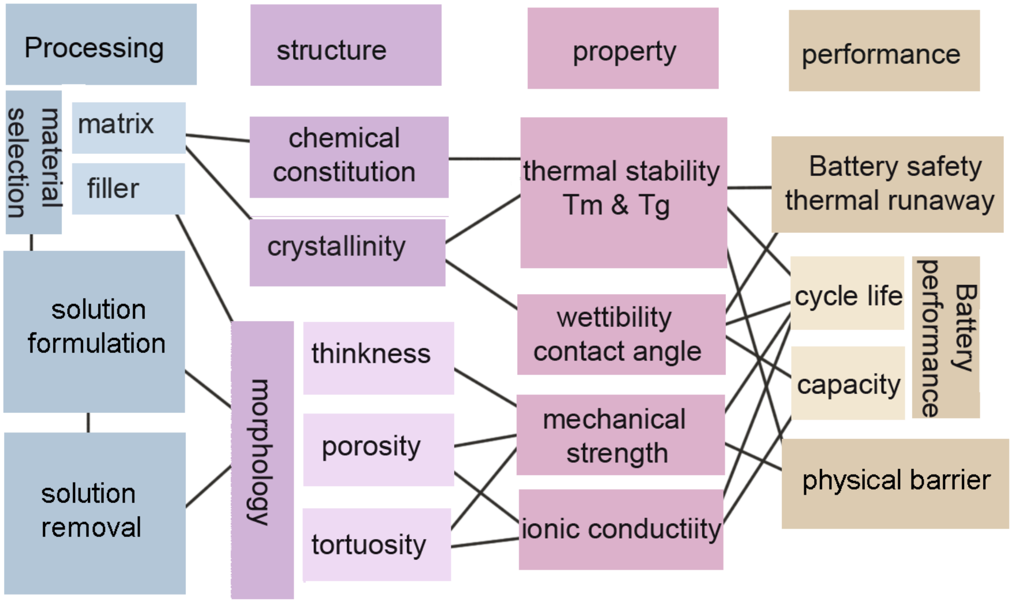


Figure 2: The system design chart used by our group to identify features of interest for our material.

Generally, the capacity, energy density, and cycle life of the battery are mainly determined by the electrode material, and the safety of the battery is determined by the electrolyte and separator. Here, we'd like to explain our design chart in terms of security and performance separately.

With the continuous expansion of its application direction, the safety problems that may be caused by its thermal runaway have also been highlighted. When improperly operated, the chemical energy stored in LIBs is suddenly released as thermal energy, which can cause fires or explosions and pose safety problems for individuals and public health. A common cause of battery combustion is due to the large internal ion current caused by an internal or external short circuit passes through the battery, causing uncontrolled electrochemical reactions between the cathode and anode. In the thermal runaway process, as the temperature approaches the melting point of the separator, its size shrinks, resulting in direct contact between the positive and negative poles, allowing for direct electronic transfer and thus short-circuiting the battery. The large amount of heat generated by the current can cause a series of exothermic side reactions between electrodes and liquid electrolytes, causing the temperature to increase, and opening the "positive feedback loop" which is out of control.

From this process, we can reason that, if the membrane can be designed to have a higher melting point, T_m, and better mechanical properties, it can fundamentally limit the opening of the thermal runaway positive cycle and effectively improve the safety of the battery. In order to have higher T_m, we can choose polymers with high crystallinity with less 'soft' chemical constitutions, and using inorganic fillers like SiO_2.

Considering that the battery cycle will make the separator bear the compressive stress and heat caused by the volume expansion of active materials and electrodes, the battery separator with higher mechanical strength, thermal stability, and more stable highly ordered nano-porous structure will undoubtedly have better cycle performance and higher capacity under high discharge rate. More specifically, the reduction of battery capacity (due to repeated or rapid charging and discharging) is related to the transmission behavior of lithium ions in the separator. Due to the influence of pressure and heat in the charging and discharging process, the morphology of the separator will be damaged gradually, resulting in the reduction of ionic conductivity, which will ultimately have an irreversible impact on battery performance.

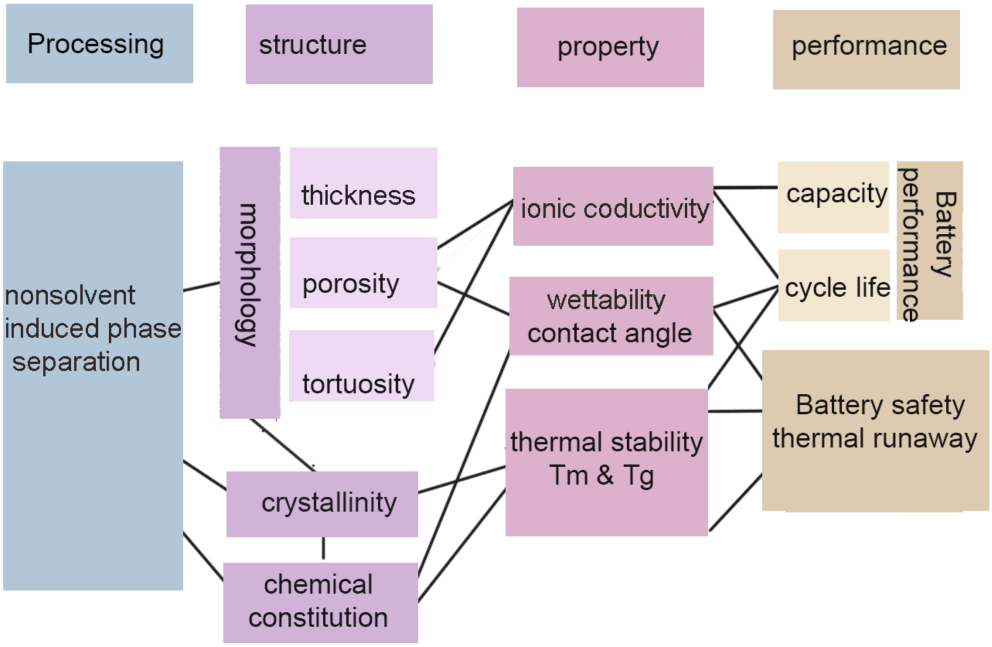


Figure 3: A sub-chart of the SDC which contains specific features of interest to our separator film design.

By deducing the properties of interest from the performance of the membrane, we confirmed that a porous film assisted with the inclusion of an inorganic filler using a polymer material with high melting temperature would be an ideal separator. Considering that the filler needs to be fully mixed with the polymer to ensure its uniform distribution in the whole matrix and that we are interested in examining methods with the potential of being scaled up to commercial application of our battery separator diaphragm design, we are convinced that the use of a phase-separation method, non-solvent induced phase separation (NIPS), as the processing method for our design is the most suitable choice since NIPS - a method involving the formation of two phases through an exchange of the solvent from the polymer solution through a non-solvent from a precipitation bath - can effectively control the pore size and other surface characteristics of the membranes with the help of additives and allow for our filler to be mixed perfectly with the help of solvent.

Materials Selection

CES/Granta EduPack offers a materials database and tools for identifying and filtering out materials of interest. Given a property of interest, it allows for a user to remove materials that fall outside of a desired range such that one can narrow down the potential materials of interest for their application. For our separator material, we use the property targets commonly seen for commercial PP separators listed in Table 1 to help us find suitable material candidates [2].

Property	Minimum	Maximum	Units
Tensile Strength	98.06	—	MPa
Porosity	40	60	Percent
Pore Size	—	1	μm
T_m	150	—	^oC
Thermal Shrinkage	5	—	Percent
Electrolyte Uptake	75	—	Percent
Ionic Conductivity	0.001	—	S/cm

Table 1: Desirable ranges for properties that are desired and measured in battery separators

Not all properties present in the table are capable of being applied into the EduPack software, however: the software is limited in capability to purely intrinsic properties of each material that do not vary as a function of other species, and as such diffusivity, ionic conductivity, and electrolyte uptake were not available data points. Similarly, some properties that were processing-dependent such as porosity, puncture strength, mixed penetration strength were similarly not able to be directly measured through the EduPack database. This left our group with a small range of properties that were able to be parameterized for use in EduPack, consisting of the tensile strength (which needs to be at least 98.06 MPa to pass battery separator standards), a melting point of at least 150C, and a thermal expansion/thermal shrinkage of 5 percent at 90C. Out of these limitations, we were then able to return 281 viable materials.

Explicitly, a limit was applied restricting:

- Tensile Strength greater than 98.06 MPa
- Melting Points between 150 and 450 ^{o}C
- Thermal expansion coefficient of a maximum of 555 μstrain/^oC

This allowed for filtering of 281 acceptable materials, which could then be plotted for Toughness versus Melting Point and Cost respectively.

While not a property we directly are observing, the fracture strength of the material has a positive correlation with the mixed penetration and puncture strengths of the separator, and as a result we seek materials of higher fracture strength if possible, and similarly desire materials of lower cost. This results in the formation of Figure 4, in which these two are the metrics in the Ashby plot that we use to examine the materials. Figure 4 changes the price axis for a melting point, in order to further visualize the melting points of the materials. A limitation to solely using EduPack to finalize the materials we plan on using is that the materials selection software is blind to many of the additional properties that we require for our separator material, and as such, it can only act as a complement to semi-holistically selecting materials based on current materials being used in separator materials.

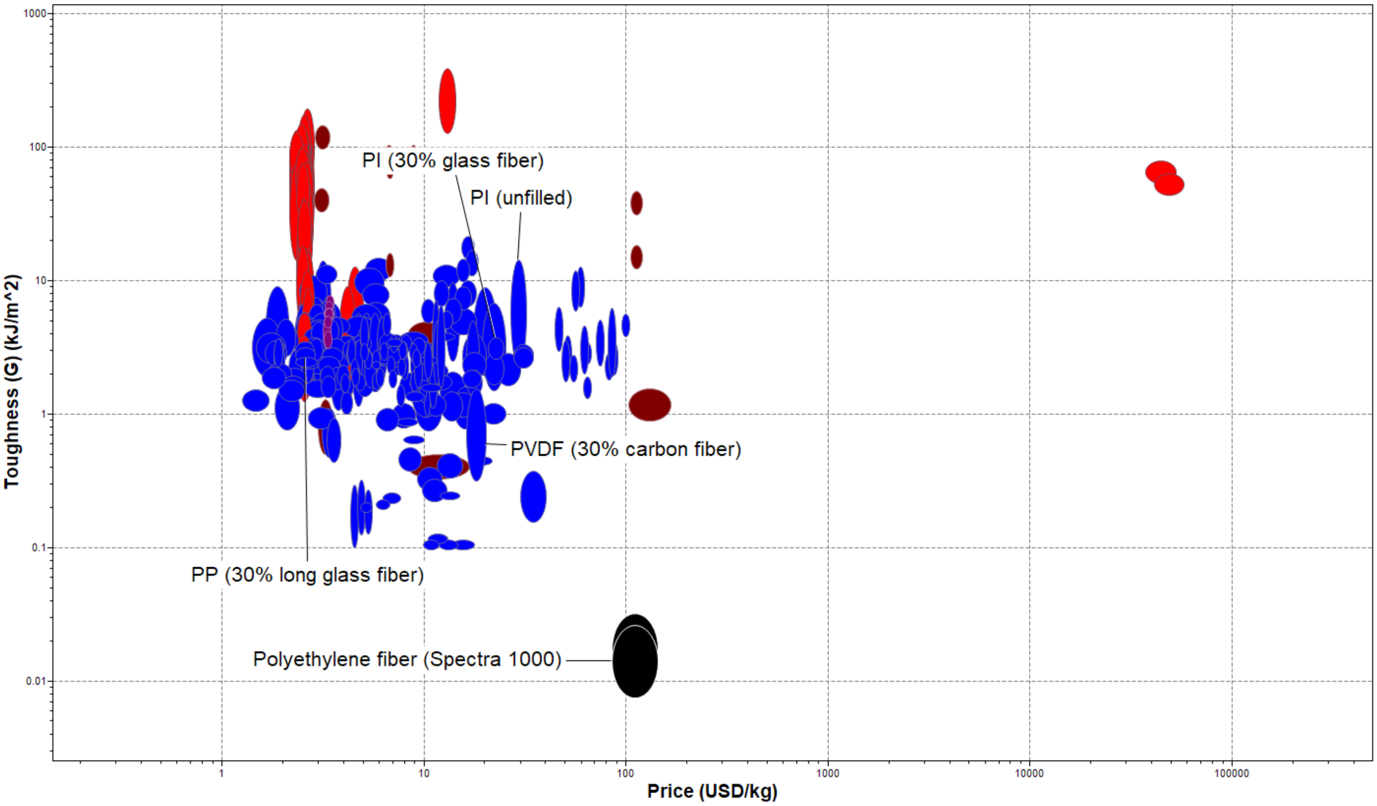


Figure 4: Plot of various materials with desirable properties as a function of Toughness versus Cost

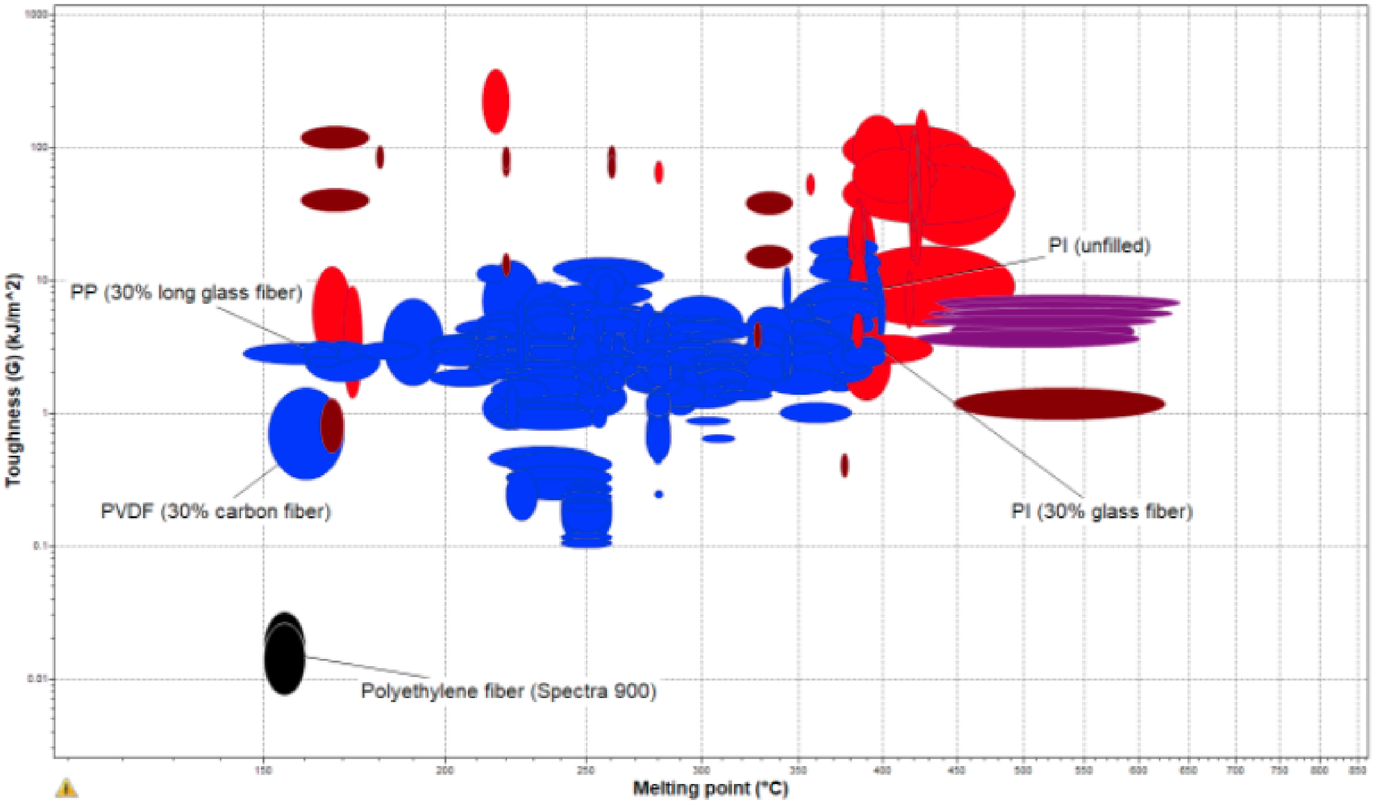
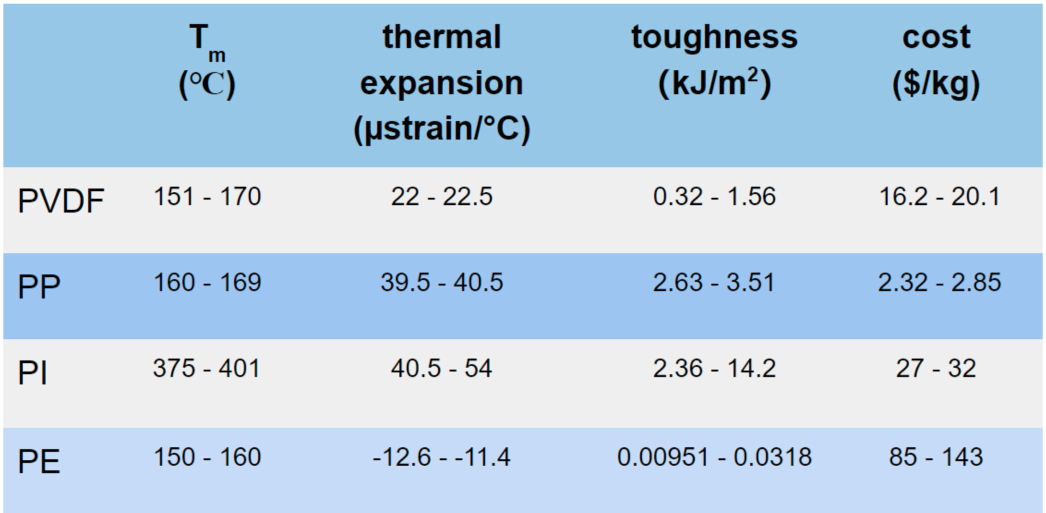


Figure 5: Plot of various materials with desirable properties as a function of Toughness versus melting Temperature

Based on the material options given by the software as well as literature searching, the four most optimal polymer options, polyvinylidene fluoride (PVDF), polypropylene (PP), polyimmides (PI), and polyethylene (PE), are shown in the table of Figure 6. From the values, we can identify PP and PI as the two polymers of greatest interest, but PI shows far greater promise with regards to our design, as the significant improvement in melting temperature will correspond to an enhanced thermal stability and protection against the risk of thermal runaway.



	T_m (°C)	thermal expansion (µstrain/°C)	toughness (kJ/m^2)	cost ($/kg)
PVDF	151 - 170	22 - 22.5	0.32 - 1.56	16.2 - 20.1
PP	160 - 169	39.5 - 40.5	2.63 - 3.51	2.32 - 2.85
PI	375 - 401	40.5 - 54	2.36 - 14.2	27 - 32
PE	150 - 160	-12.6 - -11.4	0.00951 - 0.0318	85 - 143

Figure 6: Selected values of some properties for four polymers of interest

The selection of fillers incorporated into the PI membrane was chosen similarly through selection and literature. Many studies have shown that the SiO_2 nanofillers display excellent mechanical properties and heat tolerance, suggesting dimensional flexibility and good thermal stability. Yang et al. synthesized a SiO_2/Al_2O_3-coated electrospun polyimide fibrous separator with a major decrease in interfacial resistance and contact angle for wettability enhancements due to the addition of $Si - O_2$ [3].

Design Strategy

Requirements of Membrane Shape Design Based on Ionic Conductivity

The main characteristics of lithium ion battery separator that we will examine are thickness, permeability, porosity and pore size, wettability of liquid electrolyte, and mechanical and dimensional stability. For a correct description of the performance of the separator, it is necessary to consider the morphological parameters of the separator, such as porosity, pore diameter, curvature and thickness. Miranda et al. used finite element analysis simulations, considering the governing equation and boundary condition equation of the separator and electrolyte as table x show, which include all variables corresponding to the diffusion of lithium ions in the active material, the kinetics of the heterogeneous reaction at the electrode / electrolyte interface, open circuit voltage and mass transfer flux, to quantitatively evaluate the effect of diaphragm size, porosity and tortuosity on optimizing its performance in lithium-ion batteries with the same electrode (anode and cathode) and electrolyte independent solutions. [4] Through their calculation, we know that ionic conductivity of the polymer separator can be expressed as $\kappa_f = \kappa_l \epsilon_s^p$, where κ_f is the effective ionic conductivity of the polymer separator, κ_l is the ionic conductivity of electrolyte, ϵ_s is the porosity of the diaphragm and p is the Brugman index. An important parameter affecting the performance of battery separator is bending(τ), And the following relationship is usually established:

$$\kappa_f = \kappa_l \frac{\epsilon_s}{\tau^2}.$$

According to their model, we know that high porosity helps the battery to have greater capacity in rapid charge and discharge rates. In order to ensure that the battery performance does not decline rapidly even at high discharge rate, the porosity should be restricted to being more than 50%, below which we see a greater decrease in ionic conductivity with respect to porosity.

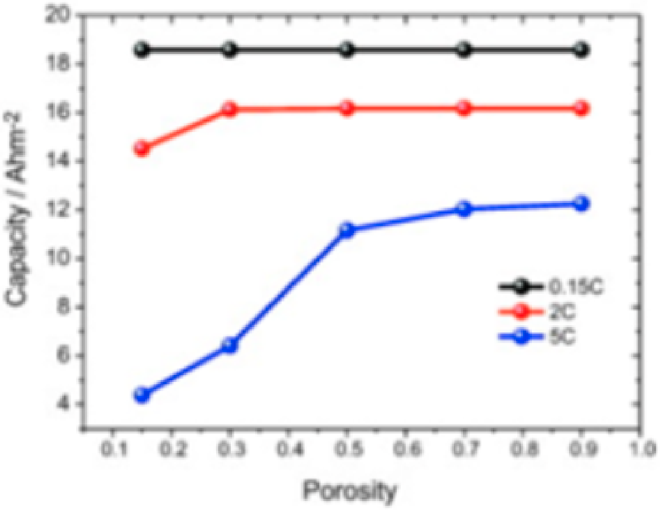


Figure 7: Capacity versus Porosity plots at different values of C.

At the same time, the tortuosity also has a great impact on the battery capacity.

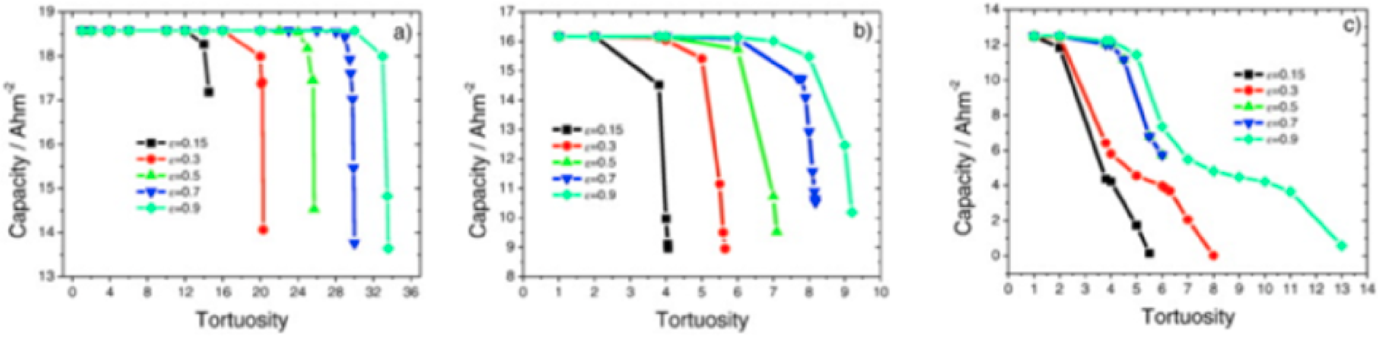


Figure 8: Plots of capacity versus tortuosity for low (left), intermediate (middle) and high (right) scan rates, with varying parameter.

The above three figures show the capacity changes of separator separators with different tortuosity under low, medium and high scan rates. Based on the performance requirements of commercial lithium batteries on the market, we can know that the designed diaphragm should ensure that the tortuosity is not greater than 4.

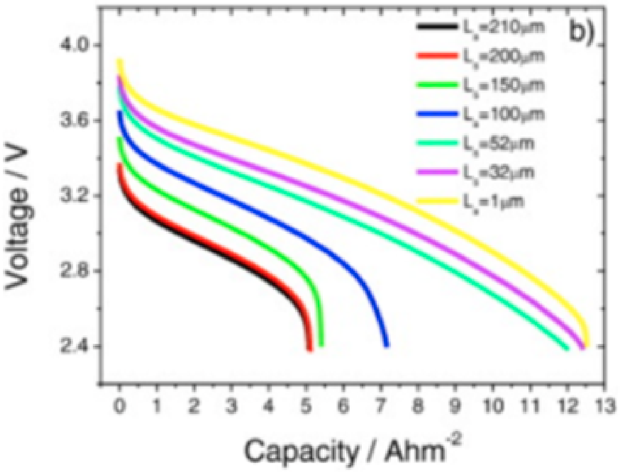


Figure 9: Plot of the Capacity and Voltage for a generalized battery separator of varying thicknesses.

Another important parameter of the separator is its thickness. With the increase of the separator thickness, the path of lithium ions through the separator must grow, resulting in the decrease of the delivery capacity. In order to maintain mechanical integrity at the same time to obtain appropriate battery performance, the separator thickness should be between 1 and 32 μm: above this thickness, significant decreases in the capacity are seen, as shown in Figure 9.

Deducting suitable processing method through morphological requirements and material selection

At present, most of the PI battery separators are prepared by electrospin deposition. However, considering that the preparation rate of electrospin deposition is difficult to meet the needs of mass production, we consider preparing our designed separator through non-solvent induced phase separation.

Over the past half century, a plethora of knowledge has been generated about phase inversion membranes formed by NIPS. Generally, the flat membrane is formed by coating a layer of polymer solution film on the porous mechanical support. The polymer solution or coating consists of at least one polymer, at least one good solvent, and may contain additives. Immerse the film and carrier in a coagulation bath, which consists of inferior solvents (i.e. non solvents) and may contain additives. The polymer film is cured by exchange of solvent and non-solvent; Therefore, the solvent - non solvent system must be miscible. [5]. Simulation of NIPS shows that selection of the non-solvent component produces dramatically different resulting morphologies depending on the interaction of the non-solvent component with the solvent-component - This indicates the tunability of the NIPS method through the selection of solvent-non-solvent interaction behavior, and consequently one can select for higher interaction to allow for the formation of phases that result in the high ionic conductivity and high ion flow through the separator that would be of interest.

For separator films, the porosity behavior will contribute significantly to the ionic conductivity of the overall battery. Because the separator material acts as a solid scaffolding through which the liquid electrolyte flows, carrying the ionic conductivity, the ionic permeability of the separator is negligible relative to the electrical resistivity of the separator, preventing short-circuit current flow from occurring between the two electrodes. From this, the separator material is shown to require open pores that can act as channels through which a suitable liquid electrolyte can penetrate the thickness of the separator.

The processing of the separator film can be controlled to produce the porosity properties desired for use in lithium-ion batteries. PP is one polymer commonly used for this purpose, favorable due to its cost and thermal resistance. A solvent (i.e. dibutyl phthalate (DBP), dioctyl phthalate (DOP), diphenyl carbonate, or N,N-bis(2-hydroxyethyl)tallow amine) is mixed with PP, and this can then be used to form suitable pores: thermally-induced phase separation allows for highly reproducible membranes [6] by first extruding the membrane to the ideal thickness, and then cooled such that phase separation occurs due to spinodal decomposition, allowing for the non-polymer components, now separated out, to be evaporated off, leaving interconnected void spaces that become the open pores of the separator membrane. With higher cooling rate and higher PP content, the pores are shrunk in size, i.e. average pore sizes at 20 wt% and 40 C/min cooling rate produces pores of 9 microns, but raising the wt% to 30% shrinks them to 5 microns, and increasing the cooling rate to 1000 C/min shrinks it to 1.5 microns [7].

PI has properties that are strongly favorable for separators but are commonly produced with electrospin deposition. This allows for greater control of porosity by controlling the fiber thickness and density but severely restricts the reproducibility and scale of production. One method to produce PI membranes has been using NIPS, adding two porogens – pore-forming modifiers – which require tape casting of liquid membrane films into ethanol solutions through which repeated washing removes these additives and leaves only the PI after being dried out [8]. The pore size was not measured, but high porosities of 80% were noted, and SEM images showed small pores, roughly 1.5 microns in size.

The selection of electrolyte will also change the ionic conductivity and contact angle with the separator membrane: For PI, the comprehensive reviews that have been performed on the electrolytes used are limited, but LiPF6 and lithium bis(trifluoromethanesulphony)imide (LiTFSI) have been used in previous literature. This makes it reasonable to treat LiPF6 as the electrolyte of interest through which we will evaluate our separator design, and the modification of electrolyte with the PI separator films proposed will likely be a source of optimization that can be worked upon once results of the design using LiPF6 as the electrolyte are shown to be successful.

In addition to the separator membrane, it is proposed that Silicon dioxide nanofillers are included as additives as previous studies have shown a significant impact on thermal stability and electrochemical performance of the separators. Therefore, SiO_2 is incorporated into the polyimide membranes in an effort to enhance their structure and cylcing stability.

Results

The conventional polypropylene membrane and the newly defined $PI - SiO_2$ membrane are compared from thermal stability to contact angle and wettability. Wettability is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. This property is measured and defined by what is known as the contact angle, the angle where a liquid-vapor interface meets a solid surface, conventionally measured through the liquid. A lower contact angle below 90^o signifies greater wettability, whereas higher contact angle above 90^o infers lower wettability. For the purpose of $PI - SiO_2$ membranes, a lower contact angle and thus, a greater wettability is desired for better electrolyte adsorption and ionic transportation.

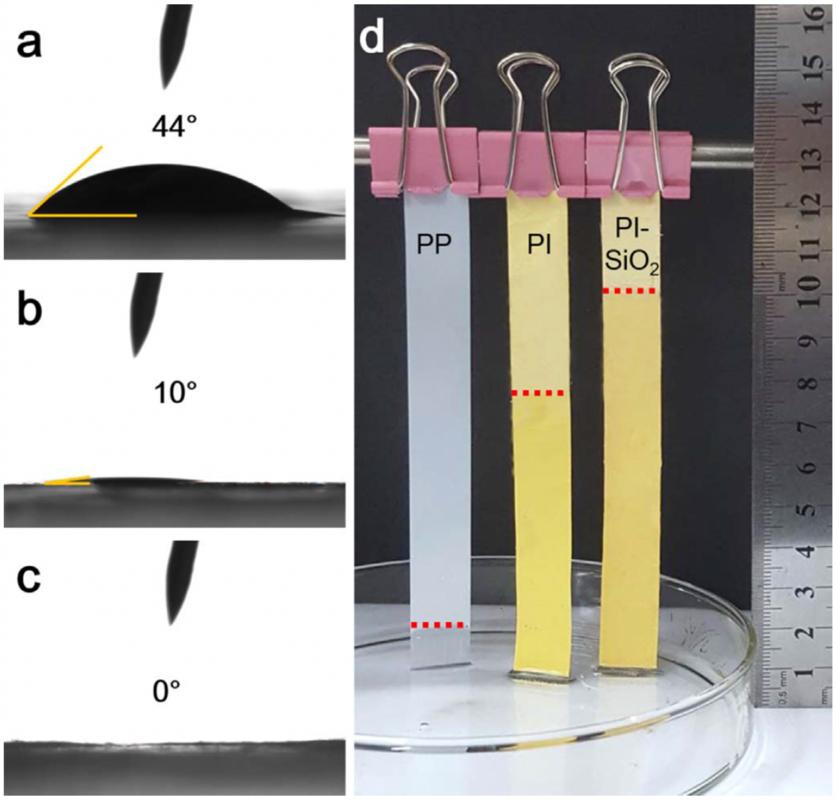


Figure 10: Contact angle images of (a) PP membrane (b) PI membrane and (c) $PI - SiO_2$ membrane (d) the electrolyte immersion-heights of PP, PI, $PI - SiO_2$ membranes

Figure 10 shows the contact angle images of PP, PI, and $PI - SiO_2$ membranes, as well as the corresponding electrolyte immersion-heights. These measurements were performed with a liquid organic electrolyte in order to characterize the electrolyte wettability of membranes. The results show that PI and $PI - SiO_2$ membranes quickly absorbed the electrolyte with a contact angle of 10^o and 0^o, whereas the PP membrane relatively did not with a contact angle of 44^o. Also, the immersion height of $PI - SiO_2$ resulted in 10.2 cm which was larger than those of PI and PP membranes, at 7.5cm and 1.7 cm respectively. We can conclude that the addition of $PI - SiO_2$ nanoparticle fillers is indeed beneficial for wetting property enhancements.

Also, the porosity of the membrane was tested by liquid absorption method. The results show that PI (91%) and $PI - SiO_2$ (90%) membranes have much higher porosities than that of PP membrane (45%), which can be explained by well-developed pores from interconnected nanofibrous structures of PI.

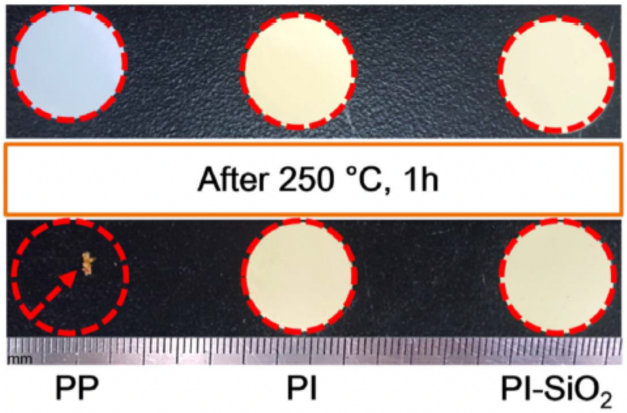


Figure 11: Dimensional stability test - thermal shrinkage after exposure at 250^oC

Now, the performance metric part of our system design chart is focused on how these enhancements in properties have an impact and affect the battery performance and safety. Recall that the morphology dimensions of our separator is a greatly important factor for battery performance as it physically separates the electrodes in order to avoid internal short-circuit thermal runways. When exposed to high temperature, separators may shrink and cause short-circuiting and thermal issues which must be avoided. To prevent this from occurring, dimensional tolerance is measured through thermal shrinkage. As displayed on Figure 11, PI and $PI - SiO_2$ membranes do not have any degradations and keep their original dimensions at over 250^oC whereas the polypropylene membrane suffers a severe thermal shrinkage and deformation due to its lower melting temperature.

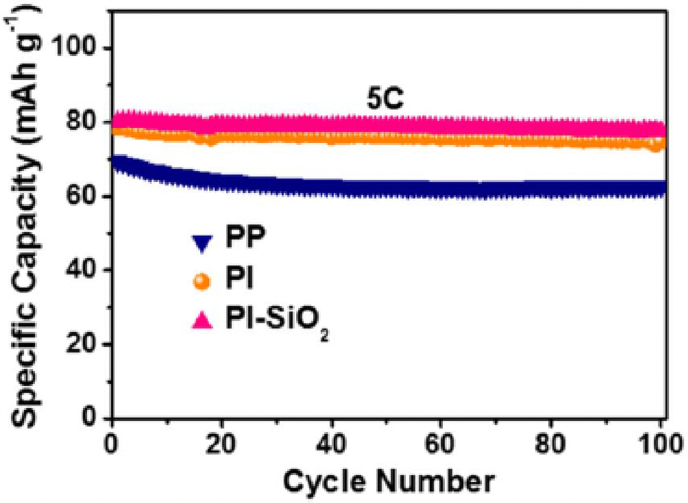


Figure 12: Cyclic performance at 5C at room temperature

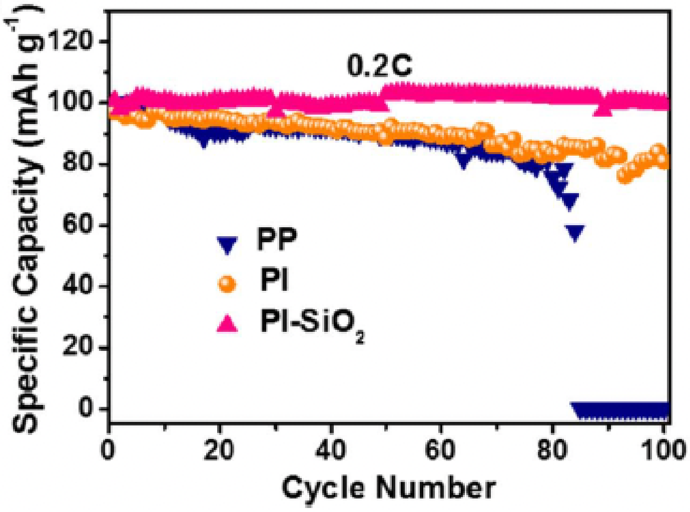


Figure 13: Cycling performance at at 55^oC

Figure 12 shows the discharge curves using different separators, displaying the cycling performances at a rate of 5C. The results indicate the cell using $PI - SiO_2$ separator exhibits an impressive intial value of $80mAhg^{-1}$ and stabilizes at $77mAhg^{-1}$ after 100 cycles, maintaining the highest specific capacity between PP, PI, $PI - SiO_2$ separators. In order to better understand the effect of adding $Si - O_2$ nanoparticles, the high temperature (55^oC) cycling performance was also tested as shown on Figure 13. The $LiMn_2O_4/Li$ cell using PP separator showed a capacity degradation in 80 cycles, while also declining sharply to $58mAhg^{-1}$ at 84th cycle. As expected, the celll using $Pi - SiO_2$ separator exhibited a much better cycling performance at almost 100% capacity retention after 80 cycles, compared to that of PI and PP separators.

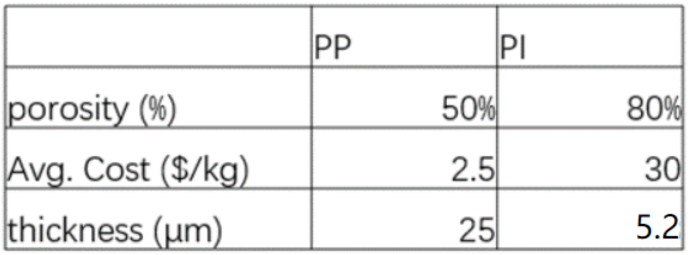
Limitations and Plans for the Future

Based on the limitations of the models that we can apply to the polymer system of choice, we are restricted to designing the separator as a single polymer in order to properly characterize the properties via modeling, but without this limitation, our ideal design would examine the potential of a two or three layer separator film, and further work would be done to experimentally identify an optimal composition for the PI during formulation which would allow for maximized tuning of the ionic conductivity and mechanical strength that relied on porosity and tortuosity control, and a more thorough examination as to the non-solvent porogen additives that could be added, and looking further into the interaction energies and miscibility with the solvent chosen for PAA/PI fabrication.

Cost

Given the porosity of PP and PI, 50% and 80% respectively, some amount of the separator is identified to be void space, indicating that the amount of volume (including the pore space) of separator produced from the same mass of polymer will be different between the two. Normalizing against this separator production potential, the average cost of PI for the equivalent amount of separator becomes $30 \cdot \frac{1-0.8}{1-0.5} = 12$, which then can be turned as a ratio of the cost of PP and the thickness of PP to find the equivalent thickness of PI necessary to balance the costs of PI identical to PP would be 5.2 μm.

This is something that has yet to be confirmed as feasible, but lies at 2x thinner than the separator film described by Li *et al.*, within one order of magnitude. Additionally, the separator fabrication method described in that study began with a doctor blade of 100 microns, which may be optimized to thinner heights - this may require a change in the porosity in order to compensate for the thinner membrane in order to preserve mechanical strength, which could lead to a decrease in performance, but none of this optimization process has been experimentally conducted, and therefore there is insufficient data to determine how much manipulation would be required to reach the thickness of 5.2 microns, and therefore this thickness can still be considered plausible with undetermined feasibility. Further costs of production would be incurred simply due to a lack of available infrastructure in battery separator markets for the fabrication of polyimide separator films, one of the biggest barriers to changing the manufacturing process, meaning that any large-scale fabrication would have to accept high short-run fixed costs up-front.



	PP	PI
porosity (%)	50%	80%
Avg. Cost ($/kg)	2.5	30
thickness (µm)	25	5.2

Figure 14: Table of the relative thicknesses for PP and PI separator films at equivalent cost.

Contributions

- Sangyoon: Background, Results, content on separator silica filler

- Mengjia: System Design Chart, Design Strategy, Significant Literature Browsing and help in the direction of design
- David: Materials Selection, Cost, Limitations, Bibliography, LaTeX coding, misc. report editing for grammatical corrections or details

References

[1] Y. Wang, S. Wang, J. Fang, L.-X. Ding, H. Wang, A nano-silica modified polyimide nanofiber separator with enhanced thermal and wetting properties for high safety lithium-ion batteries 537 (5) 248–254. `doi:10.1016/j.memsci.2017.05.023`.

[2] R. S. Baldwin, W. R. Bennett, E. K. Wong, M. R. Lewton, M. K. Harris, Battery separator characterization and evaluation procedures for NASA's advanced lithium-ion batteries (1) 70.

[3] X. Liang, Y. Yang, X. Jin, Z. Huang, F. Kang, The high performances of SiO 2 /al 2 o 3 -coated electrospun polyimide fibrous separator for lithium-ion battery 493 (3) 1–7. `doi:10.1016/j.memsci.2015.06.016`.

[4] D. Miranda, C. Costa, A. Almeida, S. Lanceros-Méndez, Modeling separator membranes physical characteristics for optimized lithium ion battery performance 278 (4) 78–84. `doi:10.1016/j.ssi.2015.05.022`.

[5] G. R. Guillen, Y. Pan, M. Li, E. M. V. Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review 50 (7) 3798–3817. `doi:10.1021/ie101928r`.

[6] Tan, Rodrigue, A review on porous polymeric membrane preparation. part II: Production techniques with polyethylene, polydimethylsiloxane, polypropylene, polyimide, and polytetrafluoroethylene 11 (8) 1310. `doi:10.3390/polym11081310`.

[7] K. V. Pochivalov, A. V. Basko, T. N. Lebedeva, A. N. Ilyasova, M. Y. Yurov, R. Y. Golovanov, V. V. Artemov, V. V. Volkov, A. A. Ezhov, A. V. Volkov, Y. V. Kudryavtsev, Thermally induced phase separation in semicrystalline polymer solutions: How does the porous structure actually arise? 28 (8) 102558. `doi:10.1016/j.mtcomm.2021.102558`.

[8] M. Li, Z. Zhang, Y. Yin, W. Guo, Y. Bai, F. Zhang, B. Zhao, F. Shen, X. Han, Novel polyimide separator prepared with two porogens for safe lithium-ion batteries 12 (3) 3610–3616. `doi:10.1021/acsami.9b19049`.