

Draining Over Blocking: Nano-Composite Janus Separators for Mitigating Internal Shorting of Lithium Batteries

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Catastrophic battery failure due to internal short is extremely difficult to detect and mitigate. In order to enable the next-generation lithium-metal batteries, a "fail safe" mechanism for internal short is highly desirable. Here, a novel separator design and approach is introduced to mitigate the effects of an internal short circuit by limiting the self-discharge current to prevent cell temperature rise. A nano-composite Janus separator-with a fully electronically insulating side contacting the anode and a partially electronically conductive (PEC) coating with tunable conductivity contacting the cathode-is implemented to intercept dendrites, control internal short circuit resistance, and slowly drain cell capacity. Galvanostatic cycling experiments demonstrate Li-metal batteries with the Janus separator perform normally before shorting, which then results in a gradual increase of internal self-discharge over >25 cycles due to PEC-mitigated shorting. This is contrasted by a sudden voltage drop and complete failure seen with a single layer separator. Potentiostatic charging abuse tests of Li-metal pouch cells result in dendrites completely penetrating the single-layer separator causing high short circuit current and large cell temperature increase; conversely, negligible current and temperature rise occurs with the Janus separator where post mortem electron microscopy shows the PEC layer successfully intercepts dendrites.

Lithium-ion batteries have enabled the consumer electronics society^[1] and are the leading candidate for vehicle electrification^[2] and grid storage.^[3] Further increase in energy density is necessary to reduce battery size, weight, and cost. In the near term, without changing active materials, the focus has been on reduction of the inactive mass in the battery. For example, the thickness of commercial battery separators has been reduced to ~10 μ m^[4] and the electrode thickness and areal specific capacity (mAh cm⁻²) continue to rise.^[5] In the long term, new electrode materials are being proposed to replace the graphite anode, first with silicon containing materials,^[6] finally with lithium metal.^[7]

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The relentless pursuit of higher energy density presents challenges in battery safety.^[8,9] A thinner separator raises the danger of puncturing and the use of lithium metal introduces the possibility of dendrite penetration and shorting. In the case of a short, Joule heating from the large current induced by rapid selfdischarge through the low resistance electronic pathway can bring temperatures to the break down point of the separator and the electrode materials (150-250 °C),^[10] setting off a chain of exothermic reactions and thermal runaway.[11,12] Internal shorting can be induced by external causes such as mechanical deformation (e.g., during nail penetration tests^[13,14]) and overcharging, but can also occur for no discernable external cause, as exemplified by recent incidents in self-ignition of parked electric vehicles.[15] Postulated mechanisms include the growth of conductive filaments in batteries which eventually penetrate the separator and short the cell.^[16] Various approaches of preventing and managing Li-ion battery

thermal runaway have been developed, which include pressure release vents,^[17] advanced battery management systems to prevent overcharging, current collectors that are designed to fracture in order to electronically isolate the short circuit,^[18] and fire retardant additives.^[19]

Among the battery components, battery separators are primarily responsible for preventing and managing battery shorting and thermal runaway. Thermally responsive separator are engineered to collapse or expand in response to high temperatures, blocking ion-flow to effectively shut off the cell.^[20,21] With the help of a third electrode, separators are able to detect a penetrating dendrite.^[22] Alternatively, mechanically robust separators can in principle block internal shorting due to lithium dendrite penetration.^[23-25] Among them, separators based on porous polymeric materials and nonwoven mats have shown improved mechanical properties over conventional polyolefins.^[26] Ceramics particles, commonly alumina or silica, are either coated on the separator or mixed into the separator to improve thermal shrinkage resistance but also have been shown to physically obstruct dendrite propagation.^[27-31] Furthermore, all ceramic solid ion conductors with high modulus can act both as the separator and the electrolyte to suppress







Figure 1. a) Schematic of the Janus separator implemented in a lithium battery. The black side is PEC and the white side is electronically insulating. The Janus separator limits the rate of self-discharge by intercepting the dendrite and increasing the short circuit resistance. b) The Thévenin equivalent circuit of the cell containing a Janus separator during internal shorting with the additional resistance, R_{PEC} , from the Janus separator. c) Schematic of a single-layer separator implemented in a lithium battery. A dendrite penetrates the separator resulting in rapid self-discharge of the cell and thermal runaway. d) The Thévenin equivalent circuit of the cell containing a single-layer separator during internal shorting.

dendritic growth.^[32] However, these more robust blocking separators often only serve to delay dendritic penetration and the subsequent shorting can result in an even more violent failure.^[33]

A separator that can allow controlled and safe shorting of a battery-while still ultimately resulting in cell failure-is an attractive alternative to separators that block and simply prolong time to catastrophic failure. Controlling the resistance of the internal short circuit (R_{Short}) is crucial to mitigating shorting and rapid self-discharge. This can be accomplished by inserting a partially electronically conductive (PEC) separator material with tunable electronic conductivity between the anode and the cathode (Figure 1a) to intercept the oncoming dendrite and effectively increase the short circuit resistance ($R_{\rm short}$). Since the layer is electronically conductive and would naturally result in a short circuit itself, an additional fully insulating separator material placed between the PEC material and the anode is required to prevent this. The PEC material can be directly coated on the electronically insulating material, resulting in a single Janus separator. When a dendrite penetrates the electronically insulating side and is intercepted by the PEC side, the additional resistance provided by the PEC side (R_{PEC}) forms the circuit seen in Figure 1b. Additionally, both are required to be sufficiently ionically conductive to leave normal battery performance unimpeded (R_{Int}). Table S1, Supporting Information, lists the nomenclatures used in the circuits. Conversely, once a dendrite has fully penetrated a conventional single-layer separator, it has no means to prevent a low-resistance internal short circuit from forming, rapidly discharging the cell and potentially resulting in thermal runaway (Figure 1c,d).

In order to easily incorporate an electronically conductive filler and reproducibly study dendrite penetration through these separators, we chose a PVdF-HFP (poly(vinylidene fluorid e-*co*-hexafluoropropylene)):SiO₂ polymer gel electrolyte as the base separator material.^[34] This system, while not as commonly seen in contemporary commercial production, was originally developed and commercialized by Bellcore^[35] and makes for an excellent proof-of-concept platform to study shorting behavior. The separator provides a high ionic conductivity (10^{-3} to 10^{-4} S cm⁻¹)^[36] and relatively poor mechanical properties with a tensile strength \approx 5 MPa (compared to polyolefins, >100 MPa) that is well suited for dendritic shorting experiments. The PVdF-HFP gel electrolyte was additionally chosen since it enables fabrication of a monolithic Janus separator— where both layers contain the same polymer gel structure.

The separators were fabricated by solution casting a mixture of PVdF-HFP, fumed silica, and a plasticizer followed by phase inversion. By incorporating multi-walled carbon nanotubes (CNTs), a nano-composite PEC layer can be formed in which Li⁺ ions diffuse through the polymer gel electrolyte and electrons conduct along the CNT network (Figure 2a). To make the Janus separator shown in Figure 2b, a polymer gel electrolyte layer containing 0 wt% CNTs is first casted and allowed to dry. Then a PEC polymer gel electrolyte layer containing 5 wt% CNTs is coated directly on top of first layer. More details can be found in the Experimental Section. Scanning electron microscopy (SEM) of the cross-section (Figure 2c) of such a Janus separator shows a defined yet intimate interface and distinct morphological difference between the 5 wt% CNTs PEC side and the 0 wt% electronically insulating side. Since the PEC layer is coated on a dry insulating layer, the CNTs appear to be unable to penetrate more than 1 µm past the interface despite being of the same base material, maintaining the integrity of the insulating side of the Janus separator. This is further supported by measuring negligible current when a DC voltage is applied across the Janus separator comparable to that seen with







Figure 2. a) Schematic of the proposed structure of the polymer gel PVDF-HFP:SiO₂/CNTs nano-composite. b) Photograph of the Janus separator: the black side is a PEC layer containing 5 wt% CNTs, and the white side is fully insulating with no CNTs. c) Cross-sectional SEM image of the Janus separator at the interface between the PEC coating (top) and the electronically insulating separator (bottom) and of the full separator showing a distinct morphology between the two sides. d) The measured resistivity of freestanding PEC polymer gel composites with various weight loadings of CNTs and the power-law model fit.

single-layer electronically insulating separator (Figure S1, Supporting Information). The overall thickness of the Janus separators is ${\approx}35~\mu\text{m}$, where the PEC side is roughly 15 μm and the insulating side is roughly 20 μm , and is comparable to thicknesses used in commercial applications.

We next characterized the mechanical, thermal, and electrochemical stabilities of the Janus separator. Tensile tests show a maximum stress of 4.2 MPa, a slight improvement of ~0.3 MPa to the tensile strength compared to a single layer 0 wt% separator. The small difference is not expected to meaningfully change the ability of the separators to block dendrite propagation or otherwise affect shorting mechanism (Figure S2, Supporting Information). Separator wettability and electrolyte uptake is unaffected by the incorporation of CNTs, although the separator no longer becomes transparent when wet and remains dark black (Video S1, Supporting Information). The addition of CNTs also had no observed effect on thermal stability as both separators show no shrinkage at temperature >280 °C (Figure S3, Supporting Information).

Linear sweep voltammetry does indicate a reaction between the CNTs and electrolyte at voltages above 4 V (vs Li/Li⁺), as is common with the conductive carbon additives use in cathodes,^[37] but passivates after multiple sweeps (Figure S4, Supporting Information). In fact, the magnitude of parasitic current between the baseline and Janus separator is negligible if one takes into account the large surface area of the CNT network. Indeed, CNTs are used as the conductive agent in the cathode for this study. Additionally, Bellcore originally applied the polymer gel electrolyte directly to construct the composite cathode containing carbon and the oxide cathode materials similar to the construction of the Janus separator—and did not report additional side reactions. Furthermore, by varying the amount of CNTs incorporated into the PEC side, control of its electronic conductivity is easily achieved and can be altered by orders of magnitude (Figure 2d) to match the demands of batteries of various formats and capacities. Freestanding PEC membranes were cast with CNT loading ranging from 0 to 50 wt% (Figures S5 and S6, Supporting Information), with electronic resistivity that varies by nearly 10^3 – $10^6 \Omega$ cm when measured using a DC voltage bias across the membrane (Figure S1, Supporting Information). The electrical conductivity follows a power-law relation with CNT wt% that is consistent with percolation theory and is modeled in Figure 2d.^[38] To test the Janus separator's ability to intercept dendrites and create a controlled short circuit, Li/NMC (LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂) coin cells with 1 м LiPF₆ in 1:1 ethylene carbonate:dimethyl carbonate (EC:DMC) electrolyte were cycled at a rate of 2 mA cm⁻² (or \approx 1.2 C). It is well known that these conditions result in a slow build-up of dendritic lithium which can eventually penetrate the separator and short the cell.^[39,40] By choosing a mechanically weak polymer gel electrolyte as the base separator material, dendrite penetration and internal shorting can be achieved long before other sources of cell failure occur (e.g., dead Li build up, electrolyte depletion, etc.).^[41] We note that dendrites do grow at much lower current densities where the Janus design will still function as designed.

Coin cells containing a Janus separator (as seen in Figure 1) were compared to cells containing $\approx 40 \ \mu m$ thick single-layer separator to test a scenario where the negative control is thicker and inherently safer than the Janus separator if the PEC layer were to not function properly. Both cell configurations showed stable cycling performance until a shorting event occurs,

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Figure 3. a) Charge and discharge capacity profile of galvanostatically cycled Li/NMC532 coin cells with a single-layer separator and a Janus separator. b) Selected voltage profiles of the cell with a single-layer separator showing stable cycling until sudden on-set of shorting followed by rapid internal self-discharge during the 59th charge. c) Selected voltage profiles of the cell with a Janus separator showing stable cycling until the on-set of PEC mitigated shorting as seen in the 60th cycle. Subsequent cycling after initial shorting results in elongated charge profiles due to increased PEC-mitigated shorting and a larger magnitude of self-discharge as seen in the 75th and 84th cycles.

around the 60th cycle for both separators (**Figure 3**a). Before shorting occurs, electrochemical impedance spectroscopy measurements show a negligible difference between the cells with single-layer separators and Janus separators (Figure S7, Supporting Information).

Despite showing similar regular cycling performance and cell Coulombic efficiencies (Figure S8, Supporting Information), there is a clear and dramatic difference between the two cells upon shorting. The single-layer separator (Figure 3b) resulted in a sudden drop of cell potential at the on-set of shorting during charge in the 59th cycle, indicating internal self-discharge. As expected, the normal separator failed to prevent a low-resistance internal short circuit and rapid self-discharge. In contrast, no sudden voltage drop occurs in the cell with a Janus separator and instead a gradual cycle-by-cycle increase of charge capacity appears-as seen in Figure 3c. After initial stable cycling, the on-set of PEC-mitigated shorting occurs sometime around the 60th cycle. This is indicated by the increase of required charge capacity to reach the cut-off voltage, which generally continues to increase each subsequent cycle. The selected voltage profiles in Figure 3c show such an increase from the

50th cycle (138 mAh g^{-1}) to the 60th cycle (165 mAh g^{-1}), then to the 75th cycle (317 mAh g^{-1}), and again to the 84th cycle (564 mAh g⁻¹). The increased charge requirement can be explained by the PEC-mitigated short circuit allowing internal self-discharge to occur at a rate less than the cell is being charged (i.e., <2 mA cm⁻²). A recent report employed neutron radiography to directly observe evidence of dendritic Li shortinduced self-discharge/charge that results in voltage fluctuation and extended charge time requirement. This is similar to what was seen with the Janus separator, corroborating the competing self-discharge/charge mechanism proposed here.^[42] The growing magnitude of internal self-discharge is attributed to increased PEC-mitigated shorting as each charge cycle continues to plate additional lithium, increasing the dendritic short penetration and contact area with the PEC side. This will lower the effective resistance of the PEC side of the Janus separator, thereby increasing the severity of shorting. During the 85th cycle, the magnitude of internal shorting and self-discharge rate becomes greater than the rate the cell is being charged (i.e., >2 mA cm⁻²), voltage declines, and the cell is unable to reach the cut-off voltage (Figure S9, Supporting Information). This

multi-cycle failure provides ample time for a battery management system to detect such a shorting event and recommend the battery be replaced. However, despite this indirect detection of an internal short, it should be noted that the primary purpose of the Janus separator is in fact to mitigate the impact of short and is not necessarily designed as a short detection separator.

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A similar effect can be achieved by coating the PEC layer directly on the cathode (Figure S10, Supporting Information). When cycling tests were repeated with a single-layer separator and an \approx 10 µm PEC coating on the cathode, very similar PEC-mitigated shorting behavior appears as marked by the increased cycle-by-cycle charge capacity requirement. The PEC layer only needs to intercept the dendrite before fully contacting the cathode and does not necessarily need to be part of the separator. However, the method used to cast the PEC polymer gel electrolyte directly on top of the cathode introduces a mechanical strain, creating cracks in the cathode visible by SEM. This detrimentally affects the capacity of the cell, likely isolating parts of active material. We expect further optimization of the coating process can remedy this issue, opening an alternative route to mitigating internal short circuiting with a PEC material.

Commonly used mechanical abuse shorting tests such as nail penetration tests or crush tests are poor surrogates to the type of internal shorting that occurs during abusive charging.^[43] Considering this, we conducted abusive 4.5 V potentiostatic charging on Li metal/NMC532 pouch cells (active area ≈28 cm²) to induce rapid controllable dendritic shorting as a further proof-of-concept of the Janus separator's ability to mitigate internal shorting. Both the electrical and thermal response of pouch cells containing a single-layer separator and a Janus separator were monitored and are shown in Figure 4a,b. A photograph of the Li-metal anode and deposition conditions is found in Figure S11, Supporting Information. Photographs of the final assembled cells and thermocouple position are found in Figure S12, Supporting Information. Initial pre-cycling data and impedance measurement of the pouch cells again show no difference in cell performance between the separators (Figure S13, Supporting Information)

Immediately upon the application of the 4.5 V (vs Li/ Li⁺) hold, both cells exhibit a brief but large charge current of nearly 1 A or >30 mA cm^{-2} . The current decays down to a diffusion-limited regime^[44] within 30 s; however, this is sufficient to deposit dendritic lithium on the anode surface and shorting occurs at around 250 s after the voltage hold is applied. Once shorting occurs, the cell with the single-layer separator experiences a short circuit current that reaches nearly 2 A, while the Janus separator cell exhibits almost no rise in current (Figure 4a). Trailing slightly behind the current, the cell temperature rises in the single-layer separator cell by more than 20 $^\circ\text{C},$ whereas the Janus separator cell remains at room temperature (Figure 4b). It is hypothesized that the ultimate decay in short circuit current in both cells is caused after all available capacity has been exhausted from the cathode; no new Li can be deposited and the existing dendrites begin to passivate, increasing the electronic resistance of the short circuit.

To explain the continuous rise in short circuit current and to better quantitatively understand PEC-mitigated shorting, we developed a simple PEC shorting model, which is seen as the dash overlayer in Figure 4a. This model attempts to capture how dendritic shorting interacts with the PEC layer of the Janus separator. Normally when dendrites penetrate through the insulating separator, an internal short circuit forms between the anode and the cathode. As charging continues, more Li is deposited at the contact point, the short grows more severe, and the resistance— $R_{Short}(t)$ —decreases. However, since electrochemical discharge of a battery requires transport of both electrons and Li⁺, the total resistance— $R_{Tot}(t)$ that dictates the short circuit current— $I_{SC}(t)$ —is the combination of $R_{\text{Short}}(t)$ in parallel with internal cell ionic resistance— $R_{\text{Int}}(t)$ —as shown in the equivalent circuit in Figure 1 and given by Equation (1)

$$R_{\text{Tot}}(t) = \frac{1}{\frac{1}{R_{\text{Int}}(t)} + \frac{1}{R_{\text{Short}}(t)}}$$
(1)

The resulting shorting circuit current— $I_{sc}(t)$ —driven by the electromotive force of the cell— $V_{emf}(Q(t))$ —and $R_{Tot}(t)$ is governed by Ohm's Law, Equation (2)



Figure 4. Abusive potentiostatic charging-induced short circuit. a) The current response of Li metal/NMC532 pouch cells with a single-layer separator and a Janus separator when a 4.5 V hold was used to charge the cell. Overlaid is modeled current response of cells with a PEC layer with varying electronic resistivity, ρ_{PEC} (Ω cm). b) Corresponding temperature response measured by a thermocouple located outside of the pouch cell at the negative current collector tab.

$$I_{\rm SC}(t) = \frac{V_{\rm emf}\left(Q(t)\right)}{R_{\rm Tot}(t)}$$
(2)

Large format cells have two primary properties that can drive a large I_{sc} : they have extremely low R_{Int} when considering the entire area of the cell, and will remain at high $V_{emf}(Q(t))$ during self-discharge due to their large capacity, Q(t). When a large format battery shorts across a sufficiently low R_{Short} , these two factors will result in the generation of a significant amount of heat.^[45,46]

Introducing the PEC layer can intercept the short and vary the rate at which $R_{\text{Short}}(t)$ develops, without affecting $R_{\text{Int}}(t)$. With proper tuning of the PEC layer, the short circuit can be controlled, and cell capacity can be slowly and safely drained. To model the effects that tuning the PEC layer has on shorting, the dynamic $R_{\text{Short}}(t)$ and resulting $I_{\text{SC}}(t)$ of 4.5 V galvanostatic abuse testing were simulated with various PEC layer resistivities— ρ_{PEC} (Ω cm).

First, the transient internal resistance— $R_{Int}(t)$ —of the R-RC equivalent circuit described in Figure 1 was estimated by fitting the potentiostatic charging data of the single-layer separator cell prior to shorting (0–250 s) to Equation (3) using the Matlab Curve Fitting Toolbox

$$R_{\text{Tot}}(t) = R_{\text{Int}}(t) = R_{\text{o}} + \left(R_{\text{ct}} - R_{\text{ct}}e^{-\frac{t}{R_{\text{ct}}C_{\text{p}}}}\right)$$
(3)

where $R_{\rm o}$ is the bulk resistance of the cell, $R_{\rm ct}$ is the charge transfer resistance, and $C_{\rm p}$ is the electrical double layer capacitance. Fitted values for each parameter are listed in **Table 1**.

Second, the fitted $R_{\text{Int}}(t)$ was inputted into Equation (1) and the remaining transient short circuit resistance, $R_{\text{Short}}(t)$ was estimated from the same potentiostatic charging data, however, now by fitting over the entire time prior to peak short circuit current (0–550 s). Resistivity of the PEC layer and the electrode, as well as the dendrite growth rate and penetration depth are considered when estimating the short circuit resistance as calculated by Equation (4)

$$R_{\rm Short}(t) \approx \rho_{\rm PEC} \star \alpha e^{-\gamma(t-t_{\rm SC})}$$
(4)

The dendrites are modeled as growing rods penetrating a PEC layer with a certain resistivity, $\rho_{\rm PEC}$ (Ω cm² cm⁻¹ or Ω cm). Here, α (cm cm⁻² or cm⁻¹) represents the ratio of rod penetration depth (cm) to the contact area (cm²) between the rod and the PEC layer. The exponential function containing γ (s⁻¹) represents the dendrite growth rate, encompassing both increasing penetration depth and growing contact area after the onset of shorting at $t = t_{\rm SC}$ (250 s). These values were also estimated using the Matlab Curve Fitting Toolbox and are listed in Table 1. It should be noted that this model allows $R_{\rm Short}(t)$ to

 $\label{eq:table 1. Fitted parameters to describe potentiostatic charging-induced shorting.$

$R_{o}[\Omega]$	$R_{\rm ct} \left[\Omega \right]$	С _р [F]	α [cm cm ⁻²]	$\gamma[s^{-1}]$
3	22.5	1.882	30.17	0.02297

approach zero and does not capture the current decay seen at the end.

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Lastly, simulations of the short circuit current response of cells during 4.5 V potentiostatic charging and shorting are performed using these fitted parameters with different $\rho_{\rm PEC}$ values. The results for the single-layer separator ($\rho = 25 \ \Omega \ cm$, representing the resistivity of cathode alone with no additional PEC layer),^[47] and with a PEC layer of $\rho_{\rm PEC} = 2500 \ \Omega \ cm$ and 2 50 000 $\Omega \ cm$ are overlaid in Figure 4a. Simply enough, the higher the PEC resistivity, the more prolonged the onset of shorting. This allows enough time for the charge capacity to be exhausted and the short to passivate.

As further confirmation of the PEC-mitigated shorting mechanism, the pouch cells were disassemble and inspected. Both separators have a large amount of dendritic lithium embedded in the anode-facing surface, which was delaminated from the Li anode during disassembly (Figure S14, Supporting Information). However, there is a clear difference visible between the cathode-facing surface of the two separators after shorting: by eye, the Janus separator maintains a black PEC surface similar to the pristine state while there is visible dendrite penetration through the single-layer separator. SEM shows a dendrite-free PEC surface whereas the single-layer separator surface is covered with cracks and lithium penetrating through those cracks (Figure S15, Supporting Information).

Additional SEM and energy-dispersive X-ray spectroscopy elemental mapping was performed on cross-sections of both separators (Figure 5). In Figure 5a, the dendrite can be seen penetrating through the electronically insulting side of the Janus separator but is then intercepted by the PEC layer. Elemental mapping of O-corresponding to oxidized Li-and F-present in the PVdF-HFP separator-further highlights the dendrite interception (Figure 5b and Figure S15, Supporting Information). Additional cross-sectional SEM along the Janus separator shows multiple locations where dendrites were intercepted by the PEC layer and can be found in Figure S17, Supporting Information. Referring again to the tensile test results (Figure S2, Supporting Information), it is highly unlikely that the PEC side possess enough additional tensile strength to mechanically suppress dendrites, and the observed dendrite interception at the interface is solely due to the PEC-mitigated shorting mechanism. Conversely, the dendrite is observed to have fully penetrated the single-layer separator in Figure 5c,d, resulting in the low-resistance internal short circuit and the current response seen during abusive charging.

In conclusion, we have designed and developed a Janus separator with one side being a PEC nano-composite layer that has the ability to dramatically reduce short circuit current when an internal shorting incident occurs from Li dendrite growth. The separator, <35 μ m thick, is fabricated by coating a PEC layer directly on an electronically insulating separator. Various electrochemical shorting tests show that the Janus separator was indeed effective in controlling and raising the resistance of the internal short circuit, thus reducing self-discharge current when compared to cells with a single-layer electronically insulting separator. Galvanostatic cycling tests resulted in a gradual failure mechanism in coin cells containing the Janus separator separators. During abusive potentiostatic charging, pouch cells

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Figure 5. Post mortem SEM of the a) Janus separator and the c) single-layer separator. EDS of separator cross-sections of the b) Janus separator and the d) single-layer separator.

assembled with the Janus separator showed little to no rise in current and temperature during shorting, whereas cells with conventional separators experienced large increase in current and more than 20 °C rise in external cell surface temperature, which could easily lead to safety incidents in larger cells.

The Janus separator presents a new approach to mitigating the impact of internal shorting. Instead of blocking the dendritic short circuit, the PEC layer allows the short circuit to occur, albeit in a much gentler and safer fashion. While the current iteration of the Janus separator remains a proof-of-concept, a similar Janus design can be applied to commercial separators (e.g., Celgard) although material and process optimization will be needed to address any differences in shorting dynamics due to the different mechanical and chemical properties of the baseline separator. The design is also expected to be effective in lithium-ion batteries where internal short circuits develop due to mechanical compression or conductive filament growth caused by manufacturing defects or overcharging. As a result, the design could find quick adoption in current battery technologies and facilitate the advancement of emerging battery technologies of higher energy density. Our work illustrates the potential of a new, generally applicable safety design mechanism that addresses the impact of internal short circuit.

Experimental Section

Separator Fabrication and Characterization: Kynar Flex 2801 PVDF-HFP co-polymer powder (Arkema) and fumed silica powder (SiO₂, Sigma-Aldrich) were combined in a 3:2 ratio. Multi-walled CNTs with an average length of 5 μ m (purchased from SWENT and used without further modification) were predispersed in acetone by ultra-sonication. The amount of CNTs dispersed was determined by the desired wt% of CNTs in PVDF-HFP/SiO₂. In a typical process, 1 g of PVDF-HFP/SiO₂ mixture was then added to 10 mL of acetone/CNT dispersion and 2 mL

of dibutyl phthalate (DBP). To ensure homogeneity, the slurry was mixed by stirring at 60 °C for 2 days in a sealed container. Finally, the slurry was mixed by an orbital mixer until the polymer was completely dissolved and the CNTs were fully incorporated. The solution was then cast using a doctor blade to form either a freestanding PEC separator, or a coating on a dry 0 wt% separator to form the Janus separator. The porosity was achieved by extracting the DBP plasticizer with diethyl ether based on the methods described in the Gozdz et al. patent.^[34]

To measure the electronic conductivity of the PVDF-HFP:SiO₂:CNTs freestanding PEC separators, they were placed between two stainless steel electrodes in a spring-loaded Swagelok cell. A voltage bias of 100 mV was applied between the electrodes. Conductivities were calculated from the current and the sample thicknesses were estimated from SEM images (Figure S1, Supporting Information)

Battery Fabrication and Testing Parameters: An 80:10:10 slurry of NMC(LiNi_{0.5}Mn_{0.2}Co_{0.3}O₂):SuperP carbon:PVDF in *N*-methyl-2-pyrrolidone (NMP) was blade coated on Al foil. After drying and calendaring, the electrodes had a thickness of roughly 100 μ m with an areal capacity of ~1.8 mAh cm⁻² for coin cells cathodes. A cathode with high capacity of 2.5 mAh cm⁻² consisted of NMC, CNT, and PVDF in a mass ratio of 100:1:1.5 on Al foil (Hunan Hong Xiang New Energy Technology CO. LTD.) was used for pouch cell fabrication.

Coin cells were assembled with 2032 stainless steel casings and used 13 mm diameter cathodes paired with a 15 mm diameter Li disk rolled onto a 1 mm thick stainless steel spacer disk. 1.0 M LiPF₆ in 1:1 vol/vol EC and DMC (LP30, Gotion) was used as the electrolyte. The cell was sealed in a hydraulic crimper at 1000 psi.

Pouch cells used a lithium anode with a capacity of 2.5 mAh cm⁻² which was prepared by electroplating lithium on copper foil at 0.1 mAh cm⁻² in 1 m LiTFSI (lithium bis(trifluoromethanesulfonyl)imide), 0.5 m LiNO₃ in 1:1 wt/wt DOL:DME (1,3-dioxolane:1,2-dimethoxyethane) using a thick Li source. This electrode was hand rolled smooth and the bare Cu edges were taped (Figure S8, Supporting Information). The laminated pouch cell was sealed using a MTI MSK-115A-S vacuum sealer in an argon-filled glove box after the electrolyte was added.

Pouch cells were placed between Teflon sheets and plexiglass plates (Figure S9, Supporting Information). The thermocouples were taped on the outside of the pouch above the negative contact, but between the plexiglass where the smaller Teflon sheet allowed space as to ADVANCED SCIENCE NEWS _____



apply pressure only to the active cell area and not to the tip of the thermocouple. A hand clamp was used to apply pressure to improve cycling of the Li-metal anodes. This set up did not allow measurement of the pressure applied, however the clamps were tightened to their maximum by hand and pressure was estimated to be >100 psi (Figure S9, Supporting Information).

Coin cells were cycled using a Landt battery tester at 0.5 mA cm⁻² for three cycles, 1.0 mA cm⁻² for five cycles, and 2.0 mA cm⁻² until failure. Coin cells and pouch cells used in the potentiostatic tests were precycled at 0.2 mA cm⁻² for two cycles (2nd cycle cut-off was set to 3.5 V). Potentiostatic holds and impedance measurements were carried with a Biologic potentiostat using a high current (10 A, 5 V) booster channel. Temperature was measured using a K-type thermocouple and HOBOware reader.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.L. proposed the idea and directed the research along with H.L. All of the authors contributed to the planning, materials fabrication, experimental design and analysis, and manuscript preparation. M.S.G. performed the majority of separator fabrication and characterization as well as cell fabrication, electrochemical testing, and model development. J.Y. and Z.W. assisted with full cell experimental design and cathode fabrication. H.Z. and N.P. aided M.S.G. in separator characterization and model development. V.P. provided insights in composing the manuscript and data organization.

Keywords

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