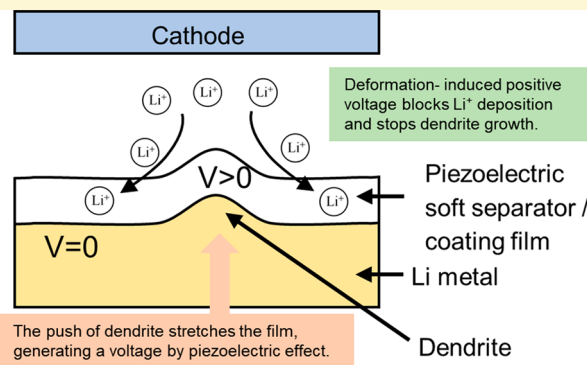


Preventing Dendrite Growth by a Soft Piezoelectric Material

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§ Supporting Information

ABSTRACT: We report a piezoelectric mechanism to stop dendrite growth, which enables inherently safe lithium metal battery. For demonstration, a polarized piezoelectric polyvinylidene fluoride (PVDF) film is used as a separator. When the film is deformed by any local protrusion because of surface instability of the deposited lithium, a local piezoelectric over-potential is generated to suppress lithium deposition on the protrusion. Our optical in situ cell shows that a polarized PVDF film ensures lithium metal depositing to form a flat surface, even when starting from an uneven surface. In contrast, a non-polarized PVDF film cannot suppress dendrite growth under the same condition, with dendrite penetrating the separator within minutes. Coin cell results further confirm that the piezoelectric mechanism is effective in practical battery applications. Analysis suggests that the effectiveness of piezoelectric mechanism by over-potential is easily 10^4 stronger than the maximum physical limit of mechanical blocking from infinitely stiff blocking materials, suggesting a new direction of material innovation.



To meet the increasing demand for energy density by consumer electronics, electric vehicles, and grid-scale storage,^{1,2} lithium metal has been studied as an anode for next generation lithium ion batteries because of its high theoretical capacity and low electrochemical potential.^{3,4} However, a key material challenge is dendrite growth during lithium deposition, which not only causes capacity loss but also leads to internal short circuit and safety hazard.^{5–8}

Stiff separator or solid electrolyte has been explored to mechanically block the growth of lithium dendrite.^{9–12} The idea is to utilize the elastic energy at the metal/electrolyte interface resulting from deformation to reduce lithium diffusion onto the dendrite tip and change electrodeposition.¹³ However, recent work showed that this does not work as desired: inorganic solids and solid polymers generally do not lead to stable electrodeposition.¹⁴ Elastic analysis shows that effective blocking demands a large elastic modulus for solid electrolyte that exceeds the capability of available materials. In addition, lithium has a low yield strength. Even with a very stiff separator, the plastic deformation of lithium metal causes the elastic energy to relax and spread rather than locally stored at the interface. The low elastic energy density has little impact on diffusion, making mechanical blocking less effective.^{15,16} This fundamental materials problem has perplexed the community for a long time. Even the use of very stiff ceramic material was unable to block the dendrite's penetration.

In this Letter, we report a discovery that the use of a soft piezoelectric film as separator can effectively suppress the formation of lithium dendrite and stabilize the lithium surface during electrodeposition. Dendrite growth is a diffusion driven process. Dendrite penetration through a membrane is not a mechanical piercing through process by a sharp object but rather a lithium growth process following the fast diffusion path. Any surface roughness, diffusion inhomogeneity or unavoidable microscopic random fluctuation can generate surface perturbations with tiny protrusions. The lithium deposition is faster on a protrusion because of the larger spherical diffusion flux comparing to the flux toward a flat surface, causing the protrusion to grow longer. Therefore, a flat lithium surface is unstable upon electrodeposition, leading to the formation of sharp dendrite tips. Our finding suggests an innovative approach to suppress dendrite formation by utilizing a negative piezoelectric feedback mechanism, where a local counter over-potential is generated when the piezoelectric film is deformed by any nucleation of surface protrusion or pre-existing protrusions such as surface defects. The counter over-potential reduces the driving force of lithium diffusion toward any protrusion and slows down the local

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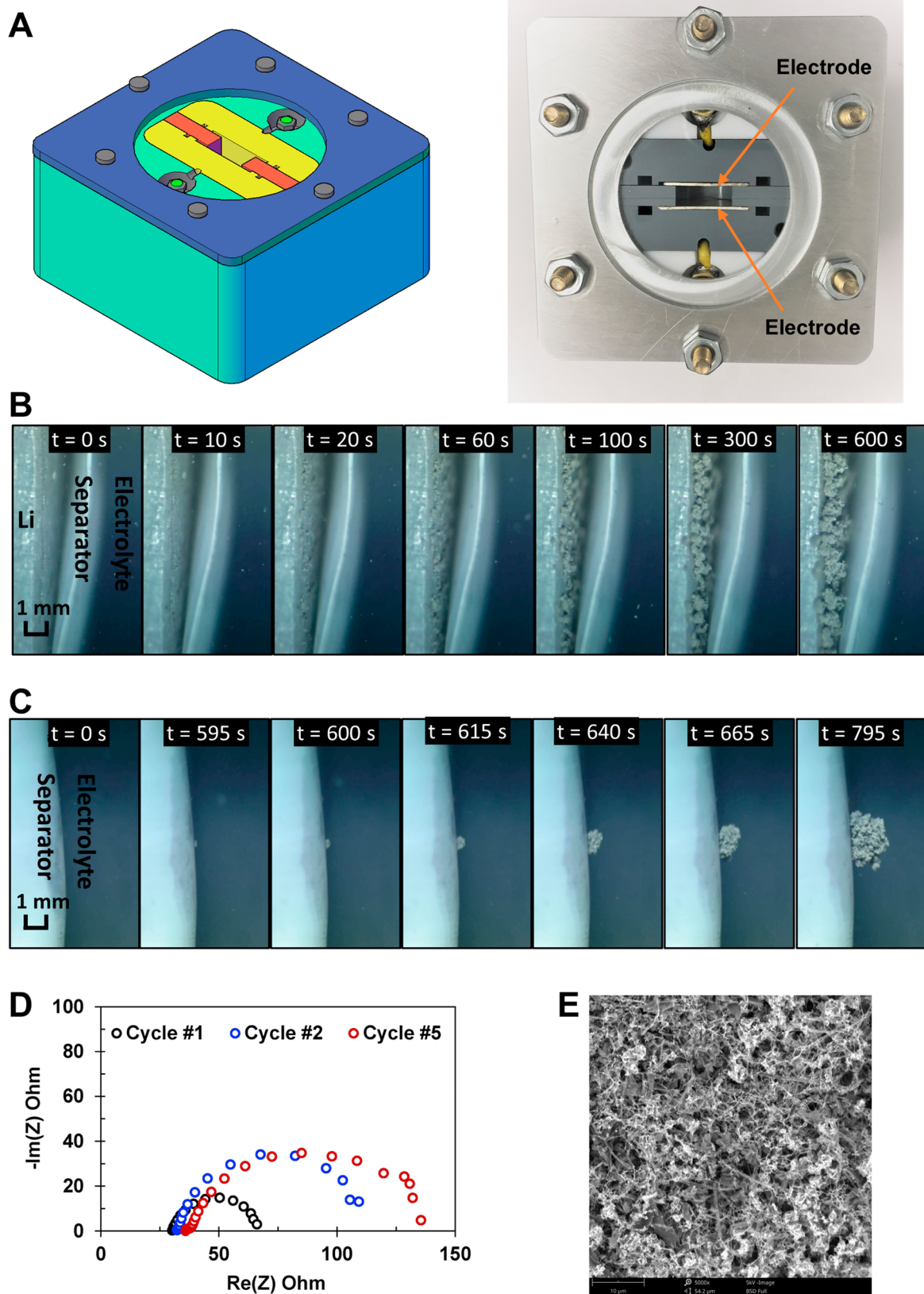


Figure 1. Optical in situ cell reveals the failure modes of a lithium metal anode. (A) Self-made in situ cell. (B) Evolution of lithium metal surface during electrodeposition under a current density of 1 mA/cm^2 . There is a gap between the lithium metal surface and the non-transparent commercial separator to observe the dendrite growth morphology until it contacts the separator. (C) Penetration through the commercial separator by lithium dendrite during electrodeposition under a current density of 1 mA/cm^2 . In this setup, the separator is directly in contact with the lithium electrode. (D) EIS results showing significant impedance increase after 5 cycles. (E) SEM image of deposited lithium surface showing sharp nano-scale needles and filaments.

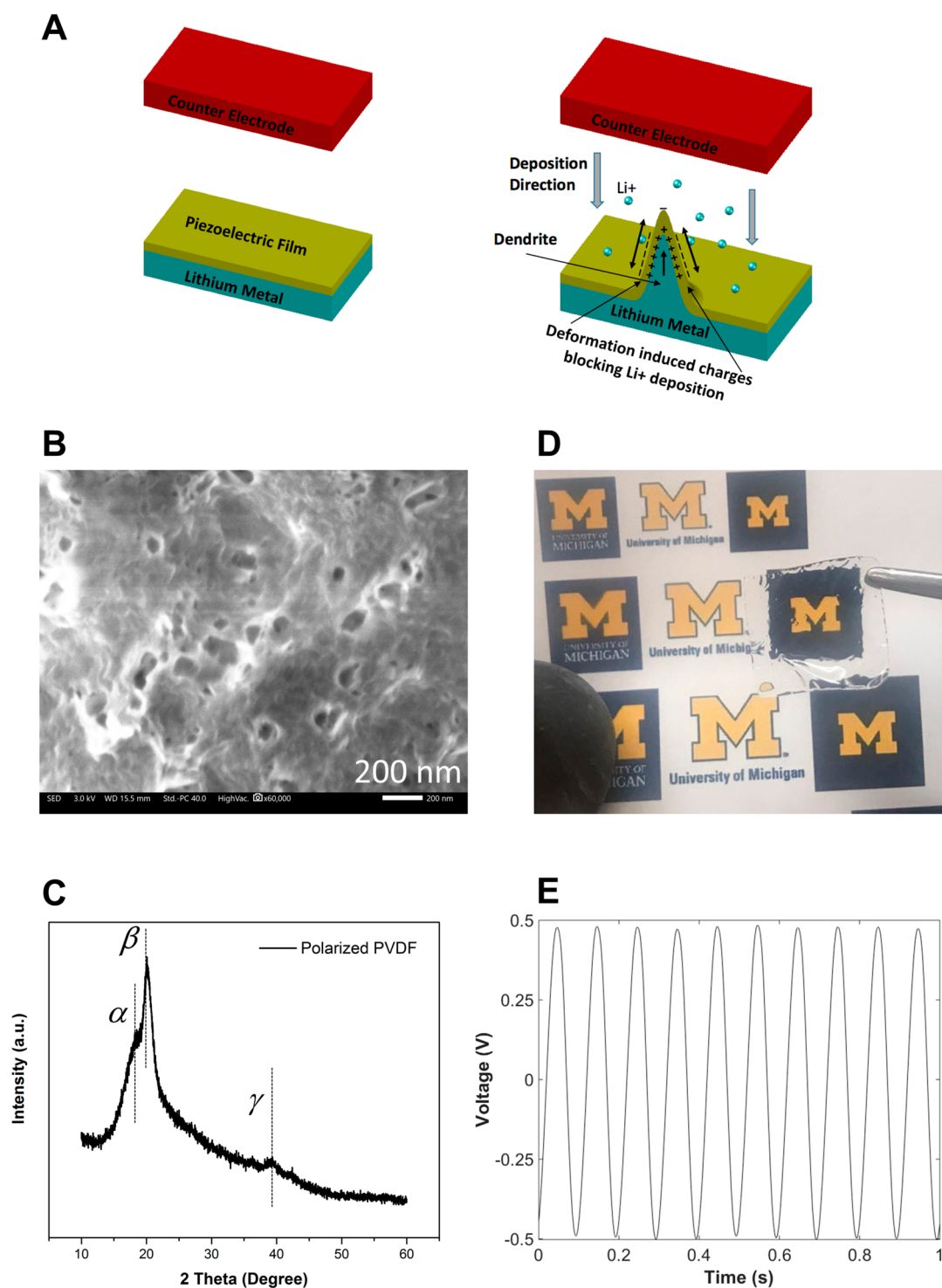


Figure 2. Concept of the piezoelectric mechanism and properties of the PVDF film. (A) Illustration of using a piezoelectric film to suppress lithium dendrite growth. (B) SEM image showing the microporous structure of a fabricated PVDF film. (C) XRD results showing the dominate β -phase PVDF and complete removal of ZnO. (D) Transparency of a PVDF film when wetted by the organic electrolyte. The block M logo belongs to the University of Michigan. (E) Characteristic piezoelectric voltage across the thickness of the fabricated porous PVDF film. The film is pre-loaded to 0.5% uniaxial in-plane strain as the reference, and cycling is centered about this reference with an amplitude of 0.5% strain, that is, cycling with 1% peak-to-peak strain.

lithium deposition on any protruded spots, eventually resulting in a flat lithium metal surface.

In mechanical blocking, the elastic energy spreads away from the interface and is fundamentally limited by the low yield strength of lithium metal. The elastic energy relaxes greatly upon plastic deformation. Therefore, the achievable elastic

energy around a protrusion is inherently limited, which is insufficient to effectively reduce lithium diffusion and deposition onto a protrusion. The piezoelectric mechanism is a very strong first order effect and is highly localized. It is very effective to stabilize a lithium surface during deposition. Analysis suggests that the effectiveness of piezoelectric

mechanism by over-potential is easily 10^4 stronger than the maximum physical limit of mechanical blocking from infinitely stiff blocking materials. This suggests a new direction of material innovation. In addition to being applied for lithium metal battery, this mechanism can be broadly applied in current lithium-ion batteries in the form of separator or coating to prevent dendrite formation during fast charging or low temperature operation, making a battery much safer.

We first investigated dendrite growth and penetration using a self-made optical in situ cell. Figure 1A shows the setup, which has a transparent quartz window for observation. Electrolyte (1 M LiPF₆ in EC: DMC (1:1 vol%)) is filled between the two lithium metal electrodes. The separator is placed on the surface of the lithium metal electrode and inserted together with the electrode in the slot. The in situ cell assembly is performed in an argon-filled glovebox (MBraun) at moisture and oxygen levels below 0.1 ppm. An optical microscope is used to observe the initiation and growth of lithium dendrite during deposition. Figure 1B shows the snapshots of a typical evolution of lithium surface under a current density of 1 mA/cm², and the entire video footage is located in Movie S1. A commercial Celgard separator is placed on top of the electrode surface. The separator is non-transparent. There is a gap between the separator and the lithium electrode so that we can observe the lithium growth morphology until it contacts the separator. Small isolated dendrites initiate at multiple locations on the lithium surface. After growing into each other, they merge and form “bush-like” mossy lithium. A large volume expansion is observed associated with lithium deposition, which ruptures the SEI layer. Figure 1C shows the process of dendrite penetrating the separator (Movie S2). In this setup, the separator is directly in contact with the lithium electrode. The current density is still 1 mA/cm². Although we cannot directly see lithium deposition inside the opaque separator, the darker shade of color in the separator around the penetration region indicates the deposited lithium and the SEI layer wrapped by the separator. The spreading of the darker shade of color indicates that electrodeposition results in a contact between the lithium and the separator. Eventually, lithium dendrite penetrates the separator at a random local spot, and quickly grows into a “bush”. This “bush” can break away from the lithium substrate and become “dead” lithium, or continue to grow and lead to a short circuit once it reaches the counter electrode. In our setup, the “bush” is far from the counter electrode. To avoid potential short circuit, we have also put another separator on the counter electrode surface as a precaution. Impedance increase is the other major failure mechanism besides short circuit. Electrical impedance spectroscopy (EIS) measurement of the in situ cell shows significant impedance increase after only 5 galvanostatic cycles (Figure 1D). Simulations have shown that dendrites can grow to penetrate the SEI at the tip area, causing the exposed lithium to form new SEI.¹⁷ Such SEI growth can contribute to impedance increase.

Our in situ study showed that mechanical blocking by the separator is only effective for a short period. Once a lithium dendrite gets in close contact with the separator as a result of quick volume expansion of lithium during deposition, the dendrite will penetrate the separator. Under SEM (Figure 1E), we can see that although seemingly harmless at the microscale, these lithium dendrites have sharp “needle” shapes at the nanoscale. These sharp tips of dendrites keep pushing the separator until penetration occurs. This observation suggests

that mechanical blocking, although intuitive, may not be effective enough to suppress the local structure of dendrites and thus is limited in short circuit prevention.

Fig. 2A illustrates our strategy of using a piezoelectric film to effectively suppress lithium dendrite growth. The intuition is to generate a counter over-potential by piezoelectricity when a dendrite protrusion nucleates to deform the piezoelectric film. This offsets the concentration over-potential caused by the spherical diffusion at the tip of the dendrite, thus suppressing the further growth of the dendrite. This ensures a stable flat surface morphology during lithium deposition. It should be emphasized that it is essential that the inhomogeneous piezoelectric over-potential (counter over-potential) is only generated at the dendrite tip that pushes the film, while no potential or minimum potential is generated in other lower or flat regions. This slows down the growth of the dendrite while the flat or lower regions can catch up, making the lithium metal surface flat. Therefore, uniformly placing a layer of charges on the surface of a lithium metal would not help since it will not selectively slow down the dendrite tip growth. For the same reason, uniformly distributed positively or negatively charged atoms in a film, either being intrinsic components of the film or being added to the film, would not help suppress dendrite. The piezoelectric suppression mechanism is further confirmed by the dependence on film orientation, where accelerating effect is observed when the piezoelectric film is flipped on the lithium surface. Related discussions can be found later.

The over-potential due to mechanical blocking can be estimated by $\Omega\sigma/F$,¹⁸ where Ω is the molar volume of lithium atom (1.3×10^{-5} m³/mol), σ is the stress on the lithium metal, and F is Faraday constant (96485 C/mol). This over-potential competes with the concentration over-potential to stabilize the lithium surface. The equation was derived by rigorous consideration of the effect of mechanical stress on electrochemical potential. Loosely speaking, $\Omega\sigma$ can be viewed as the work done to pile up the volume of 1 mol of lithium atoms on a lithium metal surface under stress σ . Dividing the work by F gives the additional over-potential needed to deposit lithium ions into lithium atoms on a lithium surface since the atoms need to pile up under stress. The equation shows that a stiffer blocking material is better for mechanical blocking, which generates a larger stress when a dendrite pushes against the material. The maximum physical limit is given by an infinitely stiff blocking material, so that the upper bound of σ is limited by the yield strength of lithium metal, which is about 0.655 MPa.¹⁵ With this, the equation gives the maximum physically possible over-potential in the order of 0.1 mV. In contrast, a thin and soft piezoelectric polyvinylidene fluoride (PVDF) film can easily generate hundreds of mV over-potential across its thickness under deformation. Figure 2E shows 1 V under a uniaxial strain of 1%. This is 10^4 larger than the maximum physical limit of mechanical blocking over-potential. In fact, a soft piezoelectric film can easily accommodate much larger local strain so that the local piezoelectric over-potential can be even higher. At the same time, a protrusion can induce significant strain and is subjected to strong suppression by the associated piezoelectric over-potential. The exact amount of induced local strain depends on the shape of protrusion. For a very rough estimation, growing a semispherical protrusion of radius R from a flat surface can induce a nominal average surface stretching in the order of $(\pi R - 2R)/2R = 57\%$. The protrusion will be suppressed to be much flatter.

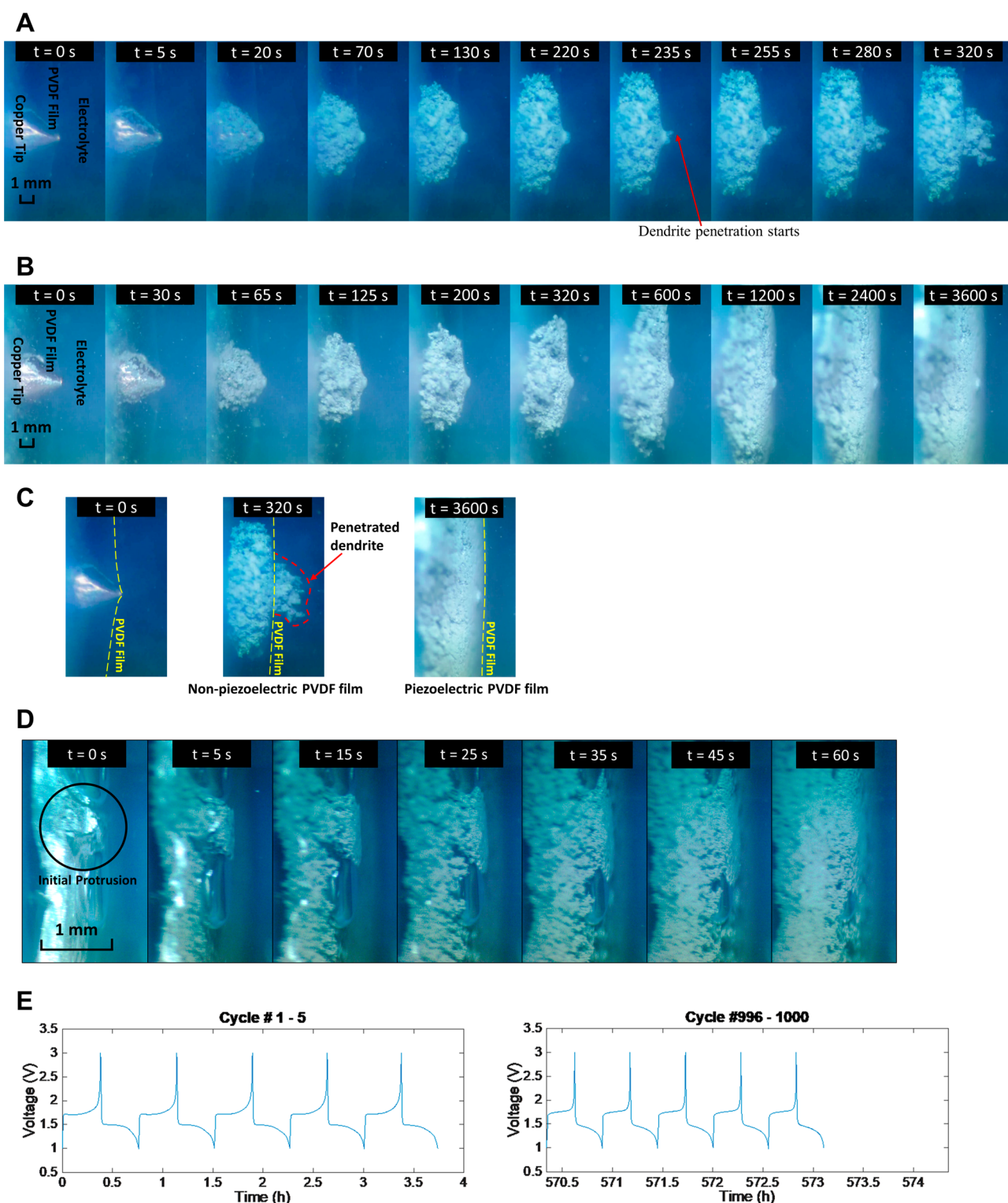


Figure 3. (A–C) Comparison between nonpolarized (NP) and polarized (P+) PVDF film under the same applied current of 2.5 mA (current density ~ 200 mA/cm²). (A) Nonpolarized PVDF film gets penetrated within 5 min. (B) Piezoelectric polarized PVDF film successfully suppresses dendrite penetration, confining deposited lithium into a flat surface. No penetration after 1 h. (C) Comparison of morphology. The only difference between NP and P+ films is the presence of piezoelectricity. With the nonpiezoelectric NP film, dendrite penetrates within 5 min. With the piezoelectric P+ film, no dendrite penetration occurs after 1 h. (D) Highly non-flat lithium surface automatically grows flat under the dendrite suppression effect of a piezoelectric film. (E) LTO P+ cell survives 1000 cycles without any sign of short circuit.

The commercial PVDF film has a very low porosity, which is difficult for lithium ions to pass through. We synthesized porous PVDF films by adding ZnO particles and PVDF

powder into a solvent, drying it, and then etching away the ZnO particles to introduce porosity (Figure 2B). The film was then polarized to make it piezoelectric. The XRD results

(Figure 2C and Figure S1) confirm the complete removal of ZnO in the film and shows a strong peak of the β -phase, which is the phase with strong piezoelectric effect. Another desired property of PVDF is that it is transparent once wetted by the organic electrolyte (Figure 2D). This allows us to observe what happens even under the film, which provides more insights on the lithium morphology evolution during deposition. The fabricated PVDF film shows ~ 1 V between its two surfaces across the film thickness under 1% uniaxial in-plane strain (Figure 2E), which is consistent with the typical d_{31} response of a piezoelectric PVDF film.

To highlight the piezoelectric mechanism in suppressing dendrite growth, we compared the nonpolarized (NP) PVDF film with the polarized (P+) PVDF film under the same deposition condition. The PVDF film is non-piezoelectric before polarization. After polarization, the film becomes piezoelectric. Here “P+” refers to that the polarized PVDF film is put on the lithium surface in the orientation that suppresses dendrite growth. The polarization direction of the film is determined by the poling electric field direction during piezoelectric film fabrication (see Experimental Methods) and is marked on the film (Figure S2). A porous PVDF film was cut into two pieces, with one piece going through polarization by an applied electric field so that it becomes piezoelectric. Therefore, the only difference between NP and P+ is the presence of piezoelectricity. Dendrite can form at random locations on a flat lithium, making it difficult to focus with a microscope and compare between experiments. For a controlled experiment, we replaced one electrode of the in situ cell with a copper needle as the deposition substrate. This allowed us to focus on the tip of the copper needle, where dendrite growth and penetration will occur. The setup also accelerated the experiment since the current density was large at the tip area. Note that the same needle, which was thoroughly cleaned after each test, was used for the experiments of NP and P+ films, so that the experimental condition was the same. Before applying the current, the PVDF film was loosely placed in contact with the copper needle. The assembled cell was examined under a microscope to make sure of no damage to the film before testing. We also made sure that the shapes of the film on the tip were consistent between experiments so that there was no difference in contact force, although this condition is not critical since lithium deposition will push the PVDF film and reduce the influence from any initial difference.

Under a current of 2.5 mA (current density ~ 200 mA/cm²), the NP film gets penetrated within 5 min (Figure 3A). In comparison, piezoelectric P+ film effectively suppresses lithium deposition at the tip area, ensuring a flat lithium surface after 1 h deposition with no sign of penetration (Figure 3B). Figure 3C gives a direct comparison of the morphology. A full side-by-side video footage comparison of NP and P+ films is located in Movie S3.

This result shows direct evidence that the piezoelectric mechanism is highly effective in dendrite suppression. For both the NP and P+ cases, the initial lithium deposition onto the copper tip is fairly unconstrained since the PVDF film is not in tight contact with the copper electrode surface. Because of spherical diffusion, the lithium deposition rate will be higher in the tip region than in the base region of the copper electrode. This explains the similar morphology of deposited lithium in the two experiments during the early stage, until a close contact is established between the lithium surface and the film.

As the gap between the film and the copper tip gets filled by the deposited lithium and SEI, the film is locally deformed. In the case of NP film, the deformation at the tip will generate a small elastic energy, which would only slightly affect the reaction kinetics since the film is compliant. It is known that even very stiff films have failed preventing dendrite growth. Therefore, it is not a surprise that dendrites constantly grow and eventually penetrate the film. This will immediately lead to short circuit in a real battery, in which the counter electrode is in close contact with the separator. In the case of P+ film, a piezoelectric over-potential is generated due to deformation in the tip area. By placing the piezoelectric film in the correct orientation (pressing the film will generate an electric field pointing in the direction from the copper electrode to the film, noted as P+), the piezoelectric over-potential causes the deposition at the tip region to be slower than other regions. Since this piezoelectric mechanism is local and strong, the lithium dendrites are successfully suppressed. In the end, the deposited lithium is confined nicely by the film into a flat surface.

It should be noted that the applied current density of ~ 200 mA/cm² in Figure 3 is much higher than the current density of 1 mA/cm² in Figure 1D. The sharp nanoscale needles in Figure 1E shows that aggressive dendrite growth already occurs at a current density of 1 mA/cm². This also confirms that penetration is not by the mild mossy dendrite but by diffusion limited sharp dendrites. The high current density in Fig. 3 ensures that the studied dendrite growth is in the regime of aggressive diffusion limited growth. The result highlights the effectiveness of the piezoelectric film in suppressing even the would-be very aggressive dendrite growth. Polarized PVDF piezoelectric films are known for their superior piezoelectric stability without self-dissipation of charge within its structure and are widely used in commercial pressure sensors. The electrolyte has no electronic conductivity so there are no free electrons to neutralize the piezoelectric potential. Therefore, the film can maintain any generated piezoelectric polarization for a long time. It should be noted that in dendrite suppression, the counter over-potential is generated instantaneously upon dendrite pressing the film. Then dendrite growth is suppressed immediately. The feedback is so fast that there is even no need for the piezoelectric film to keep its polarization for any long time. The lithium surface simply keeps flat during growth. If we halt dendrite growth and resume it later, the suppression effect resumes accordingly. Even if there is a large pre-existing protrusion of hundreds of micrometers long (much longer than a dendrite) so that it takes longer time to suppress it and level it off with the rest of the surface, we show next that the piezoelectric film is still highly effective. Therefore, potential charge dissipation in the piezoelectric film is not an issue, making the approach applicable using diverse piezoelectric materials. We also found that placing the polarized PVDF film in the reverse direction promoted dendrite penetration (Figure S4), which further confirms the significant effect of piezoelectric mechanism on dendrite growth.

To test the capability of piezoelectric film in suppressing dendrite growth in even more extreme conditions, we used a deformed non-flat lithium foil with large irregular protrusions as the deposition substrate. Figure 3D shows that as the deposition proceeds, the lithium surface becomes flattened by the P+ film. For practical lithium metal battery applications, manufacturers will try their best to produce a flat surface for the lithium metal. However, the lithium surface might become

uneven due to scratches during the cell assembly process or become significantly deformed by the cell enclosure. Our result shows that even with an uneven lithium surface, the P+ film is highly effective to confine the deposited lithium to become a flat surface, eliminating any threat of potential short circuit due to unevenly distributed lithium deposition.

To test the performance of piezoelectric PVDF films in a full cell configuration, we chose $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the cathode material as it does not suffer from intercalation stress and has a stable voltage plateau at around 1.5 V against Li. LTO/Li coin cells were assembled with one P+ film at the lithium surface (LTO P+). The cell was charged/discharged with 1C rate during each cycle to potentially form dendrites and cause short circuit. Figure 3E shows that the LTO P+ cells can survive 1000 cycles without short circuits. The contact of the piezoelectric separator with the cathode does not affect its effectiveness in suppressing dendrite. This demonstrates the feasibility of using piezoelectric PVDF films in a full cell setup, and proves the long-term cycling stability of polarized PVDF separators.

In conclusion, we discovered that using a piezoelectric polarized PVDF film as the separator can greatly suppress lithium dendrite growth and stabilize the lithium metal surface morphology in a lithium metal battery. This can be explained by the counter over-potential generated by the piezoelectric mechanism from the PVDF film when it is deformed by surface protrusions. The concept of using piezoelectric material to suppress lithium dendrite growth provides a new direction to solve the challenges in realizing lithium metal battery.

EXPERIMENTAL METHODS

We used a nanoparticle-template method to make porous PVDF films.¹⁹ PVDF powder (Sigma-Aldrich, MW ~534 000) was first completely dissolved in the *N,N*-dimethylformamide (DMF, Sigma-Aldrich, >99.9%) solvent (10 wt %) at 25 °C. Then the same mass (as the PVDF) of ZnO particles (Sigma-Aldrich, 99.99%, avg. 100 nm size) were added to the PVDF solution. The suspension was stirred at high speed and then processed in an ultrasonic bath for 1 h to form a uniform dispersion. A glass substrate was pre-cleaned with acetone, and the uniform mixture of PVDF and ZnO was coated on the substrate. A doctor blade was used to produce a film of uniform thickness. The film was dried at 60 °C in an oven to make the solvent evaporate. After this, the film was immersed in an aqueous hydrochloric acid (37 wt %) and etched for more than 12 h to completely remove the ZnO particles. Deionized water was then used to wash the film several times. These steps produced highly porous thin PVDF separators (~25 μm thickness) with well-constructed paths for Li ion transport. The area loading of PVDF film was about 2.35 mg/ cm^2 . Finally, these separators were purged with argon gas in a glovebox for 1 h at room temperature. Polarization was performed by sandwiching the film between two parallel aluminum plates and applying a voltage of 1200 V (Glassman WK) for 45 min. This process aligned the randomly orientated microscopic polarization domains in the film to the same direction so that the film exhibited macroscopic piezoelectricity.

The surface morphology of the porous PVDF film was characterized using a scanning electron microscope (Phenom Pro). The crystalline phases present in the thin film was identified by X-ray diffraction (Rigaku MiniFlex) operating in the continuous scanning mode with $10^\circ < 2\theta < 60^\circ$.

PTFE plastics block was milled into the shape of the outer shell. PVC plastics bar was milled and used as the electrode holders and spacers. The cover of the cell was made out of aluminum with a quartz glass as the optical window. The cell was sealed using Viton O-rings. Two copper screws served as the electrode poles to conduct current from the electrodes inside the cell to the outside.

The in situ cell was tested using a Biologic VMP3 potentiostat under galvanostatic condition. Cycling was performed by setting the current at 3 mA/ cm^2 , with EIS conducted after each cycle. EIS measurement was performed in the frequency range from 1 Hz to 10 kHz.

Stainless steel 2032 coin cells were assembled to test the performance of PVDF separator. LTO versus Li coin cells used the LTO electrode as cathode, which comprised 80 wt% LTO, 10 wt% carbon black, and 10 wt% PVDF binder, and used the lithium metal foil (Alfa Aesar, 0.75 mm thickness) as anode. The area loadings were 6.9 mg/ cm^2 for the LTO cathode and 40.1 mg/ cm^2 for the Li metal anode. The powder was dissolved in *N*-methylpyrrolidone and thoroughly mixed into a slurry. A doctor blade was used to coat the slurry onto a clean aluminum sheet (15 μm thickness). The coating was dried under vacuum overnight and cut into electrodes for cell assembly.

Coin cells were tested on a Maccor 4000 battery testing system after assembly. LTO versus Li coin cells were cycled under CCCV condition between 1 and 3 V with 5 formation cycles using C/10 rate, followed by 1C rate normal cycles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00289.

- Material characterization and sample preparation (PDF)
- Dendrite growth morphology (MP4)
- Dendrite penetration through a regular separator (MP4)
- Dendrite growth morphology comparison of unpolarized and polarized film (MP4)

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Notes

The authors declare no competing financial interest.

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