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Stretchable Lithium-Ion Batteries Enabled by Device-Scaled Wavy Structure and Elastic-Sticky Separator

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Fast developments and substantial achievements have been shaping the field of wearable electronic devices, resulting in the persistent requirement for stretchable lithium-ion batteries (LIBs). Despite recent progress in stretchable electrodes, stretching full batteries, including electrodes, separator, and sealing material, remains a great challenge. Here, a simple design concept for stretchable LIBs via a wavy structure at the full battery device scale is reported. All components including the package are capable of being reversibly stretched by folding the entire pouch cell into a wavy shape with polydimethylsiloxane filled in each valley region. In addition, the stretchable, sticky, and porous polyurethane/poly(vinylidene fluoride) membrane is adopted as a separator for the first time, which can maintain intimate contact between electrodes and separator to continuously secure ion pathway under dynamic state. Commercial cathode, anode, and package can be utilized in this rationally designed wavy battery to enable stretchability. The results indicate good electrochemical performances and long-term stability at repeatable release–stretch cycles. A high areal capacity of 3.6 mA h cm^{-2} and energy density of up to 172 W h L^{-1} can be achieved for the wavy battery. The promising results of the cost-effective wavy battery with high stretchability shed light on the development of stretchable energy storages.

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The ever-growing demand of customer electronics has driven the development of smart and wearable electronics ranging from flexible smart phone to sensitive robotic skins and soft surgical tools, which fulfill the various functions and can also be integrated with clothes or conformally attached to skin.[1–3] Lithium-ion batteries (LIBs) are one of the most promising candidates to supply power for the wearable electronics, due to their high-energy density and good long-term stability.[4–6] Although the recent advances in the flexible LIBs with reliable bendable characteristic have been achieved, the bending function has not yet met the requirement for the batteries to power stretchable electronic devices. Therefore, increasing effort has been devoted to LIBs that can be stretched while maintaining their electrochemical performances. Additionally, enhancing mechanical performance and safety, exploring large-scaled and industrial production technologies to lower fabrication cost of stretchable LIBs, is also a challenge.[7–9]

To realize the stretchable batteries, the current rigid key components should be either replaced by intrinsically stretchable materials or designed into stretchable structures for heterogeneous integration of hard and soft materials. A pioneered work[10] demonstrated stretchable MnO_2-Zn alkaline batteries based on stretchable fabric with embedded active particles. Up to date, a handful of studies have demonstrated stretchable LIBs, but only on stretchable electrodes using the strategies such as embedding active materials in elastic scaffold,[10] wavy/buckled/wrinkle design,[11,12] and helically coiled spring configuration.[13] Our previous works have successfully demonstrated stretchable electrodes based on porous polydimethylsiloxane (PDMS) sponge[7] and self-healing elastic polymer foam.[9] Peng et al.[11] demonstrated a highly stretchable LIB based on arched structure that could effectively accommodate large strain, but the areal capacity was only around 0.11 mA h cm^{-2}. The pioneer work on the stretchable LIBs by Rogers group[6] could enable reversible levels of stretchability up to 300%, while maintaining capacity densities of about 1.1 mA h cm^{-2}, but it indicated only 20 cycles of recharging without the results about long-term stability. Despite the progress on stretchable electrodes, for stretchable batteries, one of the most difficulty challenges is to have stretchable

packaging. Since stretching would result in internal structure change, it can easily induce leakage. Thus far, there has not been demonstration of stretchable diffusion-blocking packaging or full stretchable battery devices including packing.

In the present work, we introduce a simple method to fabricate full stretchable LIBs based on a wavy shape at the battery device level (It should be noted here that our wavy structure is in macroscopic not microscopic level as indicated in the literature[11,12]) where all the components including cathode, anode, separator, current collectors, and even packaging can be stretched equally for the first time. We also demonstrated the highest energy density up to date and long-term reliability.

Figure 1 indicates the schematic illustration for the wavy battery based on periodically sinusoidal shape. Two key novelties here are important: the device-scaled (millimeter-sized not micrometer-sized wavelength) wavy structure and the stretchable-sticky separator. It should be noted that stretchable batteries have been reported based on wavy/wrinkled/buckled-shaped electrodes in the micrometer-sized scale.[12,14–17] However, the micrometer-sized wavy shape with a large number of wrinkles could lead to the aggregation and detachment of electrode materials under repeatedly dynamic state and the sealing polymer could not guarantee water-preventing, which are both addressed by using the millimeter-sized wavy shape in our study. During stretching, the wavy shape is extended by shape deformation at the macroscopic level, and no components are stretched at the microscopic level. PDMS filled in the valley regions is able to provide reversible deformations of tension and compression. The stretchability for the wavy battery depends on amplitude and wavelength of the repetitive wavy unit. In addition, first used as separator in LIBs, the electrospun polyurethane/poly(vinylidene fluoride) (PU/PVdF) membrane was stretchable, sticky, and porous, which is capable to stick to electrodes together and confirm a good ion contact for the battery especially at dynamic state. Moreover, commercial cathode, anode, and sealing materials could be simply utilized in the wavy battery.

The stretchable-sticky PU/PVdF separator was prepared by electrospinning. PU is considered as a promising candidate for the polymer matrix for the gel electrolyte due to its high elasticity, high tensile strength, and low crystallinity.[18] PVdF could also be adopted as solid or gel polymer electrolyte in LIBs with high mechanical and anodically stability.[19,20] **Figure 2**a shows the scanning electron microscopy (SEM) image of the electrospun PU/PVdF membrane, which is highly porous that could provide a high Li-ion transport and good electrochemical performances. The differential thermal analysis/thermo-gravimetric (DTA/TG) curves (Figure S1, Supporting Information) for the PU/PVdF separator indicates that the composite polymer is thermally stable up to 300 °C. The digital photos in Figure S2 (Supporting Information) show that the PU/PVdF separator could be stretched to 100% strain. The tensile stress versus strain for the PU/PVdF separator in Figure S3 (Supporting Information) indicates that it can afford 120% strain. This good stretchability of PU/PVdF can avoid its break and detachment in the wavy battery by repeated stretching/releasing cycles.

To test the performance of the PU/PVdF separator compared with the commercial Celgard separator in LIBs, coin full cells using commercial $LiCoO_2$ (LCO) cathode coupled with graphite anode have been assembled and tested. The typical discharge/charge voltage profile of the LCO/graphite full cell using the PU/PVdF separator, together with the profile for the cell using regular untreated Celgard separator, is compared in Figure 2b. A higher areal capacity of 3.1 mAh cm^{-2} could be achieved for the cell using the PU/PVdF separator, which is as a result of better wettability (Figure S4, Supporting Information) and smaller electrolyte resistance (Figure S5, Supporting Information) compared with using the Celgard separator.

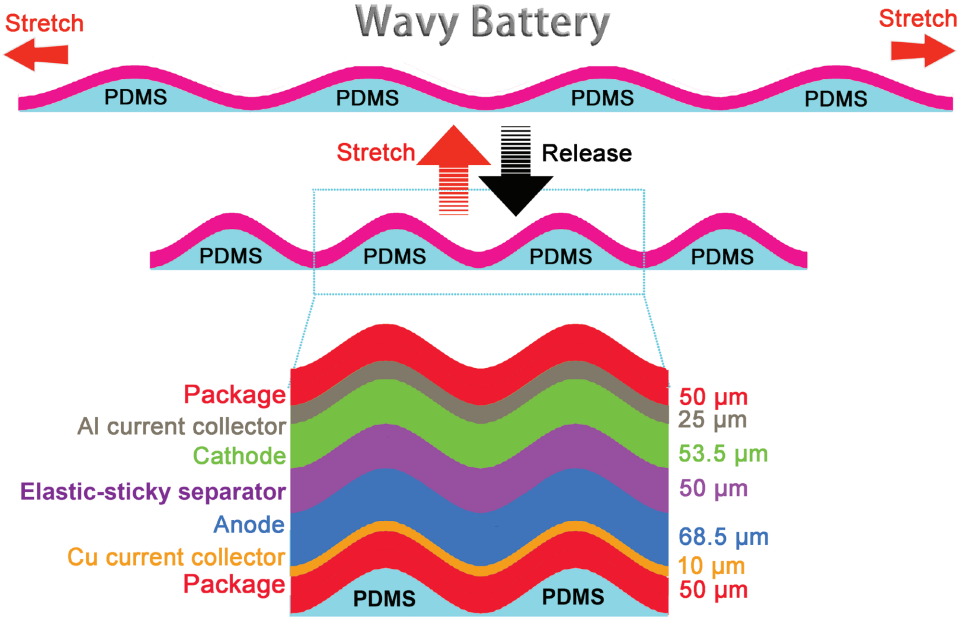

Figure 1. Schematic illustration for the stretchable battery based on device-scaled wavy structure and elastic-sticky separator. Noting that all components including cathode and anode and package are stretchable.

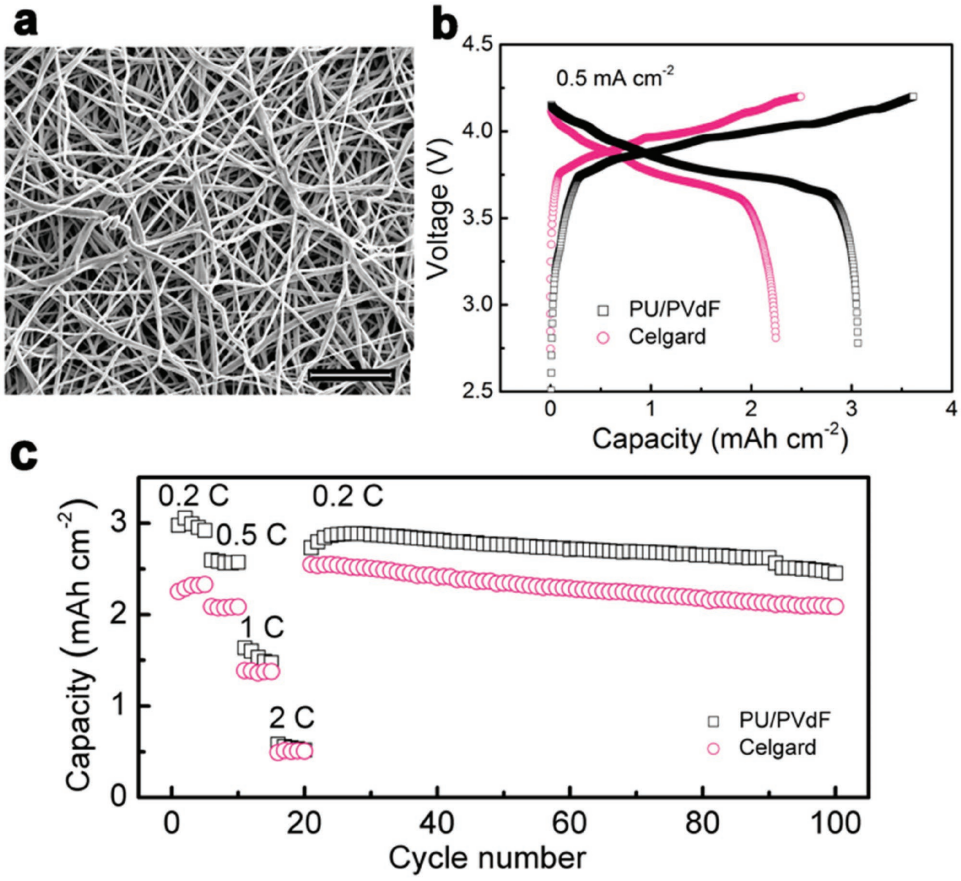

Figure 2. Morphology and electrochemical performances of coin cell using the PU/PVdF separator. a) SEM image of the PVdF/PU separator. Scale bar: 10 μm. b) Comparison of the discharge/charge voltage profiles for the LCO/graphite full cell using the PU/PVdF separator and the Celgard separator. c) Rate capability for the LCO/graphite full cell using the Celgard separator and the PU/PVdF separator.

Rate capability of the cell using the PU/PVdF separator discharged at various current rates from 0.2 to 2.0 C and then to 0.2 C for long cycles is shown in Figure 2c, indicating higher areal capacity and better long-cycle performance in comparison to the cell using the Celgard separator. Figure S6 (Supporting Information) exhibits the full cell cycling performance using the PU/PVdF separator and Celgard separator, which shows a higher areal capacity for the former over 100 charge/discharge cycles at 0.2 C.

In addition, the reason that the PU/PVdF separator is a determining factor for the stretchable-wavy battery is its sticky feature. After calendaring at a high temperature of 60 °C, the multilayers of cathode, anode, separator, and current collectors could be adhesive together tightly. **Figure 3**a shows that the LCO cathode layer with Al current collector could be firmly attached to the sticky separator. It can be seen that the graphite layer was strongly stuck to the PU/PVdF separator after peeling off the Cu current collector (Figure 3b). As shown in the SEM image (Figure 3c), the multilayers of Al current collector, cathode, anode, separator, and Cu current collector (from top to bottom) were bonded tightly. The bonded multilayers therefore could assure a good ion contact for the wavy battery especially under dynamic motions. As displayed in Figure 3d, the amplitude and wavelength of the repetitive wavy unit are 1.6 and 2.4 mm, respectively. The area of the cathode and anode is 200 mm^2 by 20 mm × 10 mm, and the width of the pouch cell is 15 mm.

The electrochemical performances for the wavy battery (pouch cell) using the PU/PVDF separator and LCO/graphite electrodes have been carried out (**Figure 4**). Aluminum-based sealing film was used to offer the capability of blocking molecules diffusion. Figure 4a shows the discharge/charge voltage profiles of wavy battery at released and stretched status, indicating nearly constant areal capacity of about 2.2 mA h cm^{-2}. This good stability for the wavy battery under both the released and stretched status is due to the good contact between separator and electrodes. Moreover, an areal capacity of 3.6 mA h cm^{-2} could be achieved by stacking double mono-cells in parallel, as shown in Figure 4b. Compared to the Celgard separator (Figure S7, Supporting Information), the PU/PVdF separator showed an obvious advantage in the wavy battery, due to its stretchable and sticky ability. Figure 4c shows the discharged areal capacity for the wavy battery at released state at various current rates from 0.25 to 1.0 C and then to 0.25 C, indicating a good rate capability.

The wavy battery with high areal capacity has been achieved, and its electrochemical performance at dynamic state is demonstrated in **Figure 5**. The intensity of the light-emitting diode powered by the wavy battery remained stable when 50% strain

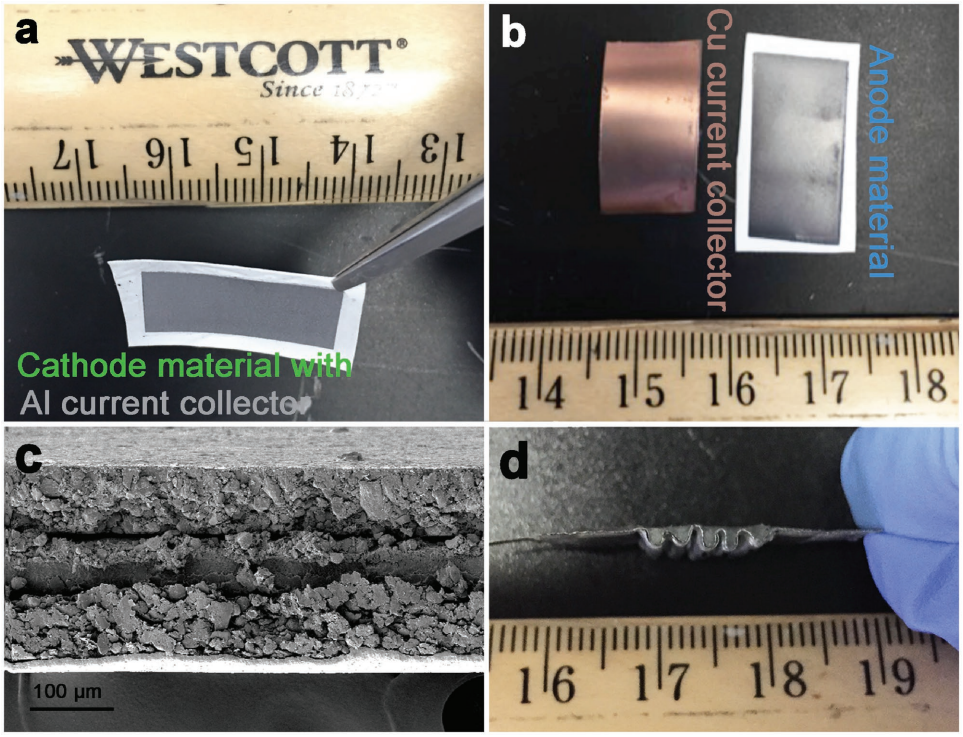

Figure 3. Photos showing that the cathode and the anode can be strongly attached on two sides of the sticky PU/PVdF separator, to assure a good electrical contact. a) The LCO cathode with Al current collector could be firmly attached to the PU/PVdF separator. b) The graphite layer was strongly stuck to the PU/PVdF separator by peeling off the Cu current collector. c) Cross-sectional SEM image of the multilayers of Al current collector, cathode, separator, anode, and Cu current collector (from top to bottom) for the wavy battery. d) Digital photograph of the wavy battery.

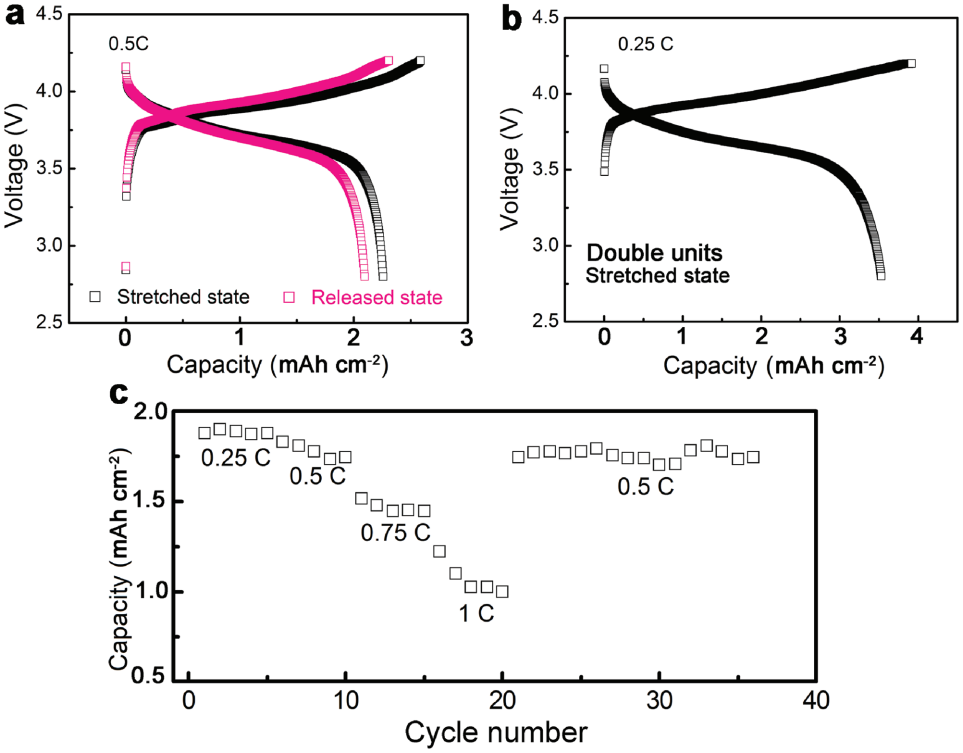

Figure 4. Electrochemical performances of the wavy battery (LCO/graphite full cell) using the PU/PVdF separator. a) Discharge/charge voltage profiles of the wavy battery at stretched and released states. b) Discharge/charge voltage profiles of the wavy battery stacking of double mono-cells. c) Rate capability of the wavy battery using the PU/PVdF separator.

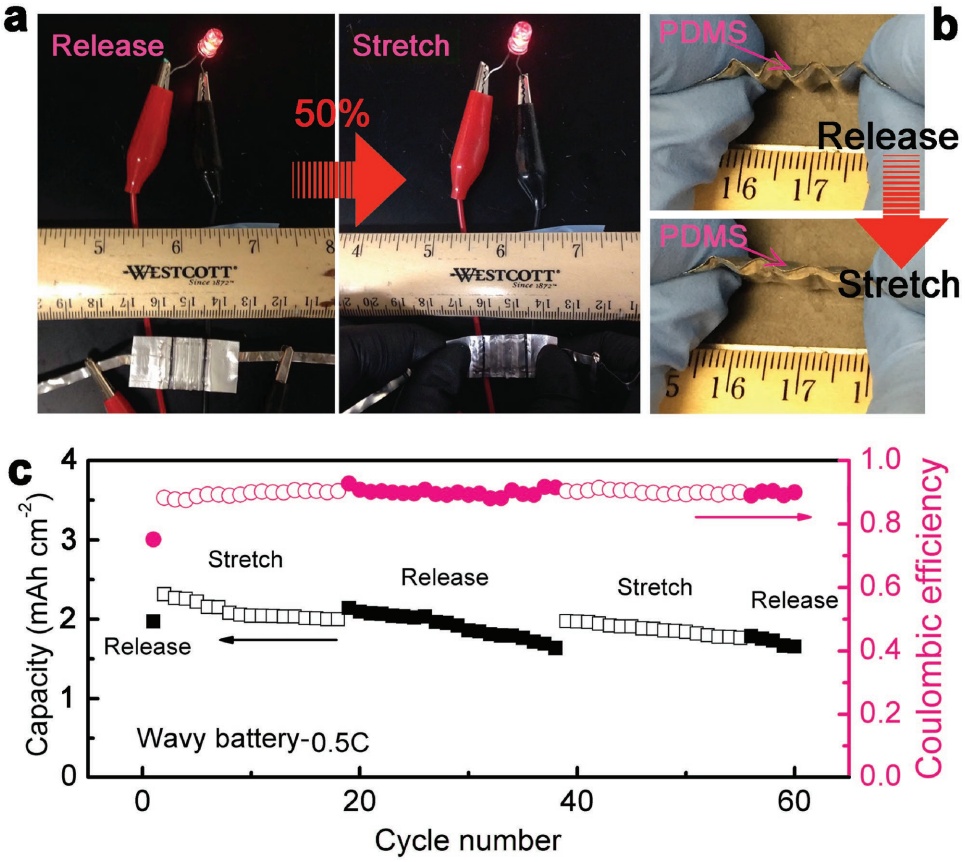

Figure 5. Electrochemical performances at dynamic state of the wavy battery. a) Digital photographs of the wavy battery powering a light-emitting diode at released and stretchable state at 50% strain. b) Photographs showing that when stretching the wavy battery, PDMS was stretched to accommodate the deformation. c) Cycling performance and Coulombic efficiency for the wavy battery under releasing and stretching states (50% strain).

was applied on the battery (Figure 5a). Moreover, long-term cycling of charge/discharge of the wavy battery at 0.5 C rate under dynamic state was carried out as shown in Figure 5c. The first charge/discharge cycle for the wavy battery was performed at released state, and then the battery was run at alternates of stretched (50% strain) and released states till 60 cycles. The results demonstrated that the wavy battery processed highly stable electrochemical performance at dynamic state of repeatable release/stretch cycles. A high areal capacity of about 1.65 mA h cm^{-2} at the 60th cycle under released state was achieved with an 85% capacity retention, which showed a better performance than reported results.[6] It should be noted that this capacity fading is due to the loss of Li deposition at the edge of graphite anode that has equal size to LCO cathode, which could be reduced by the use of anode with larger area than cathode in cell assembly. The liquid electrolyte evaporation may also reduce the cycle ability. Figure 5b clearly shows that when stretching the wavy battery, PDMS filled in each valley region could be strongly attached on the package without detachment, which ensures stretchable ability for wavy battery. Movie S1 (Supporting Information) clearly shows that the wavy battery can be stretched and released reversibly and repeatedly.

Furthermore, for the wearable energy storage systems, large stretchability has been reported in stretchable LIBs or supercapacitors; however, high energy density is still desirably required. The energy density (E, per unit volume) for the wavy battery could be calculated based on the following equation

$$E = c\times(2d_1\times a)\times 3.7/(d_0\times d_2\times b)\left(\text{mW h cm}^{-3}\right)$$
$$= 5.3\times c\times d_1/(d_0\times d_2)\left(\text{W h L}^{-1}\right)$$

where a is the electrode width = 1 cm, b is the package width = 1.5 cm, c is areal capacity, d_0 is half of the wavelength for each wavy unit, and d_2 is the amplitude (Figure S8, Supporting Information). The amplitude and wavelength of the repetitive wavy unit are 1.6 and 2.4 mm, respectively. The energy density of the wavy battery based on LCO cathode and graphite anode is calculated to be about 110 W h L^{-1} (based on the areal capacity of 2.2 mA h cm^{-2}). Moreover, the energy density of wavy battery can be improved by stacking multilayers of the cathode, anode, and separator. The energy density of the wavy battery with double single cells in parallel therefore could even improve to ≈172 W h L^{-1}, which is the highest value among the reported data to the best of our knowledge.

In summary, we have successfully developed stretchable LIBs based on a wavy structure of device scaled level. All components in the battery including the cathode, separator, anode, current collectors, and sealing material were successfully stretchable. A stretchable and porous PU/PVdF membrane

was first used as separator in LIBs, which could stick to electrodes to assure a good ion contact especially during dynamic motions. High electrochemical performance and long-term stability for wavy battery at repeatable release/stretch cycles were demonstrated. A high areal capacity of 3.6 mA h cm^{-2} and a large energy density up to 172 W h L^{-1} could be achieved for the wavy battery by packing double units in series. Collectively, the results represent that the preparation method is simple, and commercial LCO/graphite electrodes and sealing materials could be easily utilized, which can be easily scaled up for commercial fabrication at low cost and high efficiency without complicated procedures. The wavy battery concept can extend to new classes of devices representing promising directions for future research.

Experimental Section

Preparation of PU/PVDF Separator: Commercial PU and PVdF powders with 1:1 wt. ratio were dissolved in the mixture solvent of tetrahydrofuran and dimethylformamide with 1:1 vol. ratio. A transparent solution with a concentration of 10 wt% PU and PVDF was obtained by vigorous stirring. For the electrospinning procedure, the precursor solution was loaded into a 1 mL plastic capillary with a stainless-steel needle. A high voltage of 15 kV was applied by dipping a charged silver thread into the precursor solution. Served as a counter electrode, an aluminum foil was placed 15 cm beneath the needle to collect as-spun composite fibers. The PU/PVDF porous membrane could be obtained by peeling it from the aluminum foil, which could be used as a separator after drying in high vacuum over night at 50 °C.

Fabrication of Stretchable-Wavy LIBs: Commercial cathode (90 wt% $LiCoO_2$, 5 wt% carbon black, 5 wt% PVDF) and anode (95.5 wt% graphite, 2.5 wt% CMC, 2.0 wt% SBR) electrodes were kindly supplied by Samsung Electronics. Before assembly, the stretchable-sticky separator was sandwiched by cathode (20 mm × 10 mm) and anode (20 mm × 10 mm) foil and then calendared at a high temperature of 60 °C, so that the electrodes could be strongly glued on two sides of the separator. The pouch cell consisting of cathode/separator/anode multilayers was sealed using aluminum-plastic membrane with a small opening for later electrolyte injection and then folded into wavy structure by a plastic mold. The width of the package is 15 mm. Subsequently, after injection of electrolyte and sealing, the mixture of silicone elastomer and curing agent at a weight ratio of 10:1 (Sylgard 184, Dow Corning Corporation, Midland, MI, USA) was cast in the valley region of each wavy. A thin layer of polyvinyl alcohol was first deposited on the package material to make sure that the later cast polydimethylsiloxane (PDMS) could be strongly attached. By curing overnight, the stretchable-wavy LIB could be completed. The amplitude and wavelength of the repetitive wavy unit could be controlled to achieve various stretchability for the wavy battery.

Characterization and Electrochemical Measurements: DTA/TG (STA 449, Netzsch) were conducted on the samples under simulated air atmosphere (20 vol% O_2 in Ar, 99.99% pure gases from Airgas). An FEI XL30 Sirion SEM was used to investigate the morphologies of samples. Stress loading–unloading curves were obtained by using dynamic mechanical analysis (TA Instrument Q800). The electrical conductivity investigated using AC impedance spectroscopies was recorded by a Biologic VSP potentiostat over the frequency range of 0.10 Hz to 1 MHz. The coin cells (CR2032, MTI Corporation) are assembled using 1 M solution of $LiPF_6$ in EC:DEC (1:1, w/w) liquid electrolyte. All the assemblies were carried out in a dry glove box filled with argon. Galvanostatic measurements are performed using a 96-channel battery tester (Arbin Instruments). Multiple cells were tested to ensure reproducibility.

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.

Keywords

polyurethane, poly(vinylidene fluoride), sticky separator, stretchable batteries, wavy structure

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