Washable and Stretchable Zn–MnO₂ Rechargeable Cell

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A cell that can operate even when doubled in length, and that withstands washing is demonstrated. The cell employs rechargeable and safe zinc/ manganese dioxide chemistry. It incorporates a biocompatible poly(styrene – isobutylene – styrene) (SIBS) polymer as encapsulation, and in all layers. The SIBS-based separator, made using solvent evaporation-induced phase separation, has an ionic conductivity of 0.05 S m⁻¹. Electrodes contain carbon black, combined with active particles and SIBS as the binder. Stretchable current collectors are carbon black/carbon nanofiber/SIBS composites and exhibit a sheet resistance of 27 Ω⁻¹ under 100% strain. These components are encapsulated by SIBS membranes into a full cell, thin-film configuration, creating a single, polymer-based intrinsically stretchable battery. The resulting cell has a reversible specific capacity of 160 mAh g⁻¹ cathode active mass. Capacity retention is 75% following 500 charge and discharge cycles. Owing to the low permeability of SIBS and the excellent adhesion between its layers, the battery has a good shelf-life (22% mass loss of electrolyte after 523 days) and can withstand 39 washing cycles. The high capacity relative to other stretchable cells, along with the low materials cost, safe chemistry, durability, and washability, make this SIBS cell attractive for wearables and other applications that benefit from stretchability.

1. Introduction

As applications for flexible and stretchable electronics continue to emerge, the need for integration of cost-effective built-in energy storage devices that can endure deformation, while retaining performance and safety, has become apparent. In particular, stretchable batteries have attracted significant interest for powering systems such as wearable devices, electronic skin, strain sensors, and implantable medical devices. Based on the reported work on stretchable and flexible energy storage devices and their proposed applications, Yang et al. has categorized the batteries into two major groups: unidirectional deformable (bendable) batteries, with lithium as the dominant chemistry often researched for high power and capacity applications (>100 mAh), and omnidirectional deformable (soft) batteries, suitable for low power and capacity applications (<10 mAh), where high comfortability, safety, and medical compatibility are required. Advances have been made in recent years in the development of various structural configurations and internal stretchable components, including electrodes, electrolyte, current collectors, and separator membranes. What is missing so far, is the development of stretchable packaging. Such encapsulating material should offer (1) a barrier to gas and liquid exchange in order to minimize the molecular transport in and out of the battery, (2) low modulus to maximize conformability when integrated with stretchable electronics, (3) compatibility with the battery components as well as biocompatibility, particularly in applications where seamless integration of the device and the human body is applicable, (4) ease of fabrication, preferably using the existing manufacturing processes, and (5) mechanical and chemical robustness during the lifetime of the device even under mechanical deformation and during washing.

Research on intrinsically stretchable batteries to date has used polydimethylsiloxane (PDMS), Ecoflex, polyurethane (PU), and butyl rubber as packaging material. Despite high biocompatibility and elasticity, the PDMS cell exhibits limited mechanical strain capability. Ecoflex and PU offer biocompatibility and large strain – however, they demonstrate significant water permeability, affecting cycle life and releasing materials that may not be compatible with the human skin or body. Butyl rubber is widely used as an excellent sealant, due to its low gas and moisture permeability. However, it exhibits low resilience (ratio of released energy after unloading to the deformation energy) and low strength. So far, no effective washable and stretchable encapsulant and cell has been put forward.

It is highly desirable to explore novel packaging materials that enable sealing of functional stretchable batteries. In this study, the use of poly(styrene–isobutylene–styrene) (SIBS) is explored – a triblock thermoplastic copolymer used widely in biomedical applications to fabricate an aqueous stretchable zinc manganese dioxide (Zn–MnO₂) secondary battery. In addition to high chemical stability and biocompatibility, SIBS offers amongst the lowest moisture permeabilities of any elastomer, due to controlled distribution of isoprene and butadiene monomer units in its mid-block. We demonstrate a method to fabricate a multilayer intrinsically stretchable Zn–MnO₂ battery, using SIBS as the unifying component,
enabling stretchability of all the cell layers, as well as offering chemical bonding between the elements. SIBS, with the lowest product of elastic modulus of \( \approx 3 \text{ MPa} \) and water vapor transmission rate (WVTRn) of \( 0.24 \text{ g mm m}^{-2} \text{ day}^{-1} \), and high elongation of \( \approx 680\% \), is used as i) the elastomeric polymer binder in electrode and current collector composite structures, ii) a new class of porous membrane separator material, iii) a heat pressed encapsulating layer, and iv) an adhesive to facilitate binding and sealing of the multilayer stretchable Zn–MnO\(_2\) cell structure. We present the first single-polymer-based stretchable battery, facilitating energy storage, while demonstrating superior long-term washability, and robust mechanical and electrochemical performance under frequent strain cycles. The environmentally friendly Zn–MnO\(_2\) chemistry is chosen for its cost effectiveness, high energy density, low toxicity, and safety.

2. Results and Discussion

In the following sections, we report a simple and cost-effective approach to fabricate all the key components of an aqueous stretchable cell, followed by electrochemical and mechanical characterization.

2.1. Fabrication and Characterization of SIBS/Carbon/Carbon Nano Fiber Conductors

Fabrication of conductive and stretchable conductors is a key challenge in the development of stretchable energy storage devices. Blends of polymers such as Ecoflex\(^{[13]}\) and polystyrene-co-isoprene-co-styrene\(^{[14]}\) with carbon black (CB) and carbon nanotubes (CNT), reported as commonly used intrinsic conductors in stretchable batteries, exhibit sheet resistance of \( \approx 150 \Omega \square^{-1} \) respectively. Introduction of metal based materials (e.g., silver microflakes,\(^{[25]}\) gold nano mesh,\(^{[26]}\) and silver nanowire\(^{[27]}\)) significantly reduces the value to a range of 0.53 to 15 \( \Omega \square^{-1} \). However, the sheet resistance tends to substantially increase during stretch. The best performing stretchable current collector so far, reported by Song \textit{et al.}\(^{[28]}\), is a bilayer composite consisting of Au nanosheets, polystyrene-block-polysoprene-block-poly styrene (SIS), and Ag flakes, with an overall conductivity of \( 1.3 \times 10^5 \text{ S cm}^{-1} \) and a ratio of stretched to unstretched resistance, \( R/R_0 \), of 2.4 after 2000 biaxial strain cycles. We seek an impermeable and stretchable alternative that allows washing.

We start with the highly stretchable SIBS block copolymer (e.g., \( \approx 620\% \) for SIBSTAR 103T MW 100000, 30\% styrene content).\(^{[22]}\) It is mixed with highly conductive carbon black/ carbon nano fibers (CB/CNF) to demonstrate an intrinsically stretchable current collector with excellent mechanical cycling capability and good electrical properties. Initially, different weight ratios of CB are homogeneously mixed with a SIBS/ toluene matrix. The 4:10 weight ratio CB:SIBS (the sample is denoted as SC) demonstrates the highest conductivity (120 \( \Omega \square^{-1} \)) without any cracks across the current collector (Section S1.1, Supporting Information). To further increase the conductivity, CNF is added to the mixture with 1:10, 2:10, and 3:10 weight ratios (denoted as SCC10, SCC20, and SCC30). Large cracks are observed on the surface of SCC30 after curing (Section S1.1, Supporting Information), making this mixture unusable.

![Figure 1. Properties and morphologies of different current collectors. a) Conductivity stand-alone and bonded to a SIBS substrate and b) Young’s moduli. SEMs of c) SC and d) SCC10’s cross sections (scale bar 10 \( \mu \text{m} \)) showing the presence of the fibers, and e) resistance of conductors under strain of up to 100\%, relative to their unstrained resistances. The inserts show SCC10 conductor at 0\% and 100\% strain. f) Conductor’s normalized resistances changes as a function of repeated strain cycles.](image-url)
ratio of additives is essential to keep an appropriate balance between conductivity and stretchability – with the right mix being dependent on the application, and the competing needs of power and compliance.

Scanning electron microscopy (SEM) is used to investigate the morphologies of the conductors with and without CNF (Figure 1c,d). The micrograph of SC’s cross section in Figure 1c shows a homogeneous distribution of CB particles (bright spots) on the surface. The introduction of CNF (Figure 1d) results in creation of linear paths for electron transfer through long fibers, compared to the complex, multi-junction paths created through CB particle contacts in SC. This observation likely explains the conductivity increase in the SCCs.

The robustness of SC, SCC10, SCC20, and SCC10 bonded to SIBS substrate is investigated under various mechanical loadings. Examining resistance changes and mechanical response of the stretchable conductors adhered to the SIBS layer is crucial as these films are bonded to the encapsulation layers in the final cell configuration. The resistance of each sample is measured under gradual imposed strain up to 100%. As shown in Figure 1e, SCC10 bonded to SIBS exhibits a maximum of 80% resistance increase under the applied strain, which is lower than the other samples. The resistivities, however, are decreased when the electrodes are released from stretched state (Figure 1f). The resistance of SCC10 bonded to a SIBS layer increases ~1.8 times from 15 $\Omega$ to $27 \Omega$ after 500 cycles at 100% strain. SEM images of the SCC10 surface before stretching, after stretching, and stretched at 100% strain, shown in Section S1.2, Supporting Information, demonstrate no noticeable cracks or active material delamination from the surface of the current collector. To our knowledge, this is the simplest fabrication and one of the best stretchable polymer-based conductors at retaining conductivity after numerous stretching cycles, reported to date. SCC10 is used as the current collector in this work since the aim is to fabricate a structure that undergoes 100% strain, which can adapt with the maximum strain of human skin varying from 20–100% depending on the location. Nevertheless, increasing initial conductivity and $R/R_0$ of 1.5 under strain, is a better choice when there is less stretchability, for example 40% strain, is desirable.

2.2. Fabrication and Characterization of Stretchable SIBS Separator Membrane

Development of stretchable separators with high porosity and electrical isolation capability is essential for the fabrication of stretchable batteries. In this work, a scalable and simple phase separation process$^{31-34}$ is proposed to prepare a highly porous stretchable SIBS membrane via solvent evaporation-induced phase separation (SEIPS)$^{15-37}$ In this method, phase separation takes place upon evaporation of solvent in a mixture of a polymer dissolved in a volatile solvent and a less volatile nonsolvent.$^{15-37}$ To the best of our knowledge, this is the first report on the fabrication of a stretchable separator using the SEIPS process.

The fabrication process of the SIBS separator, including mixture preparation, casting steps, and pore formation mechanism, is shown in Figure 2a. As illustrated, DMSO is added dropwise into a solution of SIBS and toluene under continuous stirring. The mixture is then cast on a glass slide and dried in an ambient environment. During the evaporation process, the clear mixture becomes turbid due to phase separation between DMSO and SIBS. After complete toluene evaporation, the resulting film is dried in fume hood to remove the remaining DMSO.

Although there are many parameters that affect the membrane morphology (i.e., porosity, pore size, and pore distribution) formation, three key factors namely miscibility, evaporation rate differences, and solution concentration are discussed in this report. DMSO is a widely used polar solvent that is miscible with many polar and nonpolar compounds including toluene. Hansen, Hildebrand solubility parameters along with corresponding miscibility values ($R_v$) with toluene for eight common solvents are presented in Table S2, Supporting Information. As evident by $R_v$ values, DMSO and toluene have a relatively high $R_v$ indicating that the two solvents have low affinity compared to the THF and DMSO solvent pair. This property leads to a slow formation of DMSO-rich droplets and contributes to sponge-like membrane structure, as shown in Figure 2e.

Another important factor contributing to porosity is the difference in volatilities of the solvents. By comparing relative evaporation rate (RER to n-butyl acetate) of the eight solvents, also (Table S2, Supporting information), it can be seen that DMSO has a much lower evaporation rate than toluene, which explains the slow nucleation, growth, and coalescence of DMSO.

Polymer concentration is another parameter affecting the phase separation process. Low polymer concentration reduces the solution viscosity and facilitates convection, benefiting the growth and coalescence of DMSO-rich droplets. Taking into consideration these three factors, the SIBS: toluene: DMSO (9:6:85.4:8.6) system has been examined (different concentration combinations of SIBS: toluene: DMSO and morphologies of resulting membranes are discussed in Figure S2.1, Supporting Information).

The ternary phase diagram (Figure 2b) is constructed by experimental measurements to help predict the phase transition of the (SIBS/toluene/ DMSO) solution during membrane formation. After casting, the composition path (black arrow) crosses a binodal line indicating transition from one phase to two-phase area during toluene evaporation. The phase separation starts from the solution/air interface and then moves downward to the bottom of the cast solution.$^{35}$

As shown in Figure 2c,d,e,f, the membrane has a sponge-like morphology with non-homogeneous pores distributed across the thickness. A highly porous structure is formed on the top surface with pore diameters of ~5 to 10 µm, while a more solid morphology with smaller pore diameters (1–5 µm) is formed at the bottom surface.

The membrane’s ionic conductivity as the function of strain, shown in Figure 2g, is measured using a four-point
electrochemical impedance spectroscopy (EIS) technique (Section S3, Supporting Information). The ionic conductivity of the unstretched membrane is measured as 0.05 S m\(^{-1}\). This value rises to 0.4 S m\(^{-1}\) at 20% strain and is maintained up to 100% strain. In addition to offering stretchability, the membrane exhibits thicknesses (50–250 µm) and a conductivity range (0.01–0.5 S m\(^{-1}\)), and comparable to other reported membranes fabricated by phase inversion method, such as a polyvinylidene fluoride (PVdF) membrane using acetone and ethanol, a PVdF membrane using dimethylformamide (DMF), triethyl phosphate, n-methyl-2-pyrrolidone (NMP), and water, a poly(hydroxyethyl acrylate-co-acrylonitrile) membrane using DMF and water, poly(vinyl chloride), and a poly(methyl methacrylate) membrane using ethylene carbonate and propylene carbonate.

As it is demonstrated in the next sections, the separator exhibits excellent electrical isolation while the battery undergoes mechanical deformations, as well as good electrochemical stability after 700 charge and discharge cycles.

### 2.3. Cell Fabrication Process

A key fabrication challenge for achieving an intrinsically stretchable battery that exhibits functionality for a long period of time under various loading conditions is to provide proper binding in the multilayer structure. This challenge arises from the fact that different stretchable materials with different chemical properties and stiffnesses are often used to fabricate the components of the battery. Under mechanical loading, these components tend to delaminate, which results in life cycle reduction of the battery. Due to the material incompatibility challenges, we have examined the fabrication of an intrinsically stretchable Zn–MnO\(_2\) battery based on a SIBS as the single unifying polymer. In this method, the chemical bonding between layers provides good resistance to cyclic mechanical loading. The cross-section of the proposed stretchable battery is schematically illustrated in Figure 3a.

Solvent casting and hot pressing are examined for encapsulation layer preparation. In the first method, a solution of SIBS...
and toluene is coated on a glass mold. The solution is left in a fume hood for a week to allow full evaporation of toluene. Hot pressing of thermoplastic SIBS involves pressing SIBS pallets at 200 °C for 3 min under 70 kPa pressure to achieve a 200 µm thin film, as illustrated in Figure 3c. This thickness has been reported to exhibit very slow transport across the barrier, and SIBS is close to, if not the best elastomer encapsulant for polar solvents. Hot pressing encapsulation shows loss percentage over 80 days in both solvent cast and hot-pressed encapsulations. While the hot-pressed encapsulation shows loss that reaches 4% after 80 days, the solvent casted packaging proves to be less effective in blocking water evaporation, with a loss percentage of 22%. The increased loss rate could be due to formation of micro voids as the result of micro bubble formations in the SIBS/toluene solvent (a cross section of SIBS layer prepared by both solvent casting and hot press is shown in Section S4, Supporting Information).

The current collector paste is doctor bladed on aluminum foil and then dried in 70 °C for 24 h. Anode and cathode slurries are then directly deposited on current collector layer using doctor blading and then dried at 70 °C for 24 h (Figure 3b). The SIBS heat pressed films, current collector/anode, current collector/cathode, and separator are then assembled using the SIBS/toluene mixture as an adhesive, forming a single-polymer-based battery. Finally, an electrolyte composed of 2 M ZnSO₄ + 0.2 M MnSO₄ is injected into the battery. The presence of MnSO₄ in aqueous solution increases cycling stability significantly by suppressing the dissolution of Mn²⁺ from the cathode into electrolyte during discharge. The battery used for characterization in this paper has the dimensions of 15 mm × 40 mm × 1 mm and the active mass loading on both cathode and anode is 6 mg cm⁻². The electrolyte volume is 400 µL (the weight percentage of battery components is shown in Section S7, Supporting Information).

Microstructure and composition of the anode and cathode are examined using SEM with energy-dispersive X-ray spectroscopy (EDX) (Figure 3d,e). Both Zn and MnO₂ particles...
are dispersed homogeneously on the surface of the electrodes as shown in the EDX. Due to the size difference between Zn (≈15 μm) and MnO2 (≈7 μm) particles, the anode exhibits a rougher topology with similar weight percentage of SIBS and carbon black in both electrodes. Both electrodes display micro-cracks on their surfaces, nevertheless, SSC10 current collectors that are bonded to the electrodes facilitate low impedance electrical connections, even under 100% strain. As evident in the SEM images of the cathode surface before and after stretching at 100% strain (Figure S1d,e, Supporting Information) and the video recording of the cathode during stretching (Video S3, Supporting Information), no signs of delamination of MnO2 particles are observed from the surface of the electrode.

2.4. Cell Electrochemical and Electrochemomechanical Testing

The electrochemical properties of the stretchable battery under normal and shear mechanical loadings are investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests. The CV curves of the battery are obtained at scanning rates of 0.1, 0.5, and 1 mV s⁻¹ between 0.8 and 1.8 V versus Zn/Zn²⁺ (Figure 4a). Two distinct reduction peaks are observed, one at 1.35 V and the other at 1.22 V, agreeing with the reports for co-insertion of Zn²⁺ and H⁺ ions into the MnO2 cathode.[45–49] The discharge curves of stretchable battery at different C-rates are shown in Figure 4b. The highest galvanostatic discharge capacity of the battery, under 0% strain, reaches 6.2 mAh or 160 mAh g⁻¹ active mass at C/12 (3 mAh cm⁻²) or 37.2 Wh L⁻¹ for the coplanar configuration battery) based on MnO2 theoretical capacity of 308 mAh g⁻¹ for 1 e⁻ transfer reaction.[46,47] Based on the chemistry of Zn/MnO2, slight capacity change in the first plateau at ≈1.4 V (faster kinetic reactions) and substantial capacity reduction in the second plateau at 1.3 V is expected when the discharge rate increases.[48,49] However, Figure 4b shows a more dramatic voltage and capacity reduction when the C-rate increases. This could be the result of substantial current collector resistance, which causes significant ohmic drop with the increased charge/discharge rate. An estimate of the resistance for a 15 mm × 30 mm battery gives ohmic drop of 206, 413, and 826 mV at C-rates of 0.5 C, C, and 2 C due to the resistivity of the current collectors, whereas the actual voltage drops are 350, 580, and 840 mV, respectively (refer to Section S9, Supporting Information for detailed calculation of ohmic drop).

Following the electrochemical characterizations at 0% strain, the electrochemical and mechanical properties of the battery are evaluated under various tensile strains. Figure 4c clearly shows that the battery exhibits excellent open circuit voltage (OCV) retention (less than 10 mV fluctuation and recovery after ≈30s) under twisting and stretching on both directions. At C/4, the discharge capacity drops by 25% and 50% and the output voltage is reduced to 1.55 and 1.49 V (value at 0% strain: 1.62 V) under 50% and 100% uniaxial strain, respectively (Figure 4d). This is mainly attributed to rise of the current collectors' internal resistance under mechanical strain. The capacity and voltage loss are recovered when the battery is released to original state, as a result of the current collector regaining full conductivity, as evidenced from Figure 4f. The changes in internal resistance are further verified by EIS measurements shown in Figure 4e. At a scanning frequency of 10 kHz, the internal resistance increases from 77 Ω in an unstretched state to 130 Ω at 50% and 147 Ω at 100% strain, evidencing resistance of current collector is the dominant rate limiting factor. A key to obtain high power is to balance between stretchability and conductivity.

The galvanostatic discharge profiles of the battery are investigated as a function of mechanical loading cycles. As demonstrated in Figure 4f, after 50 and 100 stretching cycles at 100% strain, a respective increase of ≈10% and 50% in the discharge capacity is observed. The capacity reaches stability after ≈150 cycles. It is highly possible that chemical reactions are facilitated under stretching-release cycles through formation of cracks in the electrodes which could result in a significantly larger active interface between the electrolyte and the electrodes, in turn resulting in larger capacity.

The cycling performance of the unstretched battery is tested at a rate of C/3 (Figure 4g). The initial specific capacity of ≈75 mAh g⁻¹ per active mass of MnO2 is doubled after 100 cycles and then gradually fades to ≈43 mAh g⁻¹ after 800 cycles. The Columbic efficiency decreases from 110% to 92% in the first 100 cycles and then ranges from 92–98% in the next 700 cycles, proving that the cell is functional for a large number of cycles with high efficiency. It is important to highlight that a higher than 100% Coulombic efficiency and an increase in capacity in the first 100 cycles is evident. This is likely due to the slow electrode wetting process and additional MnO₂ deposition on the surface of the cathode. The slow wetting process results in higher MnO₂ exposure to the solution in the consecutive discharges and in turn, an increase in both the Coulombic efficiency and capacity.[51] Moreover, additional MnO₂ deposition during charge as the result of addition of MnSO₄ into the electrolyte, partially contributes to an increase in the capacity.[54] The compromised capacity and cycling stability in Zn/MnO₂ have been a subject of study by many research groups. According to Hao et al.[55] during battery operation, Zn²⁺ transport is blocked due to zinc corrosion (zinc corrosion product Zn₂SO₄(OH)₆·5H₂O) and hydrogen evolution, resulting in the formation of a passivation layer on the surface of the anode, and partially irreversible reactions disturbing the surface of cathode in mildly acidic electrolytes. The effect of these kinetically limited irreversible side reactions is more pronounced at lower C-rates as these reactions are reported to be kinetically limited.[50] Mo et al.[56] proposed the use of zwitterionic sulfobetaine/cellulose hydrogel to improve the cycling stability of Zn/MnO₂ chemistry, owing to the existence of both positive and negative charge groups on the polymer backbone. The charge separation is reported to redirect anions and cations of the salt solution independently. This separation could provide higher ionic conductivity and reduce the by-product formation on the anode. Incorporating such hydrogel into our current membrane might improve the cycling stability of the reported battery in this paper.

2.5. Sensibility, Washability, and Capacity as a Function of Temperature

For integration of a stretchable battery into a wearable or implantable device, study of mechanical response is important.
Figure 4. Electrochemical performance of the battery. a) Cycling voltammogram at different scan rates. b) The voltage profiles at different discharge C-rates. c) Final battery structure under twist and +/- 100% strain, with the measured open circuit voltage indicated at the bottom of each photo. d) Voltage discharge profiles (at C/4 rate), and e) EIS from 0.01 Hz to 10 kHz under different strains. f) Voltage discharge profiles (in resting state) of the battery before and after 50, 100, and 150 stretching cycles at 100% strain (at C/2 rate). g) Specific discharge capacity and Columbic efficiency of first 800 charge and discharge cycles.
The schematic illustration in Figure 5a shows a battery under back and forth bending, causing the alternating extension of one electrode and compression of the other. The inset graph demonstrates a typical OCV response to a bend and then holds in the bend state action. The small OCV drops quickly upon bending excitation that induces 18.3% strain difference between the two electrodes, and then recovers to its original value after 100 s (the strain calculation is detailed in Section S6, Supporting Information).

A linear relation between the instantaneous voltage drop and strain is demonstrated in Figure 5a. It is observed that regardless of the bending directions, the OCV always drops. Even though the voltage drop is small (≈15 mV at 18.3% strain), such instant reduction can be employed as a sensing signal, allowing the detection of mechanical loadings. The drop and subsequent OCV recovery may be the result of a disturbance of the double layer capacitance at the electrode/electrolyte interface. This is followed by a slow ion rearrangement (25 s over which the potential restored by 90% of the dropping value) to establish a new dynamic equilibrium. Unlike symmetric Li-alloyed Si electrodes, where the voltage polarity is reversed when the two electrodes system are bent in reserved direction, it is unclear why the voltage polarity does not change in this battery. A possible explanation is due to the non-symmetric geometry of the battery, where the positive electrode (MnO2) and negative (Zn) electrode always attract negative charges and positive charges, respectively.

Figure 5b shows a potential application for the stretchable battery in which the original battery inside a digital watch is replaced by two stretchable batteries in series, integrated into a watchstrap. The watch demonstrates a stable performance with the strap undergoing various mechanical deformations as shown in Videos S1 (stretching) and S2 (twisting and stretching), Supporting Information. This strap allows the watch to run for 2 years of storing in ambient conditions, the watch strap cells are recharged. The digital watch shows full functionality, demonstrating that the battery is still in working condition.

At present, batteries are removed from wearables prior to washing. Smart garments such as smart t-shirt and smart yoga pant have batteries sealed in hard case that need to be removed from the garments before washing. Here, we demonstrate that the highly deformable battery can withstand the wash process. The stretchable battery demonstrates high capacity retention under various wash tests. For wash testing, several stretchable batteries are examined under a variety of wash cycles, having differing temperatures, and while exposed to pure water or water and detergent mix. The open circuit voltage and weight of the battery are measured after each cycle.

During the initial test, a heat-sealed battery was stirred continuously (400 rpm) in a mixture of water and commercial washing detergent (Tide) at 80 °C for 30 min during each cycle. Voltage reduction of ≈30 mV and weight reduction of 20 mg (1%) were observed after eight cycles (Section S5, Supporting Information). The voltage drop is likely the result of accelerated shelf discharge of the battery due to immersion in hot environment.

A home washing machine was used to evaluate the mechanical and chemical durability of a heat-sealed battery under 24 wash cycles. Details of the washing test are summarized in Table 1. Owing to SIBS stretchability and strong chemical bonding between battery components, no signs of electrolyte leakage or material delamination were observed. The discharge capacity, however, increased by ≈41% after these cycles (refer to Section S10, Supporting Information, for details on capacity of the cell before and after washing). This may be due to increased active materials exposure within electrodes resulting from the mechanical agitation of the washing, similar to the effect of deformation seen in Figure 4f. Finally, accelerated wash tests (at 40 °C with detergent added, each cycle lasts for 15 mins) were performed on five cells, including: the cell that withstood the home washing machine tests, three solvent sealed cells, and a heat-sealed cell. The solvent sealed cells showed signs of packaging delamination after 10, 15, and 20 wash cycles. The heat-sealed batteries lasted 25 cycles before showing any signs of electrolyte leakage. The delamination in both cells is observed at the point where solvent is injected between the top and bottom encapsulation layers, prior to complete sealing. This small injection region is solvent sealed. A total of 24 standard and 15 high temperature agitation washes were obtained from the first sample. The test results suggest the commonly accepted
Table 1. Heat sealed stretchable battery home machine wash test conditions.

| Cycle type | Total number of cycles | Temperature | Number of cycles in pure water | Number of cycles in Clorox bleach [pH: 13] |
|------------|------------------------|-------------|-------------------------------|------------------------------------------|
| Cold       | 5                      | 30 °C       | 2                             | 3                                        |
| Warm       | 5                      | 40 °C       | 2                             | 3                                        |
| Very warm  | 5                      | 50 °C       | 2                             | 3                                        |
| Hot        | 5                      | 60 °C       | 2                             | 3                                        |
| Sanitize   | 4                      | 70 °C       | 1                             | 2                                        |

40 to 60 cycles target longevity for clothing \cite{61} can be reached, and that heat sealing works better than solvent sealing. Further optimization of the seal appears to be the key further improvement of washing cycle life.

Next steps with this technology include optimization of the sealing methods, further exploration of the trade-off between electronic conductivity and stretchability – with higher power application potentially benefiting from more conductive but stiffer current collectors – and exploring the application of SIBS in other chemistries (See comparison details with recently reported stretchable batteries in Table S11, Supporting Information).

3. Conclusion

In summary, we have reported a stretchable Zn/MnO$_2$ battery, demonstrating a robust performance under bending, twisting, stretching, and washing. The key to the electrochemical and mechanical stability of the battery is the use of SIBS elastomer as an encapsulant, membrane separator, and adhesion agent, which facilitates the thermal or solvent induced bonding of components. The battery comprises: 1) current collectors made from carbon black/carbon nanofiber/SIBS composite, offering good conductivity even after multiple stretching cycles at 100% strain, 2) highly stretchable and ionically conductive porous SIBS separator that has good ionic conductivity, 3) anode and cathode composites containing active materials (Zn and MnO$_2$)/carbon black /SIBS, and a SIBS packaging layer that enables the cell to keep operating for two years in ambient conditions, and to withstand washing. The resulting battery has a capacity of 160 mAh g$^{-1}$ of active material. The battery is fully functional after 150 cycles of 100% strain, is washable, and could even be used as a sensor to detect mechanical loadings (bending, stretching). SIBS can be similarly applied to other stretchable electrochemical energy storage devices, possibly including lithium-ion batteries and supercapacitors for use in applications where flexibility and stretchability is valued.

4. Experimental Section

Chemicals and Reagents: SIBSSTAR103 (Kaneka), carbon black Super-P Conductive, and zinc sulfate heptahydrate were obtained from Alfa Aesar and used as received. Carbon nanofibers, zinc powder, manganese (IV) oxide, manganese (II) sulfate monohydrate, toluene, and DMSO were from Sigma–Aldrich.

Stretchable Current Collector and Electrodes Preparation and Characterization: The stretchable SIBS-based current collector paste was prepared by dissolving 1 g of SIBS pellets in 5 g of toluene with a magnetic stirring mixer for 4 h. This mixture was used as a base solution to make the current collector and electrode plates, and as a glue to laminate the battery layers together. Current collector slurry was made using 0.4 g of carbon black, 0.1 g of carbon nanofibers, and 6.6 g of the solution using a planetary centrifugal mixer (Thinxy mixer) at 2000 rpm for 3 min followed by a defoaming step to remove all the bubbles formed during mixing, creating a homogenous blend. The Zn paste was prepared by adding 4.5 g of Zn powder and 0.25 g of carbon black into 1.5 g of the base solution. A homogenous slurry was obtained using planetary centrifugal mixer at 2000 rpm for 3 min. The MnO$_2$ electrode was prepared by adding 3.3 g of MnO$_2$ and 0.33 g of carbon black into 2 g of the base solution, using the same mixing procedure as the anode. Once the toluene evaporated, the composition of the current collector was 25%: 6.3%: 68.7% CB: CNF: SIBS, of the anode was Zn: CB: SIBS 90%: 5%: 5%, and of the cathode was MnO$_2$:CB:SIBS 85%: 7.9%: 7.1%.

Stretchable Separator Fabrication and Characterization: The stretchable separator was prepared by first dissolving 1 g of SIBS grains in 15 g toluene with a magnetic stirring mixer for 4 h. 1.5 g of DMSO was then slowly added to the mixture using a pipette while the solution was being stirred. 2 h of stirring took place to ensure the homogeneity of the slurry. Once the toluene evaporated, the composition of the separator was 6.5%: 23%: 70.5% CB: CNF: SIBS. The composite was then applied to the sample and sealed using SEIPS method. The battery components were then packaged using either SIBS solution sealing or hot pressing to bond the edges of the packaging layers.

Electrochemical Testing: Each electrode was subjected to a three-electrode cyclic voltammetric study, where the reference electrode and counter electrode were a standard Ag/AgCl electrode and a zinc plate, using Solartron electrochemical module. The working electrode could be either Zn or MnO$_2$ stretchable electrode. The electrochemical cycling tests were conducted with a battery tester (Landt instrument CT3001A). The EIS was carried out using a 0.01 Hz–10 kHz frequency range with a 10 mV AC voltage amplitude.

Mechanical Characterization: The current collector was subjected to a strain of 20%, 40%, 60%, 80%, and 100% applied using a Bose Electroforce planar testbench under sinusoidal excitation, while the resistance was measured using a multimeter (Fluke 117 true RMS multimeter). The battery mechanical cycling tests were performed using a computer-controlled stepper motor (Compumotor Motor 57-51-MO controlled by a L–N driver) driven linear stage (Daedal 6”x6”) that stretches the samples by 50% and 100% in length. The mechanical stretching frequency was 0.01 Hz, corresponding to strain rates of 1% per s and 2% per s. In bending experiments, the battery was bent around cylinders by hand with different radii from 0.5 to 2 cm in which the cylinder radius determined the induced strain on each electrode. The bending frequency was ~1 Hz. For each radius, the measurement had
been done at least three times. The error bars were different between the minimum and maximum values.

Thermal Characterization: The battery was heated up to 50 °C using a Blue M laboratory oven and cooled down in a Maytag refrigerator, while the capacity was measured using Solartron electrochemical module.

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.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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stretchable batteries, washable batteries, wearable devices, zinc ion batteries

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