Intrinsically stretchable supercapacitors composed of polypyrrole electrodes and highly stretchable gel electrolyte

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Abstract

There has been an emerging interest in stretchable power sources compatible with flexible/wearable electronics. Such power sources must be able to withstand large mechanical strains and still maintain function. Here we report a highly stretchable H_3PO_4-poly(vinyl alcohol) (PVA) polymer electrolyte obtained by optimizing the polymer molecular weight and its weight ratio to H_3PO_4 in terms of conductivity and mechanical properties. The electrolyte demonstrates a high conductivity of 3.4×10^{-3} S cm^{-1}, and a high fracture strain at 410% elongation. It is mechanically robust with a tensile strength of 2 MPa and a Young's modulus of 1 MPa, and displays a small plastic deformation (5%) after 1000 stretching cycles at 100% strain. A stretchable supercapacitor device has been developed based on buckled polypyrrole electrodes and the polymer electrolyte. The device shows only a small capacitance loss of 5.6% at 30% strain, and can retain 81% of the initial capacitance after 1000 cycles of such stretching.

Keywords

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Intrinsically Stretchable Supercapacitors Composed of Polypyrrole Electrodes and Highly Stretchable Gel Electrolyte

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ABSTRACT: There has been an emerging interest in stretchable power sources compatible with flexible/wearable electronics. Such power sources must be able to withstand large mechanical strains and still maintain function. Here we report a highly stretchable H_3PO_4-poly(vinyl alcohol) (PVA) polymer electrolyte obtained by optimizing the polymer molecular weight and its weight ratio to H_3PO_4 in terms of conductivity and mechanical properties. The electrolyte demonstrates a high conductivity of 3.4×10^{-3} S cm^{-1}, and a high fracture strain at 410% elongation. It is mechanically robust with a tensile strength of 2 MPa and a Young's modulus of 1 MPa, and displays a small plastic deformation (5%) after 1000 stretching cycles at 100% strain. A stretchable supercapacitor device has been developed based on buckled polypyrrole electrodes and the polymer electrolyte. The device shows only a small capacitance loss of 5.6% at 30%strain, and can retain 81% of the initial capacitance after 1000 cycles of such stretching.

INTRODUCTION

Stretchable electronics, also known as elastic electronics or elastic circuits, is a technology for building electronic circuits by depositing stretchable electronic devices and circuits onto or embedding them completely into stretchable substrates.[1] Research on stretchable electronics is motivated by the need for electronic systems that can sustain large mechanical strain. They have found broad applications in stretchable devices, such as p-n diodes,[2] polymer light-emitting diodes,[3,4] transistors,[5-7] electronic eyes,[8] active matrix displays,[9,10] and strain sensors.[11,12]

To achieve an integrated stretchable electronic system, a stretchable power source is required. Recently, there has been an emerging interest in stretchable energy storage including supercapacitors[13-16] and batteries.[17-19] Combining such stretchable energy storage devices with the energy harvesting systems to capture energy from human body heat or movement is a promising solution for future wearable electronics.[20] Supercapacitors have attracted tremendous attention due to their high power density and long cycle life.[21] Single-walled carbon nanotube (SWNT) macrofilms on pre-strained poly(dimethylsiloxane) (PDMS),[13,14] SWNT coated textile[15] and polypyrrole coated fabric[16] were developed as stretchable supercapacitor electrodes. Buckled SWNT macrofilms on PDMS showed a specific capacitance of 54 F g^{-1} without strain and 52 F g^{-1} with 30% strain at a current density of 1 A g^{-1}, the specific capacitance did not change up to 1000 charge-discharge cycles. A stretchable supercapacitor fabricated by using SWNT coated textile exhibited a specific capacitance of 62 F g^{-1} at a current density of 1 mA cm^{-2}, and no obvious capacitance loss was observed after being subjected to 100 stretching cycles with 120% elongation. The specific capacitance on polypyrrole coated fabric without strain was 108.5 F g^{-1}

and this increased to 125.1 F g^{-1} with 60% elongation. However, the leakage of liquid electrolyte is a risk when those fabricated supercapacitors are integrated into electronic system.

An intrinsically stretchable supercapacitor requires each device component including electrodes, separator and electrolyte to be stretchable. Compared to liquid electrolyte, polymer electrolytes have several advantages over liquid electrolytes including the ability to minimize percent leakage of electrolytes and ensure non-flammable reaction products at the surface of electrodes.[22-24] They have been widely used in energy conversion and storage devices.[25-28] Currently, there are only a few stretchable solid electrolytes reported such as graft copolymer poly[(oxyethylene)$_9$methacrylate]-g-poly(dimethylsiloxane) doped with LiCF$_3$SO$_3$,[29] poly(methyl methacrylate) networks solvated by the ionic liquid 1-ethy-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMI.TFSI).[30] The fabrication of these electrolytes involves complicated chemical reaction/polymerization, and their conductivities are low (10^{-5}-10^{-4} S cm^{-1}). H$_3$PO$_4$-PVA or H$_2$SO$_4$-PVA is a commonly used gel electrolyte in flexible energy devices.[31,32] Very recently, a stretchable H$_2$SO$_4$-PVA gel electrolyte has been used to prepare stretchable integrated supercapacitor which can sustain 120% strain.[33] It is fabricated by a solvent casting method. However, there is no report on the mechanical properties and stretchability of this electrolyte available. The lack of such knowledge will limit its wide application as a stretchable electrolyte.

Here, we report a highly stretchable electrolyte with high conductivity and mechanical properties. PVA with a molecular weight of 124,000-186,000 g mol^{-1} was chosen and the PVA/H$_3$PO$_4$ weight ratio was optimized. The optimized electrolyte was then coupled with buckled, stretchable polypyrrole electrodes to form an intrinsically stretchable supercapacitor device. The polypyrrole electrode was prepared using a facile electropolymerization method as

described in our previous report.[34] Such supercapacitor can sustain 1000 stretching cycles with 30% strain applied.

EXPERIMENTAL SECTION

Materials. Pyrrole was sourced from Merck, *p*-toluenesulfonic acid and PVA were obtained from Sigma-Aldrich. Orthophosphoric acid (85%) and acetonitrile were purchased from Ajax Finechemicals. Pyrrole was freshly distilled, while all the other chemicals were used as-supplied.

Preparationof stretchable polymer electrolyte. Stretchable polymer electrolyte was prepared by solvent casting method. PVA (1 g) was dissolved in Milli-Q water (10 mL) at 90 ℃ under vigorous stirring until the solution became clear, then an appropriate amount of H_3PO_4 was added into the hot solution and stirred at room temperature overnight. The viscous solutions were cast onto Teflon molds and dried in a vacuum oven at 40 ℃ for 24 h. The dried films were peeled off from the molds and cut into 30 mm×10 mm specimens for further tests.

Preparation of stretchable polypyrrole electrodes. Buckled, stretchable polypyrrole electrodes on Au-coated elastomer poly (styrene-*block*-isobutylene-*block*-styrene) (SIBS) substrate were prepared using a procedure established previously.[34] Briefly, SIBS substrate was prepared by solvent casting from a solution in toluene. A thin Au film of about 30 nm thickness was sputter coated on pre-strained SIBS substrate using an Edwards Auto 306 Sputter Coater, followed by release of the strain to obtain buckled Au microfilms. Polypyrrole with dopant of p-toluenesulfonic acid was galvanstatically electropolymerized on the re-elongated conductive substrate from the solution containing 0.10 M pyrrole and 0.10 M p-toluenesulfonic acid in acetonitrile at 0 ℃ to a charge density of 0.25 C cm^{-2}. The applied current density was 0.25 mA cm^{-2}.

Fabrication of stretchable supercapacitor. The stretchable supercapacitor was fabricated by assembling the stretchable polypyrrole electrodes and stretchable polymer electrolyte in a sandwich configuration. Copper wires were attached on the uncovered gold film of the stretchable polypyrrole electrodes by silver paste for electrical contact. The H_3PO_4-PVA solution was heated to 80 ℃ then the buckled polypyrrole electrodes were immersed in this solution for 10 min, followed by leaving the electrodes in fume hood for 4 h to remove most of the water contained. Such two polypyrrole electrodes with polymer electrolyte were pressed together face-to-face to form a sandwich structure. The whole device was dried at room temperature overnight.

Characterization. The morphology of the buckled polypyrrole electrode was characterized by FE-SEM (JEOL JSM-7500FA). The mechanical properties of the stretchable polymer electrolyte were conducted using Shimadzu EZ mechanical tester with 50N load cell at a stretching speed of 25% min^{-1}, and the gauge length was 20 mm. The samples were stretched and released at a speed of 50% s^{-1} for 1000 cycles for stretchability test. The ionic conductivity was determined using AC impedance using a Gamry EIS 3000™ system in the frequency range of 100 kHz to 1Hz at 30 ℃. For this measurement, the sample was sandwiched between two stainless steel plates with a testing area of 1.4 cm^2. The ionic conductivity is estimated according to the following equation:

$$\sigma = \frac{T}{RA} \quad (1)$$

where T is the thickness of the film (cm), R is the bulk resistance (Ω) obtained from the first intercept on the x-axis of the impedance data in the complex plane, and A is the contact area (cm^2).The effects of temperature and strain on the electrolyte conductivity were investigated between 30 ℃ and 70 ℃, 0% and 100% strain, respectively.

The cross-section of the stretchable supercapacitor was characterized using an optical microscope (Leica DM6000). Cyclic voltammetry (CV) of the stretchable supercapacitor was conducted from 0V to 0.8V using CHI 650D (CHI instruments). Electrochemical impedance spectra were measured using Gamry EIS 3000™ system in the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 10 mV at open circuit potential. Galvanostatic charge–discharge tests of the stretchable supercapacitor were performed using a battery test system (Neware electronic Co.) between 0 V and 0.8 V. Specific capacitance(C_{sp}) of the supercapacitor was calculated from the constant current charge-discharge curves using the following equation:[35]

$$C_{sp} = \frac{I}{m \cdot \frac{dV}{dt}} \qquad (2)$$

Where I is the discharge current, dV/dt is the slope of the discharge curve and m is the total mass of the polypyrrole films on both electrodes.

RESULTS AND DISCUSSION

Properties of the stretchable polymer electrolyte. PVA with varying molecular weight of 30,000-50,000, 85,000-14,6000 and 124,000-186,000 g mol^{-1} were used to prepare the electrolytes investigate here. It was found that stretchable H_3PO_4-PVA film could be obtained only with high molecular weight PVA (124,000-186,000 g mol^{-1}) at the weight ratio of 1:1. No films could be formed using low molecular weight PVA (30,000-50,000 g mol^{-1}). The film obtained from the PVA of medium molecular weight (85,000-146,000 g mol^{-1}) was very sticky and didn't return to the original dimensions after being stretched and released. H_3PO_4 is known act as a plasticizer in the PVA matrix. When H_3PO_4 was added, the free volume of PVA increased, the segment in low molecular weight PVA matrix had higher mobility than that in PVA with higher molecular weight, resulting in relatively lower mechanical strength.[36] At this weight ratio, the polymer chains in low molecular weight PVA didn't come into contact with

each other, so no stable film was formed. When the molecular weight increased, the longer

polymer chains begun to overlap and entangle with each other, leading to stretchable film.[37]

The effect of the weight ratio H_3PO_4/PVA was also investigated over the range 0.5:1, 1:1,

1.5:1, 2:1 and 3:1. Stretchable films were formed only from the solution with H_3PO_4/PVA ratio

of 1:1 and 1.5:1. In the dry films, the weight ratio of pure H_3PO_4 to PVA were 0.85:1 and 1.28:1

(the concentration of H_3PO_4 was 85%), the water content was about 2%. The mechanical

properties of these two stretchable electrolytes are shown in Figure 1, together with that of pure

PVA for comparison. With the increase of H_3PO_4 content, the tensile stress and Young's

modulus decreased, while the elongation to break was enhanced, indicating that the film became

softer with increasing H_3PO_4 content. Pure PVA is partially crystalline and consists of crystalline

layers of folded chains. The interactions between H_3PO_4 and the polymer chain network lead to

an increasing portion of amorphous region.[38] According to the free volume theory,[36] the free

volume of PVA increased with the increasing content of H_3PO_4, which enhanced the PVA chain

mobility leading to the improved elasticity until the H_3PO_4/PVA ratio of 1.5. When the content

of H_3PO_4 continued to rise, the entangled polymer chains started to lose entanglement with each

other, resulting in unstretchable film, and finally no stable film was formed.

The ionic conductivity was found to increase from 9.6×10^{-4} S cm^{-1} to 3.44×10^{-3} S cm^{-1} as the

weight ratio of H_3PO_4/PVA rose from 1.0:1 to 1.5:1, this is attributed to the increased number of

charge carriers, H^+ ions from H_3PO_4.[39] This value is comparable to the conductivity of 0.05 M

H_3PO_4 (5.5×10^{-3} S cm^{-1}), and 1M LiClO$_4$ in propylene carbonate (~10^{-3} S cm^{-1}).[40] The H_3PO_4-

PVA (1.5:1) polymer electrolyte was selected for further tests due to its higher elasticity and

conductivity. The conductivity increased as the temperature went up in the range of 30 ℃ to 70

7

℃ (Figure 2a-b), indicating an Arrhenius type thermally activated process. This process can be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (3)$$

where σ_0 is the pre-exponential factor and E_a is the activation energy required for the process. The estimated values of the pre-exponential factor σ_0 and the activation energy E_a from the curve are 10.57 and 0.20 eV. Similar results were reported by Kufian and coworkers.[39] The increase in conductivity with temperature can be explained by a hopping mechanism between coordinating sites, local structure relaxation and segmental motions of the polymer electrolyte complexes. As temperature increases, the polymer chain moves faster in which bond rotation produces segmental motion. Accordingly, the ion movements become faster, leading to higher conductivity.[41] The conductivity of the stretchable electrolyte under various strains up to 100% remained fairly constant at approximately 3.4×10^{-3} S cm^{-1} (Figure 2c-d).

The electrolyte was then subjected to 1000 strain cycles with 100% elongation applied. The accumulation of plastic deformation (defined as the length increase at the relaxation state), and the variation in conductivity of the electrolyte film were investigated. No plastic deformation was observed for the first 100 cycles, and the deformation was only 5% after 1000 cycles (Figure 3), indicating that this electrolyte is highly stretchable. The conductivity remained constant after such 1000 cycles of elongation-relaxation, which was still 3.1×10^{-3} S cm^{-1}. These results clearly demonstrate that this stretchable electrolyte is mechanically robust.

Electrochemical properties of the stretchable supercapacitor. The polypyrrole electrode exhibited a buckled structure along the elongation direction with 1 buckle per μm, and polypyrrole film displayed a cauliflower morphology composed of large nodules (Figure 4a-c). The highly stretchable electrolyte layer formed between two electrodes serves as separator and

electrolyte, which enables the whole device intrinsically stretchable. The thickness of the electrolyte layer was about 100 µm (Figure 4d). The schematic configuration of this supercapacitor is also presented for easy understanding (Figure 4e).

The strain applied to test our stretchable supercapacitor was 30%, same as that used for polypyrrole electrodes in our previous report.[34] It should be also pointed out that the application of this highly stretchable electrolyte is currently limited by our stretchable polypyrrole electrodes. The supercapacitor exhibited nearly rectangular CV responses at the relaxation state (i.e. no strain applied) at scan rates up to 50 mV s^{-1} (Figure 5a), which indicated that the charge-discharge processes were highly reversible and kinetically facile. When the scan rate reached 100 mV s^{-1}, the rectangular CV shape became distorted. This may be attributed to the inclusion/ejection and diffusion of counter ions being slow compared to the transfer of electrons in the polypyrrole matrix at high scan rates.[16] With 30% strain applied, the supercapacitor maintained similar CV responses (Figure 5b), suggesting that this supercapacitor was stretchable. The specific capacitances of the supercapacitor at 0% and 30% strain at different scan rates are presented in Figure 5c for comparison. The specific capacitance decreased with the increase of scan rate, this is because at lower scan rates, there is enough time for ions to complete the redox process, resulting in higher capacitance. The supercapacitor at 30% stain delivered lower capacitance than that without strain, which might be due to the decreased electrical conductivity of the buckled polypyrrole electrodes induced by the applied strain.

Impedance spectroscopy was performed to gain an insight into the electrochemical interface properties of the stretchable supercapacitor. The Nyquist plots of the stretchable supercapacitor with 0% and 30% strain are shown in Figure 5d. The stretchable supercapacitor with 0% and 30% strain all showed a line close to 90º at low frequency, indicating a good capacitive

behavior.[42] At high frequency, the intercept point on the real axis represents the resistance of the electrolyte and the internal resistance of the electrodes, which can be called bulk resistance, and the diameter of compressed semicircle is attributed to charge transfer resistance.[43] Both the bulk resistance and charge transfer resistance increased with the applied strain, which agrees with the results from CV. The equivalent series resistance (ESR) of the stretchable supercapacitor at 0% and 30% strain was 9.9 Ω and 16.5 Ω, respectively. Accordingly, the maximum powers could be delivered were 16.2 mW and 9.7 mW, respectively. Wearable system usually contains devices with low-power requirement. For example, a wireless sensors network showed a sensitivity of - 60 dBm with a power consumption of 6.3 mW from a 1.8 V supply,[44] our device can be connected in series to meet this requirement.

The charge-discharge curves of the supercapacitor with 0% and 30% strain at a current density of 0.5 A g^{-1} are presented in Figure 6a. The specific capacitance of the supercapacitor without strain was 23.2 F g^{-1}, and 94.4% of the capacitance was retained (21.9 F g^{-1}) at 30% elongation. In the case of a single electrode, its specific capacitance without strain was 92.8 F g^{-1}. This value was slightly higher than that 84 F g^{-1} offered from polypyrrole electrodeposited on ITO glass using a H$_3$PO$_4$/PVA polymer electrolyte reported by Hashmi *et al.*[45] This stretchable supercapacitor was also investigated after being subjected to 30% strain for up to 1000 stretching cycles at a stretching speed of 2% s^{-1}. A notable IR drop was observed after 1000 stretching cycles (Figure 6b), which can be ascribed to the resistance increase induced by the cracks formed on the buckled polypyrrole film after the continuous stretching. This stretchable supercapacitor delivered a specific capacitance of 20.6 F g^{-1}, 20.0 F g^{-1} and 18.8 F g^{-1} after 100, 500 and 1000 stretching cycles with 30% strain applied, respectively (Figure 6c). It still retained about 81.0%

of the capacitance after 1000 stretching cycles, suggesting the high stretchability of our supercapacitor device.

The cycling stability of the stretchable supercapacitor was assessed at a current density of 0.5 A g^{-1} for 2000 cycles with 0% and 30% strain applied (Figure 6d). The stretchable supercapacitor retained 83.6% of its initial capacitance with 0% strain, and 74.4% with 30% strain. The capacitance loss observed can be ascribed to the mechanical degradation of polypyrrole electrodes during the volume change associated with the doping-dedoping process. It may be improved by producing nanostructured polypyrrole films[46,47] or composing it with carbon based materials such as carbon nanotubes, and graphene.[48,49]

CONCLUSION

We successfully developed a highly stretchable polymer electrolyte with high conductivity (3.4×10^{-3}S cm^{-1}) using PVA with a molecular weight of 124,000-186,000 g mol^{-1} and a weight ratio to H$_3$PO$_4$/PVA of 1.5. The electrolyte was stable and displayed only 5% plastic deformation after being stretched for 1000 cycles with 100% strain applied. The use of this stretchable polymer electrolyte as electrolyte and separator allows fabrication of an intrinsically stretchable supercapacitor with buckled, stretchable polypyrrole electrodes. Our stretchable supercapacitor exhibited comparable performance to that used traditional flat polypyrrole electrodes. This stretchable supercapacitor retained 81% of the initial capacitance even after being stretched for 1000 cycles with 30% strain applied.

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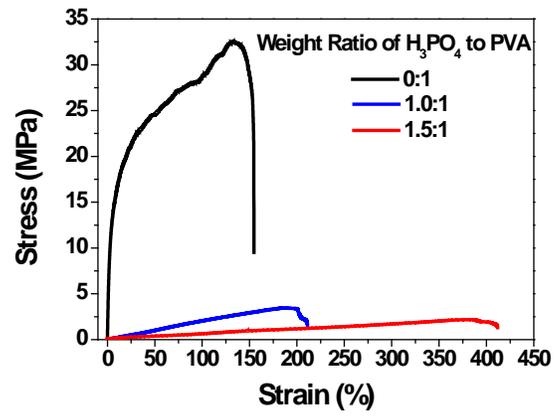(49) Li, X.; Zhitomirsky, I. *J. Power Sources* **2013**, *221*, 49-56.
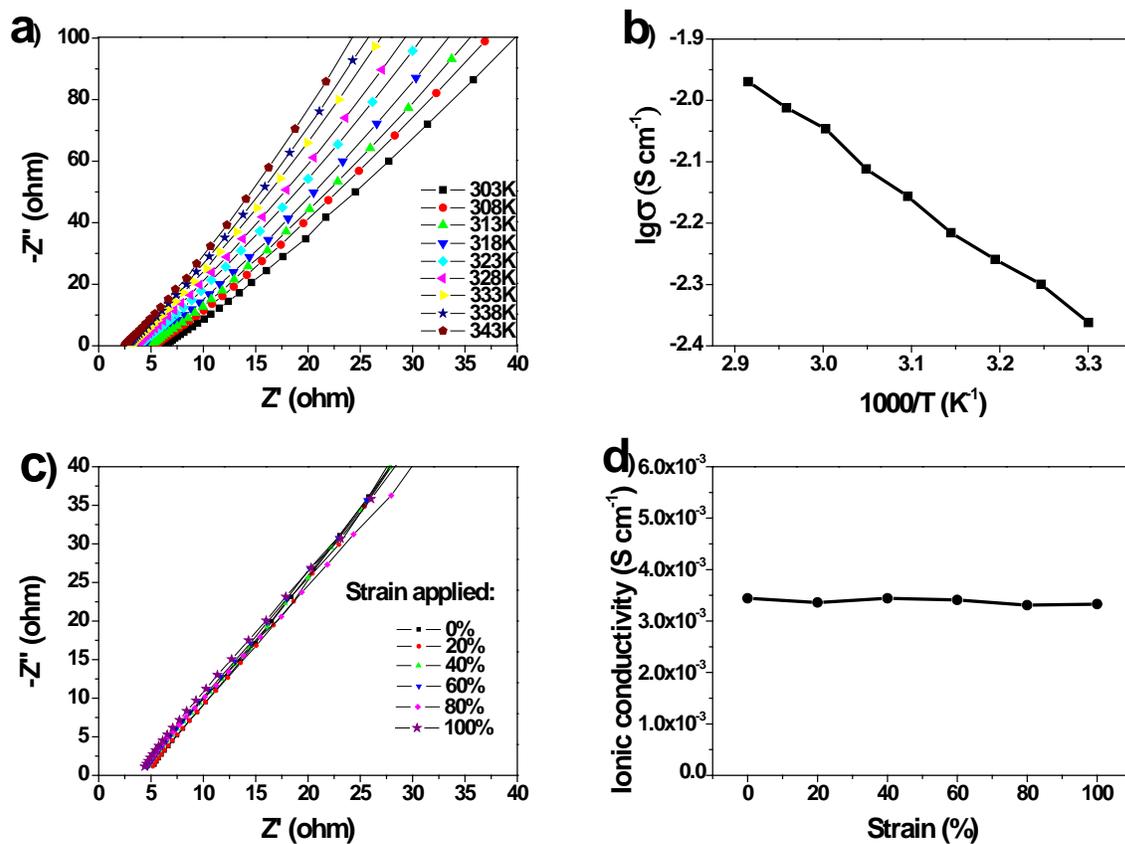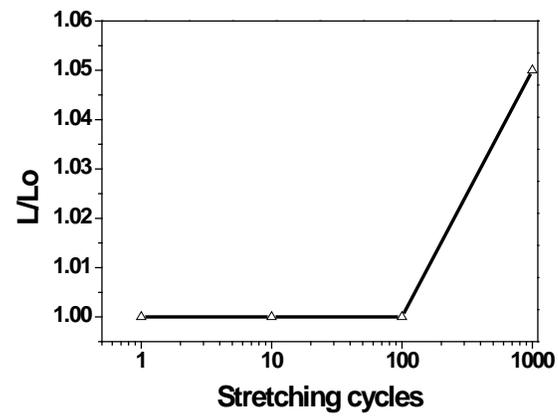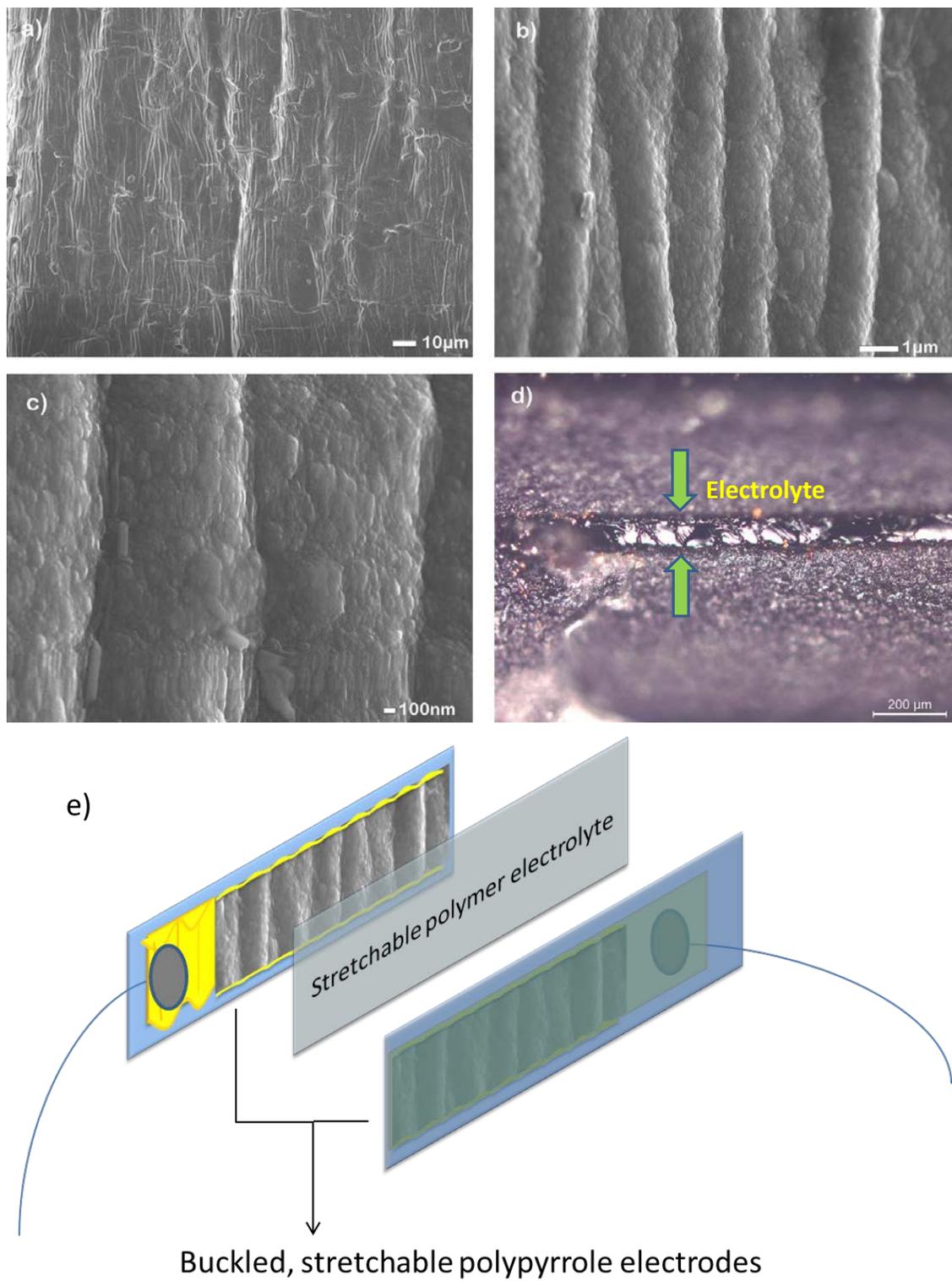
Figure 1

Figure 2

Figure 3

a) b) c) d)

Electrolyte

e)

Stretchable polymer electrolyte

Buckled, stretchable polypyrrole electrodes
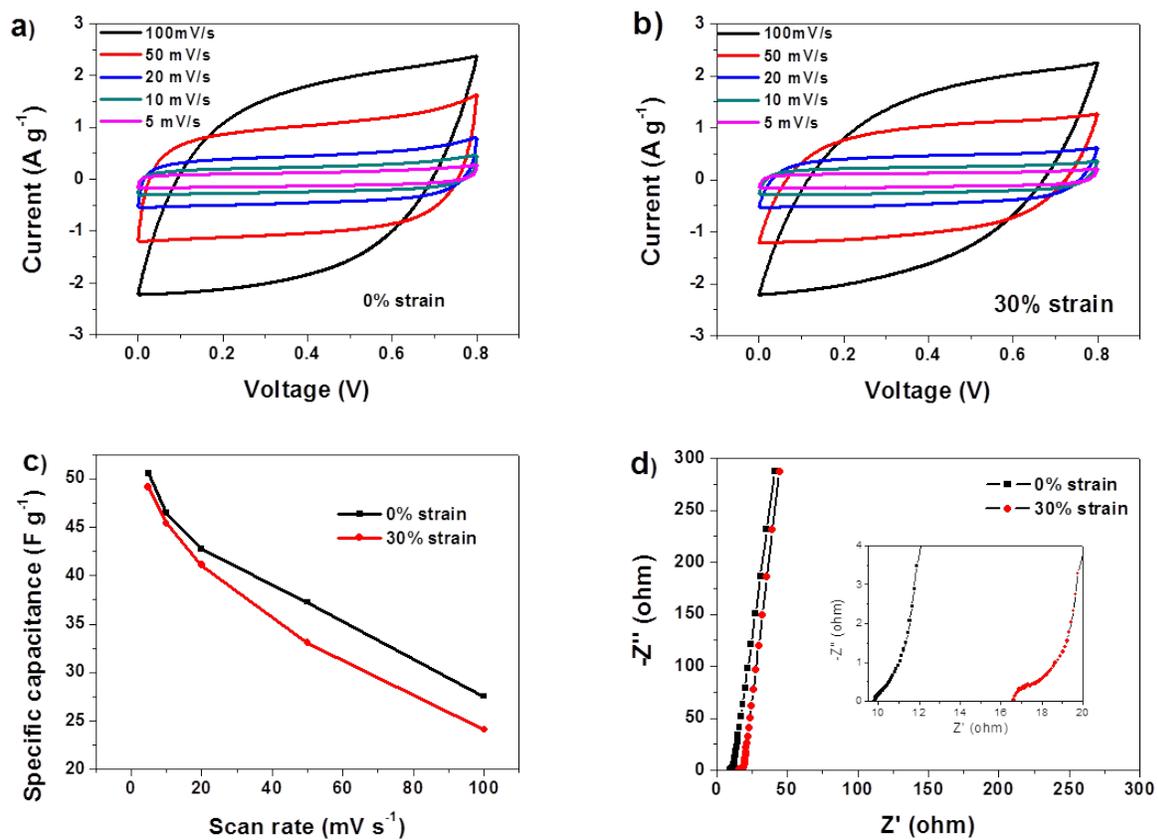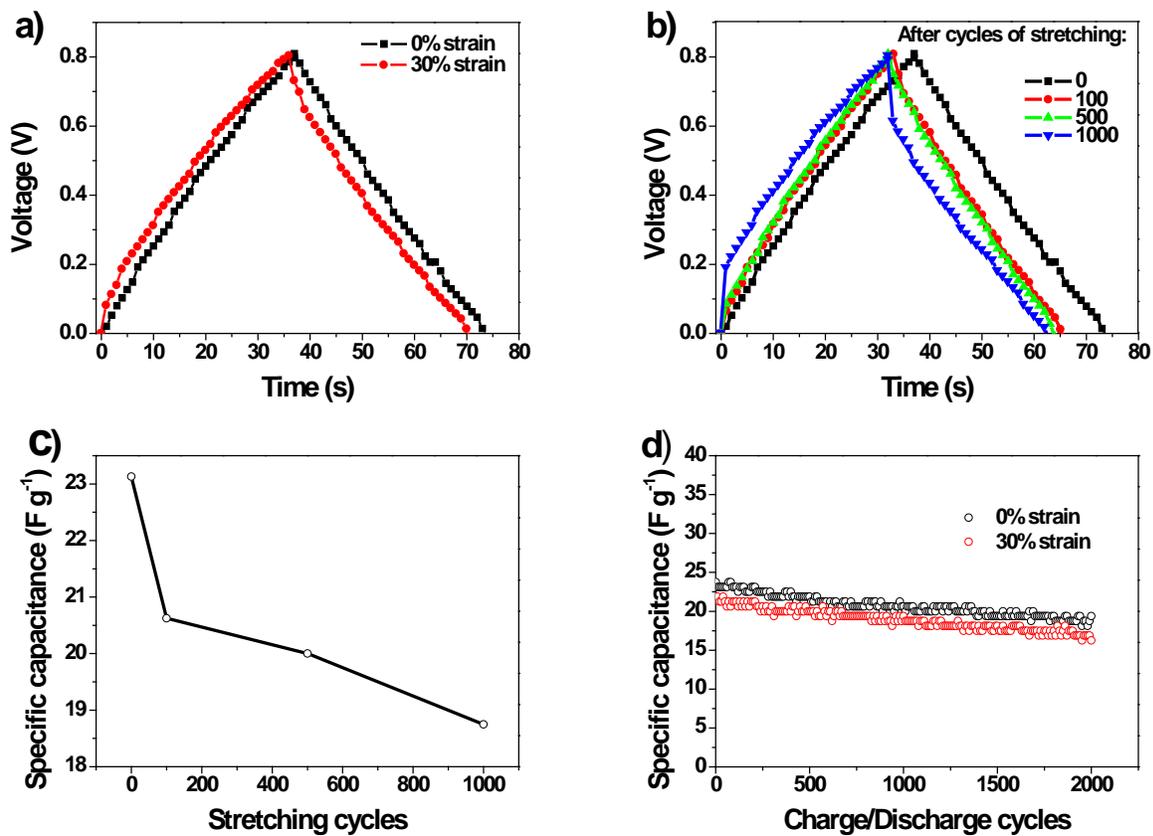
Figure 4

Figure 5

Figure 6

Captions

Figure1: Stress-strain curves of pure PVA and H_3PO_4-PVA electrolytes.

Figure2: (a) Nyquistplots of H_3PO_4-PVA electrolyteat different temperature. (b) Temperature dependence of theconductivity of H_3PO_4-PVA electrolyte. (c) Nyquistplots of H_3PO_4-PVA electrolyte under different strain at room temperature. (d) Ionic conductivity of H_3PO_4-PVA electrolyte under different strain at room temperature.

Figure 3: Plastic deformation of the H_3PO_4-PVA electrolyte with stretching cycle number at 100% strain.

Figure4: FE-SEM images of buckled polypyrrole electrodes at low (a)and high magnification(b, c). (d) Optical image of the cross-section of the stretchablesupercapacitor. (e) Schematic configuration of the intrinsically stretchablesupercapacior.

Figure5: CV curves of the stretchable supercapacitor at different scan rateswith 0% (a) and 30% (b) strain applied. (c) Specific capacitances of the stretchable supercapacitor with 0% and 30% strain as a function of scan rates. (d) Nyquist plots of the stretchable supercapacitor with 0% and 30% strain with frequency ranging from 100 kHz to 0.01 Hz.

Figure 6: (a) Charge-discharge curves of the stretchable supercapacitorwith 0% and 30%strain at a current density of 0.5 A g^{-1}. (b) Charge-discharge curves of the stretchable supercapacitor before and after stretching cycles. (c) Specific capacitances of the stretchable supercapacitor as a function of stretching cycle number. (d) Specific capacitances of the stretchable supercapacitor with 0% and 30% strain as a function of charge-discharge cycles.

Abstract graphic

Buckled, stretchable polypyrrole electrodes