Skin-Inspired Surface-Microstructured Tough Hydrogel Electrolytes for Stretchable Supercapacitors

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ABSTRACT: Double-network tough hydrogels have raised increasing interest in stretchable electronic applications as well as electronic skin (e-skin) owing to their excellent mechanical properties and functionalities. While hydrogels have been extensively explored as solid-state electrolytes, stretchable energy storage devices based on tough hydrogel electrolytes are still limited despite their high stretchability and strength. A key challenge remains in the robust electrode/electrolyte interface under large mechanical strains. Inspired by the skin structure that involves the microstructured interface for the tight connection between the dermis and epidermis, we demonstrated that a surface-microstructured tough hydrogel electrolyte composed of agar/polyacrylamide/LiCl (AG/PAAm/LiCl) could be exploited to allow stretchable supercapacitors with enhanced mechanical and electrochemical performance. The prestretched tough hydrogel electrolyte was treated to generate surface microstructures with a roughness of tens of micrometers simply via mechanical rubbing followed by the attachment of activated carbon electrodes on both sides to realize the fabrication of the stretchable supercapacitor. Through investigating the properties of the tough hydrogel electrolyte and the electrochemical performance of the as-fabricated supercapacitors under varied strains, the surface-microstructured hydrogel electrolyte was shown to enable robust adhesion to electrodes, improving electrochemical behavior and capacitance, as well as having better performance retention under repeated stretching cycles, which surpassed the pristine hydrogel with smooth surfaces. Our approach could provide an alternative and general strategy to improve the interfacial properties between the electrode and the hydrogel electrolyte, driving new directions for functional stretchable devices based on tough hydrogels.

KEYWORDS: double-network tough hydrogel, hydrogel electrolyte, microstructured surface, supercapacitor, stretchable electronics

INTRODUCTION

The emergence of electronic skin (e-skin) to mimic the skin with soft and lightweight thin film electronic devices has driven the rapid progress in intelligent human-machine interfaces, wearable medical devices, soft robotics, and bioinspired sensing and computing systems.1−3 As one of the most promising materials appealing to e-skin, hydrogels, with intrinsic properties resembling to biological tissues, have been extensively exploited to establish ion-based soft electronic devices for e-skin (or hydrogel ionotronics).4−6 In particular, double-network tough hydrogels have raised increasing interest to function as ideal candidates for wearable applications owing to their excellent mechanical properties and functionalities.7,8 These tough hydrogels consist of two polymer networks, either physically or chemically cross-linked, leading to enhanced tensile strength and high fracture energy and toughness while maintaining exceedingly high stretchability over 2000% strain, which surpass the conventional single-network hydrogels having a weak and brittle nature. Moreover, the inherent porous property of hydrogels to hold large amounts of aqueous solution affords tunable ion conductivity, good biocompatibility, mass transport capability, and so on. Therefore, tough hydrogels have been applied in a wide range of stretchable devices including stretchable substrates,5−11 fluidic channels,9,12 wearable force and temperature sensors,13−15 displays,16 triboelectric generators,17 and electrodes.18−20

To date, the request for an integrated energy storage device has become an urgent issue for fully autonomous wearable functions. Among them, supercapacitors can serve as fast charging, safe, and convenient power units for wearable...
applications in which solid-state, gel-like polymers containing aqueous electrolytes are the key elements to realize all-solid-state devices with flexibility.21,22 Thus, in addition to the design of electrode layers with buckled or other stretchable architectures to afford the device stretchability,23−25 elastic hydrogel electrolytes have attracted rising attention for stretchable supercapacitors since they can ensure efficient ion transport without electrolyte leakage while allowing high mechanical flexibility.26 For example, intrinsically stretchable and compressible supercapacitors have been fabricated based on hydrogel networks cross-linked by SiO2 nanoparticles or polyurethane.27−29 Hydrogel electrolytes can be also designed to realize self-healable and cold-resistant devices.30−36 More importantly, double-network tough gels have introduced unique functions for energy storage applications recently, for example, for the fabrication of super-tough, bendable, and compressible supercapacitors with adjustable performance.37−39 as well as safe energy storage devices.40,41 Nevertheless, while tough hydrogels possess high stretchability and strength, stretchable energy storage devices based on tough hydrogel electrolytes have yet to be fully investigated.

A key challenge for the applications of tough hydrogels in stretchable devices is the interfacial bonding between the gel and a variety of materials, which relies on the chemically adhesive interlayers in previous efforts.16,42 Inspired by the skin structure in which the dermis has an outer papillary layer for the tight connection with the epidermis (Figure 1A),43,44 we hypothesized that a microstructured tough hydrogel surface with high surface area could provide an alternative and general approach to improve the interfacial properties between the electrode and electrolyte and enable stretchable supercapacitors with enhanced mechanical stability. Herein, we examined a tough hydrogel electrolyte made of agar/polyacrylamide (AG/PAAm) double networks involving LiCl salts for the fabrication of stretchable supercapacitors in which the tough hydrogel simultaneously served as both the solid-state polymer electrolyte and the stretchable supporting substrate. The prestretched tough hydrogel electrolyte was roughened to generate microstructured surfaces through a straightforward rubbing method followed by direct coating of activated carbon (AC) electrodes on both sides to assemble a prototype monolithic and stretchable supercapacitor device (Figure 1B). By investigating the electrochemical performance of our devices under varied strains, we demonstrated that the tough hydrogel in combination with the surface structuring strategy could enhance the mechanical and electrochemical performance of the stretchable supercapacitor, in addition to the proof-of-concept demonstration of the hydrogel-based power source to drive LEDs.

**EXPERIMENTAL SECTION**

**Synthesis and Characterization of AG/PAAm/LiCl Tough Hydrogel Electrolytes.** All the chemicals were purchased from Macklin Inc. and used as received. The AG/PAAm/LiCl double-network hydrogel electrolyte was synthesized via a one-pot method following the literature.45 Typically, 3.6 g of acrylamide, 225 μL of N,N'-methylene-bisacrylamide (MBA, 10 mg mL−1 aqueous solution), 105 mg of photoinitiator 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropophenone (Irgacure 2959), 0.63 g of LiCl (1 mol kg−1), and 0.3 g of agar (gel strength 1200 g cm−1) were mixed in 15 mL of H2O and ultrasonicated for 20 min followed by degassing in a vacuum chamber. The degassed mixture was then heated at 90 °C until it turned into a clear solution. The homogeneous solution was poured out into a plastic mold, covered with a plastic thin film, and cooled for 30 min to form the first agar gel network. After that, the whole gel was illuminated by UV light (365 nm, 48 W) for 2 h to finish the polymerization and cross-linking of the second PAAm network and obtain the hydrogel electrolyte. The tensile test of the as-prepared hydrogel electrolyte was carried out using SANS CMT4204. For the tensile test, a 3.5 mm wide and 2.5 mm thick dumbbell hydrogel electrolyte sample with a gauge length of 20 mm was used, and the tensile rate was 100 mm min−1. The ionic conductivities of the sample under various strains were measured by electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (CHI 660E, Shanghai Chenhua) in which the sample was sandwiched between two steel plate electrodes with a test area of 1.77 cm2. The conductivity was calculated according to the following formula

$$\sigma = \frac{H}{RA}$$

where H (cm), A (cm2), and R (Ω) are thickness, electrode area, and bulk resistance obtained by the intercept with the X axis in Nyquist plots, respectively. The morphology of the tough hydrogel was characterized with a stereo optical microscope (Leica DVM6).

**Fabrication and Electrochemical Characterization of Stretchable Supercapacitors.** A piece of hydrogel electrolyte was cut to ∼3 × 3 cm2 (thickness ∼3 mm) and prestretched to a certain strain. The surfaces on both sides of the hydrogel were mechanically roughened by slightly rubbing with a piece of sandpaper or a toothbrush. Then active electrode materials (4 mg) consisting of activated carbon (YEC-8A, ∼10 μm particle size, Fuzhou Yihuan Carbon Inc.), acetylene black, and polyvinylidene fluoride with a weight ratio of 8:1:1 were made into slurry and coated on each side of the hydrogel electrolyte followed by the release of the device to the relaxed state. Finally, the obtained activated charcoal electrodes with a
mass loading of about 1 mg cm$^{-2}$ were dried in air for 30 min before testing of the supercapacitor performance.

All the electrochemical measurements of the supercapacitors were performed in a two-electrode system at 25 °C on the electrochemical workstation (CHI 660E, Shanghai Chenhua), including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) measurement, and EIS. The potential range was set as 0–0.8 V for CV and GCD tests. EIS was performed in the frequency range from 10$^5$ to 10$^{-1}$ Hz with a root-mean-square amplitude of 5 mV at open-circuit potential. The specific capacitance for single electrode ($C$, F g$^{-1}$) was calculated from CV and GCD tests according to the following formulas:

$$C = \frac{2lt}{A \Delta V m}$$  \hspace{1cm} (2)

$$C = \frac{1}{m(U_{\text{max}} - U_{\text{min}})} \int_{U_{\text{min}}}^{U_{\text{max}}} \frac{idU}{\nu}$$  \hspace{1cm} (3)

where $I$ (A), $t$ (s), $\Delta V$ (V), $U_{\text{max}}$ (V), $U_{\text{min}}$ (V), $i$ (A), $\nu$ (V s$^{-1}$), and $m$ (g) are discharge current, discharge time, voltage change after voltage drop during the discharging process in the GCD curve, maximum voltage, minimum voltage, current during CV, scan rate of the CV curve, and mass of activated carbon on one electrode (4 mg), respectively.

### RESULTS AND DISCUSSION

To prepare an intrinsically stretchable and tough hydrogel electrolyte, we selected agar (AG) as the first physically cross-linked network and polyacrylamide (PAAm) as the second chemically cross-linked network, in combination with 1 mol kg$^{-1}$ LiCl salts to provide the ionic conductivity. All the AG, PAAm, and AG/PAAm double-network hydrogels have been used as polymer electrolytes for supercapacitors before, showing good flexibility and conductivity.\textsuperscript{38,45} A facile one-pot synthesis approach was employed to obtain the double-network hydrogel electrolyte according to the literature, including a heating–cooling cycle followed by UV-induced polymerization and cross-linking\textsuperscript{38,45} The as-prepared tough hydrogel electrolyte was a transparent elastomeric thin film with superior stretchability and mechanical strength, allowing uniaxially and biaxially stretching, bending, twisting, compressing, and knotting (Figure 2A and Figure S1). As seen from Figure 2A, a piece of hydrogel electrolyte thin film ($\sim$2 × 2 cm$^2$ area and $\sim$2 mm thickness) can be manually stretched to above 1000% strain. In addition, it can withstand the mechanical deformation during the puncture utilizing a centrifuge tube without breakage (Figure 2B). The mechanical properties were then examined in detail from the stress–strain curve (Figure 2C) using a dumbbell-shaped AG/PAAm/LiCl electrolyte sample (3.5 mm in width and 2.5 mm in thickness). It indicated that the as-prepared tough hydrogel electrolyte typically had a fracture stress of 0.38 MPa, a fracture strain of 2185%, an elastic modulus of 0.18 MPa, and a toughness of 4.4 MJ m$^{-2}$, in well accordance with previously reported results.\textsuperscript{38,45} The mechanical properties of the tough hydrogel electrolyte could be adjusted by varying the mass ratio between AG and PAAm, the cross-linker content, and the water content, with the maximum strain varying from $\sim$500 to $\sim$2300%.\textsuperscript{45}

To evaluate the performance of AG/PAAm/LiCl hydrogel as a stretchable solid-state electrolyte, we then investigated its ionic conductivity ($\sigma$) along with mechanical stretching from 0 to 500% strain. After stretching the sample to a certain strain, the hydrogel thin film with an initial thickness of $\sim$3 mm was tightly sandwiched between two steel electrodes for electrochemical impedance spectroscopy (EIS) measurement. Utilizing the bulk resistance ($R$) from the measured Nyquist plots, the measured film thickness ($H$), and the electrode area ($A$), the $\sigma$ can be calculated by $\sigma = H/(R \times A)$. Different from the electronic conductors, the resistance of the hydrogel electrolyte exhibited almost constant values with decreasing thickness.
Figure 3. (A) Stereo optical microscope image of the pristine AG/PAAm/LiCl hydrogel. (B) Stereooptical microscope image of the surface-microstructured tough hydrogel electrolyte by rubbing. The bottom shows the typical cross-sectional profile from the optical image. (C) Photo of the tape peeling test results of two carbon-coated tough hydrogel samples with microstructured (left) and pristine (right) surfaces. The image on the right shows a remarkable loss of carbon particles on the pristine smooth surface after tape peeling. (D) Cross-sectional optical (top) and scanning electron microscope (bottom) images of the surface-microstructured hydrogel electrolyte coated with activated carbon (AC) electrodes. (E) Nyquist plots of the pristine and surface-microstructured tough hydrogel electrolytes tested with AC electrodes on both sides. (F) Photos of the prestretching and release process for the fabrication of stretchable supercapacitor. (G) 3D optical topography image of the wrinkled AC electrode surface in the as-fabricated supercapacitor.

when stretching the hydrogel thin film (Figure S2A). Therefore, the conductivity varied with the same trend as the film thickness. As seen from Figure 2D, it was found that the \( \sigma \) decreased from 13 ± 0.8 to 6.4 ± 1.2 mS cm\(^{-1}\) within the initial strain range between 0 and 300%, and then it remained at ~6–8 mS cm\(^{-1}\) independent of the following strain variation up to 500%. Since the tough hydrogel electrolyte contains a large portion of aqueous solution inside the porous polymer network structures, the ion transport behavior is similar to liquid-phase conductors in which cations and anions oppositely migrate toward the cathode and anode through the solvent under an electric field.\(^{48}\) The ionic conductivity is almost identical to the LiCl solution, and the strain-induced conductivity variation is also consistent with previous reported results on the PAAm hydrogel,\(^{48}\) possibly related to the volume expansion of the hydrogel networks. Such high ionic conductivity was sufficient for supercapacitor applications and could be further increased by using other salts. We also tested its conductivity under repeated stretching cycles and found that the conductivity of the tough hydrogel electrolyte was unchanged after stretching for 500 cycles (Figure S2). Based on the mechanical performance and good ionic conductivity upon stretching, the AG/PAAm/LiCl hydrogel can be considered as both the elastic supporting substrate and the ion-conducting polymer electrolyte with high durability in device applications.

Next, a supercapacitor can be fabricated by simply coating AC electrodes on both sides of the AG/PAAm/LiCl hydrogel electrolyte to form a sandwiched configuration (Figure 1B, see the Experimental Section for details). In order to firmly attach the electrodes to the hydrogel surface, prior to coating, we intentionally roughened the surfaces through gently rubbing with a piece of sandpaper or a toothbrush. After rubbing, the pristine smooth surfaces of the tough hydrogel (Figure 3A) were turned into microstructured surfaces exhibiting irregular microscale ridges and cavities (100–150 \( \mu \)m in width and 10–40 \( \mu \)m in height), as characterized by stereo optical microscopy (Figure 3B and Figure S3), which were in a similar length scale to the AC microparticles with a size of ~1–10 \( \mu \)m. Remarkably, the surface-microstructured hydrogel electrolyte could afford several benefits for stretchable devices. First, for a variety of tough hydrogels, it was found that the first formed polysaccharide network tended to produce a nonsticky and stiff polysaccharide thin shell at the outer surface (Figure S3). Thus, in order to improve the adhesion between the electrodes and electrolyte, mechanical removal of such a surface layer was an efficient way, which introduced microscale roughness as well as exposed the inner hydrogel components that were wetter, softer, and stickier. As proof-of-concept demonstration, we performed tape tests to peel off the AC electrodes coated on the microstructured and the pristine smooth hydrogel surfaces. It was clearly shown in Figure 3C that most of the carbon particles remained on the microstructured surface, while a large portion of the electrodes was detached from the smooth one, leaving a semitransparent surface. Furthermore, the microstructured surface also increased the surface area at the electrode/electrolyte interface, which was believed to not only allow tighter contact between carbon microparticles and the hydrogel but also enhance the capacitive behavior. Figure 3D presents the cross-sectional view of the microstructured hydrogel embedded with carbon microparticles, indicating the tight connections with enhanced contact areas. To investigate the interfacial charge transport, the Nyquist plots of the AC-coated hydrogel electrolytes with
microstructured and pristine surfaces were compared, as shown in Figure 3E. At high frequencies, the interception of the curve at the real part represented the Ohmic resistance ($R_s$) that reflects charge transport in both the electrolyte and electrode materials, while the diameter of the semicircle-like curve indicated the charge transfer resistance ($R_{ct}$) related to the interfacial resistance between the electrode and electrolyte.38 Both $R_s$ (2.8 Ω) and $R_{ct}$ (1.4 Ω) of the sample with the microstructured surfaces were relatively smaller than those with the pristine ones ($R_s = 3.3$ Ω and $R_{ct} = 3.4$ Ω), revealing better performance of the microstructured interface for the charge transport between the electrolyte and electrodes. Moreover, the slopes of the lines at the mid- and low frequencies can reflect the ion diffusion resistance and the capacitive characteristics. The microstructured sample also exhibited larger slopes than the pristine one, suggesting better ionic diffusion and a behavior closer to the ideal electric double layer capacitor. In addition to the interfacial contact, the surface microstructures could also be beneficial to the immobilization of carbon microparticles and improve the stability upon mechanical deformation owing to the microcavity topography as well as the interlocking effect.49,50

Importantly, we found that the carbon electrode layer on the pristine surface could be easily cracked and delaminated from the hydrogel surface when bending or stretching the device (Figure S4A), while losing the film conductivity. In comparison, the electrode layer on the roughened surface did not show notable changes under an optical microscope even with a 2-fold elongation, and the film resistance of AC electrodes remained unchanged within the initial 50% strain, indicating that the attached layer could be preserved to be nearly intact for electronic conduction. In addition, the rough surface was stable after stretching for 1000 cycles (Figure S4B), and the carbon electrodes on the microstructured hydrogel were still attached after cycling.

Knowing that the surface-microstructured tough hydrogel electrolyte could enable the electrode/electrolyte interface with good mechanical and electrochemical properties, we then fabricated monolithic and stretchable supercapacitors that accommodate to large strains through a prestretching and release process. Typically, a piece of AG/PAAm/LiCl hydrogel of 3 cm × 3 cm (≈3 mm thickness) was uniaxially prestretched to a certain strain, roughened by rubbing, and then coated with the AC electrodes on both sides (4 mg for each side, 2 cm² after releasing). The employed prestrain was limited to ~600% for the fabrication of stretchable supercapacitors since the tough hydrogel electrolyte with a thickness less than 0.5 mm at higher strains could undergo rapid dehydration accompanied by a loss of elasticity during the fabrication process. Still, it can well satisfy the stretchability requirement

Figure 4. (A) Cyclic voltammetry (CV) measurements of the supercapacitor prestretched to 350% strain under various strains ($\varepsilon$) from 0 to 350%. The scan rate was 0.1 V s⁻¹. (B) Galvanostatic charge–discharge (GCD) curves of the device under various strains at a constant current of 0.25 A g⁻¹. (C) Comparison of the capacitance obtained under various strains and between the microstructured and pristine hydrogel electrolytes at 0% strain. The errors were derived from the statistics of three devices. (D) Plots of specific capacitance with discharging current at 0 and 350% strains. The inset shows the corresponding GCD curves under a strain of 350%. (E) Nyquist plots for devices under various strains. (F) GCD curves of the device that was biaxially prestretched to 150% strain. The inset shows the photo of the stretched device. (G) Capacitance retention under repeated stretching cycles for devices based on the surface-microstructured AG/PAAm electrolyte (red square) and pristine PAM electrolyte (black circle). The specific capacitance was measured at 1.25 A g⁻¹ and 150% strain. (H) Photo of the yellow LED light powered by three supercapacitor devices in series at the released (left) and stretched (right) states ($\varepsilon = 150\%$).
for practical wearable applications (>100% strain). The following release process resulted in wrinkled electrode layers with a periodicity of ~200–300 μm (Figure 3F,G) in the relaxed state, which could be harnessed to render the device highly stretchable while retaining electronic functions within the range of prestrain.

The electrochemical performance of the as-fabricated supercapacitor was then measured using two pieces of carbon cloth as the current collectors. As shown in Figure 4A, we tested a supercapacitor fabricated at a 350% prestrain using a series of cyclic voltammetry (CV) measurements at a scan rate of 0.1 V s⁻¹ and varying strains of 0, 75, 150, 250, and 350%. As expected, all the CV curves under different strains presented the characteristic rectangular-like shapes in the potential range of 0–0.8 V. The CV curves had almost the same shapes that were difficult to distinguish, showing constant electrochemical performance upon stretching. Figure S5 further shows that the rectangular-like shape of CV curves could be maintained at various scan rates even as high as 0.2 V s⁻¹ for devices under the relaxed state (0% strain) and the fully stretched state (350% strain), indicating the fast ion diffusion in the electrodes. Tests on devices with 600% prestrain were also achieved, showing comparable capacitance between the relaxed and stretched states (Figure SSD).

Next, galvanostatic charge–discharge (GCD) experiments were carried out to investigate the energy storage performance of the stretchable supercapacitor. First, at a current of 0.25 A g⁻¹, the GCD curves obtained under various strains were examined. Again, it demonstrated that the charge–discharge process and the specific capacitance remained almost the same within the strain range from 0 to 350% in which the capacitance upon stretching showed a small variation of 94–105% related to the relaxed state (Figure 4B,C). Even with slight overstretching to 400% strain, the capacitance only dropped to ~90% compared with the relaxed one (Figure S6A). Notably, we also compared the GCD performances between devices based on the microstructured and pristine hydrogel electrolytes without stretching. The pristine hydrogel was shown to result in a capacitance of ~20–30% less than that of the microstructured one (Figure 4C and Figure S6B), suggesting that the microstructured electrode/electrolyte interface could enhance the capacitance with the increased contact area at the microscale. In addition, as the current altered from 0.125 to 5 A g⁻¹, the capacitance of our stretchable supercapacitor still remained similar at the relaxed and stretched states, even though a slight decrease at higher current was observed for the fully stretched device at 350% strain (Figure 4D). For instance, the specific capacitance could reach 90 F g⁻¹ at 0.125 A g⁻¹ for devices under both 0 and 350% strains, while at 5 A g⁻¹, it remained around 52% of the capacitance (47 F g⁻¹) at 0% strain and 47% (42 F g⁻¹) at 350% strain. The capacitance was similar to the reported value using AG/PAAm/LiCl and AC electrodes elsewhere.³⁸ The performance could be improved by increasing the liquid electrolyte penetration to the whole electrode materials, for instance, using thinner and more porous electrode layers.

To further illustrate the interfacial charge transport affected by stretching, impedance spectra of the stretchable supercapacitor were measured with varying strains (Figure 4E). It was found that the Rₜ showed slight variations of ±0.5 Ω between 0 and 75% strains in different batches of devices. Within this range, there was possible stress release of the hydrogel electrolytes under the wrinkled electrodes, and the hydrogel electrolyte might not be elongated too much. However, when the strain exceeded 75%, the Rₜ significantly increased by 1.5-fold or greater (e.g., from 2.5 to 3.5 Ω), possibly due to the strain effect on the ionic conductivity as well as the Ohmic contact. On the other hand, the Rₓ and the line slopes in all Nyquist curves were similar, indicating little adverse effect of the strain on the charge transfer, ion diffusion, and capacitive behavior. Besides, it is also worth mentioning that the hydrogel electrolyte can be biaxially prestretched to endowed the supercapacitor with the biaxial stretchability. As a proof of concept, we tested the GCD performance of the device with 150% prestrain in both the x and y directions, which showed comparable discharging times between the stretched and the relaxed states (Figure 4F). Overall, these results confirmed that the electrochemical performance of the supercapacitor could be well maintained during stretching and releasing based on the surface-microstructured hydrogel electrolyte and the wrinkled electrode layers.

The surface-microstructured tough hydrogel electrolyte could also afford durable performance. First, the electrochemical cycling stability is demonstrated in Figure S7, with ~80% capacitance retention over 6000 GCD cycles at a constant current of 1.25 A g⁻¹ and 150% strain (Figure S7). More importantly, the device was tested to undergo repeated stretching cycles with 150% strain for 800 times. We discovered that, for the first 300 cycles, the device could maintain 90% capacitance, and after 800 stretching cycles, it still preserved ~80% capacitance (Figure 4G). In comparison, with the pristine single-network PAAm electrolyte, which presented adhesive surfaces similar to the microstructured AG/PAAm hydrogel, the device could only withstand cycles of 500 times and was damaged thereafter, associated with a significant capacitance deterioration to ~60%. Clearly, it verified that the tough hydrogel electrolyte with microstructured surfaces could improve the mechanical stability of the stretchable supercapacitor while retaining the capacitance, regardless of the inherent adhesion of the hydrogel surface. Nevertheless, the repeated stretching cycle did lead to changes in the electrodes. As seen from the Nyquist plots of the device after different stretching cycles (Figure S8), the slopes of the line in the low-frequency regime gradually decreased, indicating the increase in the diffusion resistance of ions to the electrode surface. Meanwhile, the long-term stability of the electrolyte could be another major issue (Figure S2), which included the loss of water inside the hydrogel during either the mechanical or electrochemical cycling process lasting for several hours to several days in air (humidity <50%) without encapsulation. Also, the decrease in ionic conductivity could result from the irreversible elongation of the tough hydrogel. Therefore, to improve the device performance based on the tough hydrogel electrolyte, it is better to improve the stability of the electrode and electrolyte structures as well as employ encapsulation and anti-drying additives in future studies.

Following the performance investigation to evaluate the surface-microstructured tough hydrogel electrolyte for stretchable supercapacitors, we further explored supercapacitor devices connected in series to drive an LED as the proof-of-concept demonstration of its practical application. Thin films of conductive carbon nanotube composites (10–30 μm in thickness) were utilized as the current collectors, which were coated with AC electrodes prior to assembly. The electrode-coated thin films were pasted onto the prestretched tough hydrogel surfaces and formed wrinkles to enable the
stretchable applications. The corresponding electrochemical performance was stable with the applied strain, similar to that with carbon cloth (Figure S9). The serially connected devices could supply a voltage of 2.0 V or higher for several minutes, allowing the shining of yellow LED light at both the released and stretched states (Figure 4H and Figure S9). In addition, not only limited to the above demonstrated device, a similar transfer printing approach could be compatible with our surface-microstructured hydrogel for the fabrication of hydrogel-based microdevices. For example, a patterned microsupercapacitor was produced by transfer printing of the prepatterned AC microelectrodes from a PDMS donor substrate onto the microstructured surface of the hydrogel electrolyte (Figure S10). Such a microdevice also showed good electrochemical performance as well as mechanical flexibility, which would be investigated in detail by further studies.

**CONCLUSIONS**

In summary, we demonstrated a skin-inspired strategy to exploit double-network tough hydrogel electrolyte in combination with the microstructured surface for the construction of stretchable supercapacitors, which significantly improved the mechanical robustness and electrochemical performance of the device. The high stretchability, high toughness, and high ionic conductivity of the as-prepared tough hydrogel electrolyte allowed the stretchable devices to withstand diverse mechanical deformations, while the microstructured electrode/electrolyte interface was demonstrated as an essential innovation to enable the robust adhesion of electrode materials and improved interfacial charge transport and capacitance, as well as the performance retention under stretching. This approach can be general and allows further development to realize novel functional stretchable devices. For example, tough hydrogels with other functionalities such as self-healing, anti-freezing, or shape-adaptive properties could be explored in stretchable electronics. The microstructured surface might be rationally designed with lithographic techniques to establish a 3D interface with tunable adhesion, surface area, or optical properties.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b03410.

Additional photos and optical microscope images of tough hydrogel electrolytes and carbon electrodes after stretching, electrochemical measurements of the tough hydrogel electrolyte, stretchable supercapacitors, photos and measurements of devices in series and microdevices (PDF)

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**Funding**

Sun Yat-sen University and National Natural Science Foundation of China (No.21802171).

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is supported by Sun Yat-sen University (“Hundred Talent Plan” Grant and Lab Open Fund Project for Undergraduates) and National Natural Science Foundation of China (No. 21802171). The authors would like to thank Prof. Xuelin Tian at Sun Yat-sen University for the assistance in characterization and Prof. Zijian Zheng at The Hong Kong Polytechnic University for helpful discussions.

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