An Intrinsically Stretchable and Compressible Supercapacitor Containing a Polyacrylamide Hydrogel Electrolyte

Yan Huang, Ming Zhong, Fukuan Shi, Xiaoying Liu, Zijie Tang, Yukun Wang, Yang Huang, Haoqing Hou, Xuming Xie,* and Chunyi Zhi*

Abstract: Stretchability and compressibility of supercapacitors is an essential element of modern electronics, such as flexible, wearable devices. Widely used polyvinyl alcohol-based electrolytes are neither very stretchable nor compressible, which fundamentally limits the realization of supercapacitors with high stretchability and compressibility. A new electrolyte that is intrinsically super-stretchable and compressible is presented. Vinyl hybrid silica nanoparticle cross-linkers were introduced into polyacrylamide hydrogel backbones to promote dynamic cross-linking of the polymer networks. These cross-linkers serve as stress buffers to dissipate energy when strain is applied, providing a solution to the intrinsically low stretchability and compressibility shortcomings of conventional supercapacitors. The newly developed supercapacitor and electrolyte can be stretched up to an unprecedented 1000% strain with enhanced performance, and compressed to 50% strain with good retention of the initial performance.

Modern electronics, such as flexible and wearable energy devices and even soft robots, demand development of soft electrolytes with high stretchability, compressibility, and ionic transport. In particular, highly stretchable and compressible supercapacitors have received attention for their high power density, fast rate of charge–discharge, and long cycling lifetime. However, the widely used polyvinyl alcohol (PVA)-based electrolytes are neither very stretchable nor compressible. To make conventionally rigid supercapacitors stretchable, electron/ion-inactive stretchable substrates (for example, rubber elastomers) and strain-accommodating engineering of device structures (such as, non-coplanar buckled, coplanar serpentine, and wavy structures) have been utilized. These designs give rise to key constraints of low stretchability (most < 100%)[12–14], degraded capacitance at high strains, and low volumetric/mass capacitance because stretchable substrates are used. Compression is another common mechanical deformation for flexible supercapacitors, and yet compressible supercapacitors are rarely investigated, at least partly because widely used PVA-based electrolytes cannot be compressed.

A highly stretchable and compressible polyelectrolyte is urgently needed to realize intrinsic super-stretchability and compressibility of supercapacitor devices. Hydrogels, as hydrophilic polymer networks swollen with tunable amounts of water, are very stretchable and compressible. The water contained in hydrogels can dissolve ions, thus rendering hydrogels good ionic conductors. Consequently, incorporation of hydrogel polyelectrolytes into supercapacitors may extend super-stretchability, compressibility, and ionic conductivity properties to the supercapacitor. Herein, synthesis of a hydrogel polyelectrolyte comprising proton-incorporated polyacrylamide (PAM) cross-linked by vinyl hybrid silica nanoparticles (VSNPs) is described. The PAM was used as the hydrogel polyelectrolyte matrix because of its toughness, whereas the VSNPs were used as stress buffers to dissipate energy when large strain was applied. The prepared polyelectrolyte possesses all the advantages of tunable ionic conductivity, super-stretchability, and high compressibility; as a result, a supercapacitor containing the polyelectrolyte exhibits high capacitance (equivalent to the highest results obtained with the same electrode), intrinsic super-stretchability (unprecedented 1000% stretch with a 2.6-fold capacitance enhancement), and intrinsic high compressibility (50% compression with 99.4% capacitance is retained and a 257-fold supercapacitor weight is held).

It is difficult for pure PAM hydrogels to achieve super-stretchability. Herein, we used VSNPs to reinforce the mechanical properties of PAM hydrogels. VSNPs with an average diameter of 10 nm were obtained from a silicon source, vinyltriethoxysilane (VTES), by a sol–gel process (Figure 1a; Supporting Information, Figure S1). In the VSNPs, silica particles were functionalized by vinyl groups. Subsequently, acrylamide monomers and the as-prepared VSNPs were polymerized together to form the VSNPs cross-linked PAM hydrogel in the presence of ammonium persulfate as the initiator and phosphoric acid as the proton source (Figure 1a). The PAM polymer chains were covalently grafted on the VSNPs in the hydrogel with the aid of the vinyl groups. The strong covalent bonding between VSNPs and PAM chains rendered the VSNPs effective cross-linkers...
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As mentioned in the preceding text, we used the pre-strain approach to fabricate an intrinsically 1000% super-stretchable supercapacitor, which has never been achieved before. The wavy structure of electrodes after release has many uncontacted areas, leaving enough space for deformation and thus avoiding structural breakdown during stretching. The electrochemical performance is enhanced with an increase of strain (Figures 3c,d; Supporting Information, Figure S7). The capacitance calculated from the GCD and CV curves achieves an enhancement factor of 2.6-fold and 2.2-fold at 1000% strain, respectively. The increased contact areas between electrodes and the electrolyte provide more effective materials to participate in the electrocapacitive process and thus contribute to the increased capacitance. Moreover, the use of highly flexible electrodes also endows the supercapacitor with great freedom to deform without structural damage during significant stretching. The pre-stratched wavy structure and use of highly flexible electrodes results in a supercapacitor with enhanced capacitance at super strains; the discovery holds promise in high performance super-stretchable devices.

Because of the intrinsically soft but tough properties of the VSNPs–PAM hydrogel electrolyte, the supercapacitor is also very compressible (Figures 3e,f); it can undergo heavy loads of 257-fold weight of the whole supercapacitor device and correspondingly achieves 50% compression. More importantly, the electrochemical performance is retained at various compressive strains, as indicated by GCDs (Figure 3e), CV curves (Supporting Information, Figure S8a), or impedance spectra (Supporting Information, Figure S8b). These results suggest that our supercapacitor has both mechanical and electrochemical robustness for use in mechanically extreme conditions. Notably, the electrolyte becomes thinner on stretching and compression, which might benefit the electrochemical performance. However, we studied a wide range of electrolyte thicknesses and found that the performance of the supercapacitor was almost unaffected (Supporting Information, Figure S9), which substantiates the good ionic conductivity of our electrolyte. Thus, the effect of electrolyte thickness on the capacitance under stretch and compression is only a very minor factor.

Therefore, the demonstrated good ionic conductivity, super-stretchability, and high compressibility of the VSNPs–PAM hydrogel electrolyte achieve an intrinsically super-stretchable and highly compressible supercapacitor, (Table 1). Most stretchable supercapacitors are realized by addition of stretchable substrates with limited stretch, and few compressible supercapacitors are reported.

In conclusion, we have developed a new polyelectrolyte comprised of PAM hydrogel cross-linked by VSNPs. The polyelectrolyte can be easily stretched to 1500% strain, is very compressible, and has good ionic conductivity. Easily fabricated supercapacitors based on this polyelectrolyte possess unprecedented intrinsic super-stretchability (up to 1000% strain with enhanced capacitance) and high compressibility (up to 50% strain with retention of capacitance). The stretchability and compressibility of supercapacitors originate from the unique polyelectrolyte structure of PAM cross-linked by VSNPs. Our study of intrinsic stretchability and compressibility at the device level, easily fabricated from only...
a few components, paves the way to development of modern electronics such as flexible energy devices and soft robot systems.

Experimental Section

Synthesis of VSNPs cross-linked PAM electrolyte: VTES (3.8 g, Alfa Aesar) was first added to deionized water (30 g) under vigorous stirring until oil-like droplets completely disappeared (12 h) so that a transparent dispersion of VSNPs was obtained. The dispersion of VSNPs was diluted (0.067 wt.%). Acrylamide monomers (12 g, Beijing Chemical Reagent) and ammonium persulfate (0.06 g, Xilong Chemical) were added to the diluted dispersion (20 mL) and stirred for 0.5 h at room temperature. After magnetic stirring, the solution was degassed and sealed under N2 to remove the dissolved oxygen. Subsequently, free-radical polymerization proceeded in a water bath at 40 ± 2°C for 30 h. Finally, the as-prepared polymer was fully dried at room temperature and then soaked in phosphoric acid (500 mL, 2 wt%) for up to 2 days.

Fabrication and electrochemical characterization of the supercapacitor with the VSNPs-PAM hydrogel electrolyte: PPy was electrodeposited on CNT papers (width: 1 cm; length: 10 cm) at 0.8 V vs. Ag/AgCl for up to 2 days.

Electrochemical impedance spectra (EIS) were measured at frequencies ranging from 0.01 to 100000 Hz with a potential amplitude of 5 mV at the open circuit. The capacitance with respect to the single electrode (Cm) was calculated using the charge integrated from GCD and CV curves individually, according to the following formulae:

\[ C_m = \frac{2lt}{U_m} \]  
\[ C_m = \frac{1}{U_m} \int \frac{1}{t} dt \]  

where \( I \) is the discharge current during GCD, \( t \) is the discharge time during GCD, \( U \) is the voltage range (\( U = U_+ - U_- \)), \( m \) is the mass of PPy on one electrode, \( v \) is the scan rate of the CV curve, and \( i(U) \) is the current during CV.

Table 1: Summary of stretchable and compressible supercapacitors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Substrate</th>
<th>Maximum stretch [%]</th>
<th>Maximum compression [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>N/A</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>[14]</td>
<td>elastic fiber</td>
<td>100</td>
<td>N/A</td>
</tr>
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<td>[20]</td>
<td>stainless steel</td>
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<td>N/A</td>
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<tr>
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<td>N/A</td>
<td>100</td>
<td>N/A</td>
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<td>80</td>
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<tr>
<td>[36]</td>
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<td>N/A</td>
<td>90</td>
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</table>

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Conflict of interest

The authors declare no conflict of interest.

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S-T-R-E-T-C-H: An easily fabricated polyacrylamide hydrogel electrolyte incorporated into a supercapacitor instills the device with intrinsic and unprecedented super-stretchability (1000% strain with enhanced performance) and high compressibility (50% strain with retained capacitance).
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