TOPICAL REVIEW — Fundamental physics research in lithium batteries

Wavy structures for stretchable energy storage devices: Structural design and implementation*

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The application of wavy structures in stretchable electrochemical energy storage devices is reviewed. First, the mechanical analysis of wavy structures, specific to flexible electronics, is introduced. Second, stretchable electrochemical energy storage devices with wavy structures are discussed. Finally, the present problems and challenges are reviewed, and possible directions for future research are outlined.

Keywords: stretchable devices, lithium ion batteries, supercapacitors, wavy structure

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1. Introduction

Flexible electronic devices have emerged as an important field of modern electronics. They are essential for many innovative applications, such as wearable electronics, soft surgical instruments, and sensitive robotic skins. To meet the growing demand for flexible electronics, flexible electrochemical energy storage devices such as flexible supercapacitors and lithium ion batteries (LIBs) are needed.[1–4] So far, no clear definition for flexible electrochemical energy storage devices has been accepted. Considering the trends in electronic devices, flexible electrochemical energy storage devices can be defined as devices that can deform and work within a normal elastic range. When the external loading disappears, such devices can completely recover their original state with no additional plastic deformation or electrochemical performance deterioration.[5] Besides deformability, two features of flexible LIBs are notable: (i) ultrathin and ultra-light: compared with the conventional prismatic electrochemical energy storage devices, flexible LIBs ought to be thinner to adapt and integrate into future mobile and wearable electronic devices; (ii) various shapes: in addition to simple prismatic examples, flexible electrochemical energy storage devices should be made in various shapes to meet curved surfaces such as skin and other tissues. Among these, reversible elastic flexibility is the core feature of flexible electronics.

From the viewpoint of practical applications, the typical deformation modes of flexible LIBs include bending and stretching. In today's experience, energy flexible storage devices usually refer to bendable devices such as bendable LIBs, supercapacitors, and solar cells.[2,3,6,7] Another kind is stretchable devices, the production of which is more challenging and difficult.[8]

In general, novel elastic hybrid materials and structural designs are the main routes to stretchable energy storage systems. However, developing stretchable active materials for energy storage systems is extremely difficult, because an appropriate material should meet lots of technical requirements. On the other hand, a novel stretchable structural design can buffer large scale elastic deformation, which is a viable way to achieve stretchability based on the conventional brittle inorganic materials. One of the most popular and effective strategies for designing stretchable structures is wavy structures. Such designs permit large elastic deformation by releasing the strain. Figure 1(a) shows a familiar example of wavy structure design from daily life, a corrugated metal hose. Although they consist of the same material, this hose and the smooth tubes in Fig. 1(b) are quite distinct in their deformability. The corrugated structure is stretchable and compressible, while the smooth tubes show extremely low deformability.[9]

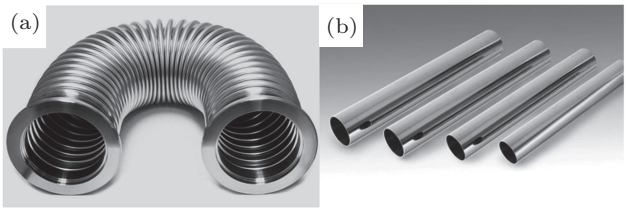


Fig. 1. (a) Corrugated metal hose and (b) straight, smooth tubes.

Recently, intense research has been conducted on stretchable energy storage devices with wavy designs, using conventional inorganic materials.[10–12] This is mainly because the

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familiar active materials in energy storage devices show good conductivity, cost little, and are amenable to fabrication by today's industrial technology. Integrating rigid inorganic materials with soft compliant substrates will become important in the development of flexible electronic devices.

In this brief review, we summarize the application of wavy structures in stretchable electrochemical energy storage devices. First, we introduce the mechanical analysis of wavy structures in flexible electronics. Second, we focus on stretchable electrochemical energy storage devices with wavy structures. Finally, we discuss the existing problems and challenges, and possible directions for future research.

2. Advantages of wavy structure

In practice, stretching-deformation is more challenging than bending-deformation mainly due to the very limited elastic strain extensibility of the conventional electrode materials ($LiCoO_2$:$< 0.1\%$,[13] graphite: $0.1 \sim 0.2\%$,[14] Si:$< 0.1\%$,[13] carbon nanotubes:$< 3.0\%$,[15,16] graphene or graphene oxide membrane: 0.6%,[17] etc.), these materials cannot accommodate large scale elastic strain. Stretching leads to fairly extensive destruction in flexible electrodes due mainly to two processes during stretching: (i) the inorganic active material itself has an extremely low elastic strain, so even a little stretching can fracture the electrode overall; (ii) the active materials may lose electronic contact due to repeated deformation.[18]

To overcome these problems, we should use innovative structures to design the electrodes. We can use structural deformation to buffer deformation of active materials during stretching. One of the most popular stretchable structural designs is the wavy or wrinkled structure. Various wavy structures have found increasingly wide utilization in flexible electronics,[19–21] and have progressively expanded into other fields. Song *et al.*[22] proposed three possible wavy structures: (i) one-dimensional (1D) wavy electrode, (ii) two-dimensional (2D) checkerboard wavy structure, and (iii) 2D herringbone structure.[19,23,24] Figure 2 shows a schematic illustration of different wavy structures.

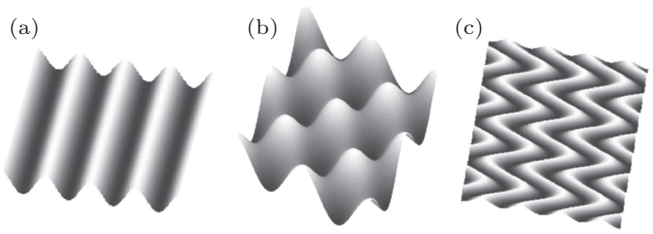


Fig. 2. Wavy designs for flexible electronics: (a) one-dimensional wavy structure, (b) 2D checkerboard wavy structure, and (c) 2D herringbone structure.[22]

Figure 3 is a schematic of 1D wavy structure fabrication via a controlled buckling process. Single silicon nanoribbons are bonded with an elastomeric substrate, and then releasing pre-strain leads to the formation of a periodic wavy structure. In this structure, when compressing and stretching, polydimethylsiloxane (PDMS) substrates undergo major deformation, which can protect the active materials (Si) with limited strain.

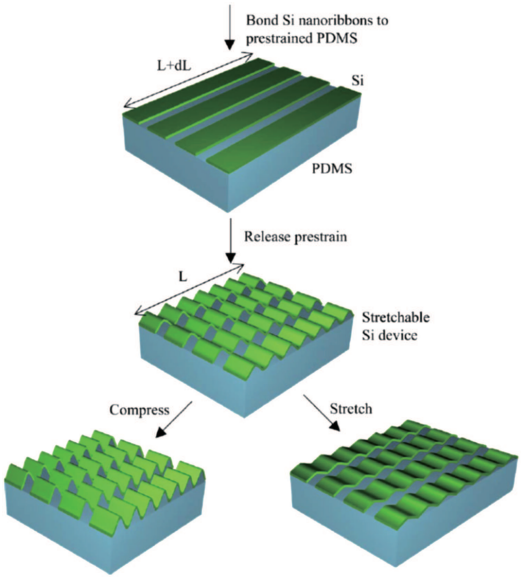


Fig. 3. Fabrication process of wavy structure.[24]

Based on the small-deformation theory, Huang *et al.*[25] developed a minimum energy method to investigate the buckling process under small pre-strain ($0.5\% < \varepsilon_{pre} < 5\%$) for a 1D wavy structure (Fig. 2(a)), which can be found in several excellent reviews.[10–12,24,26] Huang *et al.*[25] proposed that the out-of-plane displacement of the buckled thin ribbon can be represented by a cosine curve. By minimizing the total energy (sum of the bending energy, membrane energy in the rigid film, and strain energy in the substrate) of the systems, buckling wavelength (λ) and amplitude (A) can be obtained as

$$\lambda_0 = 2\pi h_f \left(\frac{\bar{E}_f}{3\bar{E}_s}\right)^{1/3}, \tag{1}$$

$$A_0 = h_f \sqrt{\frac{\varepsilon_{pre}}{\varepsilon_c} - 1}, \tag{2}$$

$$\varepsilon_c = 0.25 \left(\frac{3\bar{E}_s}{\bar{E}_f}\right)^{2/3}, \tag{3}$$

where h_f is the ribbon thickness of the film, E_f is the Young's modulus of the rigid films, E_s is the Young's modulus of the elastic substrate, ε_c is the critical strain for the buckling, and ε_{pre} is the pre-strain to induce buckling. For silicon nanoribbons on PDMS substrate, ε_c is 0.034% (calculated by using $E_f = 130$ GPa and $E_s = 1.8$ MPa).[24,26] Analytical results show that wavelength λ_0 does not depend on pre-strain and amplitude. If $\varepsilon_{pre} < \varepsilon_c$, the pre-strain does not induce a wavy structure; a wavy structure is formed when $\varepsilon_{pre} < \varepsilon_c$. The max-

imum strain ε_{peak} is the sum of the membrane strain and bending strains, and can be approximated as[26]

$$\varepsilon_{peak} \approx 2\sqrt{\varepsilon_{pre}\varepsilon_c}. \quad (4)$$

Based on Eq. (4), it is worth noting that ε_{peak} is much smaller than the pre-strain ε_{pre}. For example, when ε_{pre} is 23.8%, the induced ε_{peak} is only 1.8%. In other words, only when the applied strain is about 10 times higher than the maximum elastic strain can it cause Si nanoribbons to crack. This further proves that the wavy structure can significantly improve the flexibility of brittle materials.[26]

For large deformation and pre-strain ($5\% < \varepsilon_{pre} < 30\%$), the wavelength increases with increasing pre-strain. Jiang *et al.*[27] used finite deformation theory to analyze the buckling process. Under large pre-strain, the wavelength and the amplitude can be obtained by

$$\lambda = \frac{\lambda_0}{(1+\varepsilon_{pre})(1+\xi)^{1/3}}, \quad (5)$$

$$A \approx \frac{A_0}{(1+\xi)^{1/3}\sqrt{1+\varepsilon_{pre}}}, \quad (6)$$

with

$$\xi = 5\varepsilon_{pre}(1+\varepsilon_{pre})/32. \quad (7)$$

Here, λ_0 and A_0 are the wavelength and the amplitude, respectively, under small pre-strain. It can be seen that the wavelength under this circumstance is pre-strain dependent. According to Jiang *et al.*,[27] the maximum strain can be written as

$$\varepsilon_{peak} \approx 2\sqrt{\varepsilon_{pre}\varepsilon_c}\frac{(1+\xi)^{1/3}}{\sqrt{1+\varepsilon_{pre}}}. \quad (8)$$

Similar to the small deformation case, the maximum strain is much smaller than the pre-strain. Thus, the wavy structure provides an effective level of stretchability in materials that are intrinsically brittle.[27]

Besides 1D wavy structure, some researchers produced biaxially stretchable wavy structures on elastomeric PDMS substrate to provide full 2D stretchability. Choi *et al.*[28] fabricated herringbone 2D stretchable silicon films on elastic substrates. First, a controlled degree of bilateral isotropic thermal expansion was induced in an activated PDMS substrate, and silicon films were deposited on the substrate. The silicon nano membrane/PDMS structure was then cooled to room temperature to release the thermally induced pre-strain. This process led to the spontaneous formation of a 2D wavy structure. In order to investigate the 2D buckling patterns, Song *et al.*[22] performed an analytical study of different buckling modes, including 1D, 2D checkerboard, and herringbone structures. According to Song *et al.*,[22] the herringbone mode (Fig. 2(c)) has the lowest energy when the film is subjected to biaxial pre-strain. This explains why the herringbone mode is frequently observed in experiments with thermally induced pre-strain.

3. Implementation of stretchable energy storage devices

As stated above, electronics are mostly based on inorganic materials, such as silicon, gallium arsenide, and gallium nitride. Compatible, well developed, high performance inorganic electronic materials are a key challenge in the development of flexible electronics. Wavy structure design relies on new structural layouts based on the conventional materials and enables brittle materials to be made flexible to some extent. In accordance with the choice of materials, electrochemical energy storage devices, such as LIBs and supercapacitors have points of resemblance to ideal flexible electronics. Due to the inherently limited small strain of active materials in LIBs and supercapacitors, we can obtain only bending-deformation. Based on wavy designs for stretchable electronics, some work has been done on stretchable electrochemical energy storage devices. Table 1 characterizes the main wavy structured electrochemical energy storage devices fabricated so far, including the particular character of the wavy structure, and mechanical and electrochemical performance.

The conventional electrochemical energy storage device consists of an electrode with a polymer separator, an aqueous or organic liquid electrolyte, a metal tab, and packaging. Preparation of electrodes for LIBs is mainly based on a slurry-casting method that requires mixing active materials with binders and conductive additives, and then casting the mixture onto a metal (Al or Cu) foil. Rigid current collectors provide the structural support and electrical conductive pathways for the electrodes.[3,40] As shown in Table 1, in order to achieve flexible devices with wavy structures, metal current collectors could be replaced by lightweight, elastic polymer substrates, with wavy structures subsequently built on the elastic substrates. The three keys to achieving wavy structures with higher flexibility are: (i) an appropriate elastic substrate, (ii) a strong interface between the active material and the substrate, and (iii) optimization of the active material.

Suitable elastic substrate and interface properties are important to construct an effective wavy structure. Flexible substrates that are to replace rigid current collectors must meet the following requirements: (i) stability of the electrolyte: the substrate should not contribute any contaminants during electrochemical reactions and should be totally inert against the electrolyte and any other chemicals in the system; (ii) mechanical properties: the substrate should have a suitable elastic modulus and mechanical properties; (iii) surface pre-treatment of elastic substrate: we can introduce a conductive layer to enhance the electronic conductivity; surface pre-treatment also includes introducing functional groups on the surface of polymers, which can yield intact interface bonding between the active material and the substrate.

Table 1. Stretchable electrochemical energy storage devices with 1D and 2D wavy structures.

Flexible support	Conductive layer	Active materials	Pre-strain	Wave structure (λ, A, h)[a)]	Cycle performance under strain	Mechanical properties	Refs.
PDMS	/	SWCNT	uniaxial 30%	2.0 μm 0.4 μm 50 nm	1000 cycles under 30% strain, no fading	~ 30% stretchability	[29]
PDMS	/	SWCNT	uniaxial 100%	1.1 μm / 200 nm	1000 cycles under 120% strain, no fading	~ 140% stretchability	[30]
PDMS	/	SWCNT	uniaxial 30%	/	1000 cycles, 98.5%, under 1.11 strain s^{-1}	~ 31.5% stretchability, 4.46% strain s^{-1}	[31]
SIBS	30 nm Au	PPy-pTS		10–50 μm 1.0–5.0 μm /	2000 cycles, no fading	~ 30% stretchability, 5% strain s^{-1}	[32]
PDMS	/	SWCNT/PANI	uniaxial 100%	/ / 200 nm	200 cycles, 85%	~ 120% elongation 10% strain s^{-1}	[33]
Wavy graphene	/	PANI	none	0.5 mm 2.6 mm /	1000 cycles, 95%	~ 30% elongation	[34]
PDMS	/	graphene	uniaxial 50%	1.0 μm 1.0 μm /	10000 cycles, 100%	~ 40% elongation	[35]
PDMS	/	wavy graphene	0%	/	100 cycles, 100%	~ 40% elongation	[36]
VHB	/	crumpled graphene	biaxial 50%–400%	/ 46–78 μm /	100 cycles, 100%	~ 300% elongation	[37]
SIBS	30 nm Au	PPy		1.0 μm / /	1000 cycles, 81%	~ 30% elongation	[38]
PDMS	5 nm Ti and 50 nm Au	SWCNT	uniaxial 60%		3000 cycles, 96.6%	~ 20% elongation	[39]

[a)]Here λ is the wavelength, A is the amplitude, and h is the thickness of the buckling film. PANI: polyaniline; VHB: VHB acrylic 4910, produced by 3M company; SIBS: styrene-block-isobutylene-block-styrene; PPy-pTS: polypyrrole, containing the dopant p-toluenesulfonate anion.

Suitable substrates should have high electrolyte resistance and excellent interface properties. Due to their greater stretchability, PDMS and PET are often used as stretchable substrates. An elastomer serving as a flexible substrate inevitably contacts the electrolyte, such as liquid carbonate solvent with a high dielectric constant, H_2SO_4 aqueous solution, etc. Yun *et al.*[41] measured the stability of polymeric films against electrolytes by the amount of electrolyte taken up into polymeric films. They found that the resistance of polymeric films to electrolyte absorption is in the order of: Poly (ethylene naphthalate) PEN > poly (ethylene terephthalate) PET > (polyimide) PI > poly (ether sulfone) PES. PEN is the most stable substrate in an electrolyte solution due to its high strength, superior barrier property, and high stability at elevated temperature, associated with its low expansion coefficient. In contrast, PES losts its chemical stability owing to the high diffusion of electrolyte into it.

As Table 1 suggests, PDMS is one of the most widely used stretchable substrates. It shows excellent stretchability and durability. Aqueous solvents, alcohols, and other polar solvents such as methanol and glycerol do not swell the PDMS appreciably.[42] PDMS can be used well in combination with an aqueous supercapacitor electrolyte without substrate deformation.[43] Unfortunately, most organic solvents can diffuse into PDMS and cause swelling. This phenomenon makes the electrolytes of LIBs incompatible with PDMS substrates.[42] On the other hand, trace HF in electrolytes will attack PDMS substrates and extract PDMS oligomers from the bulk of the cross-linked polymer.[42] Therefore, the chemical and mechanical stability of PDMS in LIB systems is highly questionable, and other potential substrates for more stable LIB systems, especially flexible LIB systems, should be investigated.

As flexible polymers are usually insulators, the resistance of flexible substrates is much higher than that of Cu and Al foil current collectors. Therefore it is necessary to significantly lower the resistance of flexible substrates in order to obtain a performance comparable to metal foils.[41] In order to enhance the conductivity of a stretchable elastomer, a thin metal (Cu, Au, etc.) layer coated on a flexible polymer film may be favorable. Wang *et al.*[32] deposited gold on pre-strained SIBS substrates and released the pre-strain, obtaining buckled PPy-pTS films, as illustrated in Fig. 4. This film can endure 2000 stretching cycles with 30% tensile strain. In this design, the wavy structure provides flexibility, and the deposited Au film provides enough conductivity. Zhao *et al.*[38] prepared an SIBS substrate by solvent casting from a solution in toluene, then a thin Au film of about 30 nm was sputter-coated on the SIBS substrate, followed by release of the strain to obtain buckled Au microfilms; this sputtered Au film showed superior interface resistance. Lee *et al.*[39] pre-treated PDMS substrate by ozone, then deposited Ti (~ 5 nm) and Au (~ 50 nm) adhesion layers to obtain a 3-layer stretchable polymer substrate. This sputtered metal layer also significantly improves the electronic conductivity of the polymer substrate. Gold or titanium film can lower the resistance significantly, making it comparable to metal current collectors. Moreover, a nanometric film is favorable for forming wavy structures.

Another important property of the substrates is strong bonding between active materials and stretchable substrates. In order to ensure intact binding between active materials and flexible substrates, appropriate pre-treatment is important. The most widely used flexible substrate PDMS is composed of polymeric chains constructed with repeating units of $–OSi(CH_3)_2O–$. Figure 5 shows the surface chemistry of PDMS and reactions between PDMS and semiconducting nanoribbons. Surface $–(CH_3)$ groups give rise to the hydrophobicity of pristine PDMS substrates. This property

enables weak adhesion via van der Walls force, as shown in Fig. 5.[44,45] Exposure to UV light can introduce atomic oxygen, which reacts with PDMS to change the hydrophobic surface (dominated by $-OSi(CH_3)_2O-$ groups) to hydrophilic (terminated with $-O_nSi(OH)_{4-n}$ functional sites).[46] Pre-treated PDMS surfaces can react with various inorganic surfaces with –OH groups to yield strong chemical bonding, upon physical contact at room temperatures, as shown in Fig. 5. Yu *et al.*[29] demonstrated that UV-treated PDMS interacts strongly with functionalized single-wall carbon nanotubes (SWNTs) with –OH functional groups. Ultraviolet treatment of PDMS substrate along the direction of the pre-strain can cause covalent bonds (–C–O–Si–) to form through condensation reactions. Strong chemical bonding between the SWNTs and the PDMS substrate gives rise to excellent reversible stretchability. This stretchability is even retained through $\sim$ 1000 cycles under $\sim$ 30% strain.

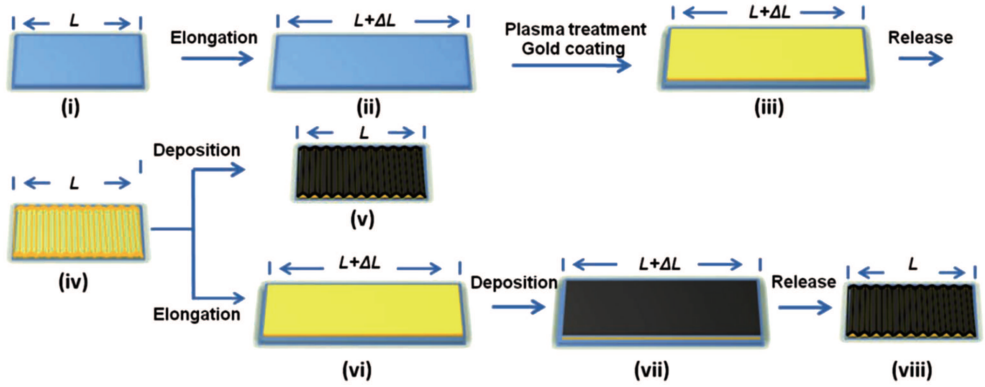


Fig. 4. Schematic procedures for the fabrication of buckled Au and PPy-pTS films on substrates.[32]

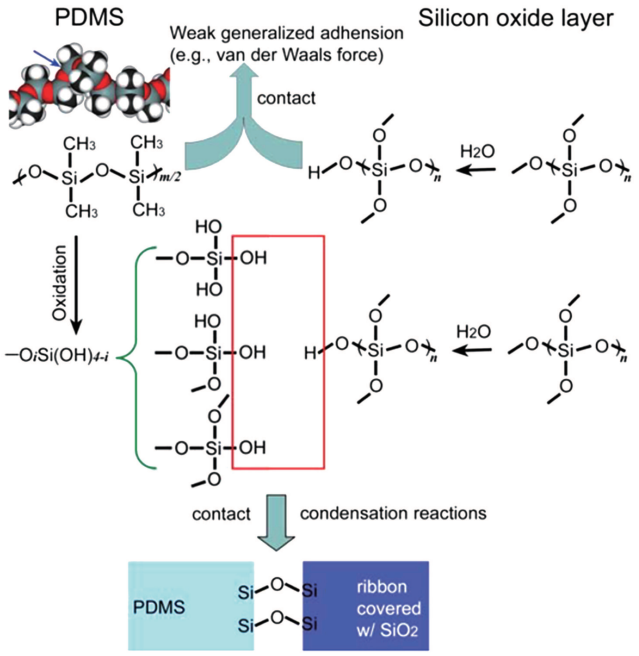


Fig. 5. Illustration of the surface chemistry of PDMS and reactions occurring at the interfaces between PDMS and semiconducting nanoribbons covered with thin SiO_2 layers.[44]

Already, wavy structures have been constructed of many dissimilar active materials, including nanocarbons (carbon nanotubes (CNTs) and graphene), polymers, and traditional LIB materials. The nanocarbons have been widely used for high energy and high power-density supercapacitors due to the materials' unique morphologies, high surface to volume ratio, and high ionic and electronic conductivities. Moreover, their higher elastic strain enables potential applications in stretchable LIBs and supercapacitors.[7,40,47,48] Yu *et al.*[29] prepared sinusoidal SWNT macrofilms on 1D pre-stretched PDMS substrates. Figures 6(a) and 6(b) show that their measured wavelength is about 2 μm and the amplitude is about 0.4 μm. The researchers also used the small deformation theory, represented by Eqs. (1)–(3), to estimate the wavelength and amplitude, arriving at results that agree very well with the experimental results. Cyclic voltammetry (CV) curves (Fig. 6(c)) show that the electrochemical performance of the stretchable supercapacitors remains unchanged even under $\sim$ 30% applied tensile strain. The specific capacitances of these stretchable supercapacitors, with or without strain, do not decline even during 1000 charge–discharge cycles (Fig. 6(d)), which illustrates the effectiveness of the buckled CNT macrofilm strategy.

So far, most of the research about stretchable electrochemical energy storage devices has only been about 1D wavy structures. However, biaxial pre-stretched PDMS substrates can effectively enhance the flexibility of devices by enabling them to stretch in two directions. Zang *et al.*[37] fabricated crumpled graphene on biaxially stretched polymer substrates. Figure 7 shows that this graphene has a herringbone structure. Its maximum linear strain is about $\sim$ 300%, and serving as an electrode, it can retain its initial specific capacitance over 1000 stretch/relax cycles. This kind of wavy structure typically has a herringbone structure, consistent with the theoretical prediction of Song *et al.*[22]

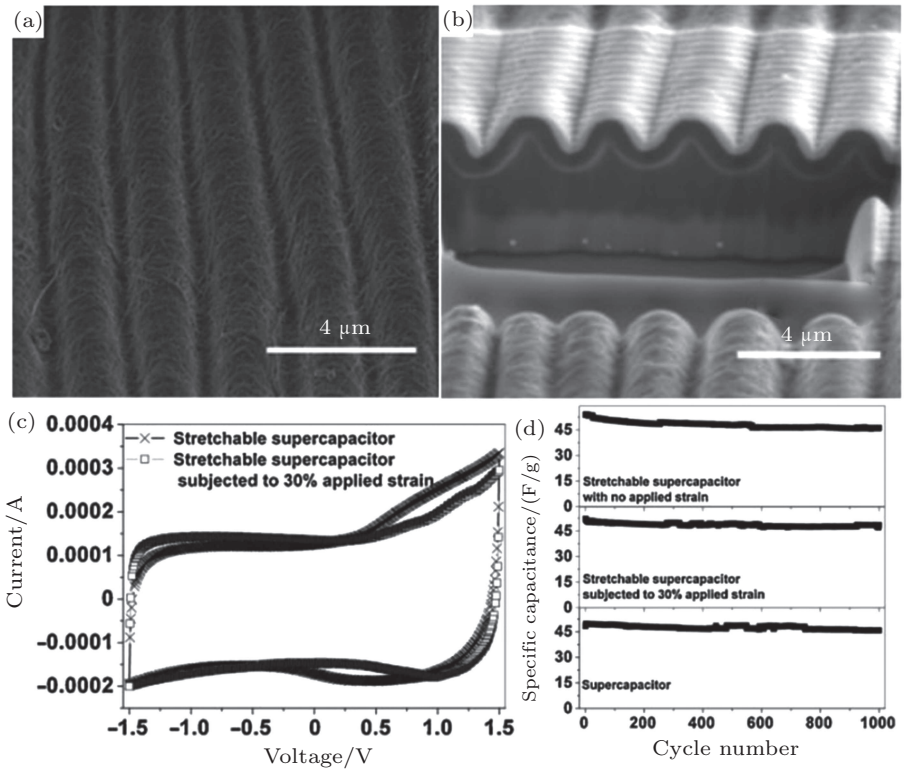


Fig. 6. (a) and (b) SEM morphologies of buckled CNTs macrofilms on pre-strained PDMS substrates; (c) CV curves of stretchable supercapacitors with and without 30% strain; (d) specific capacitance of cycled stretchable supercapacitors with and without 30% strain.[29]

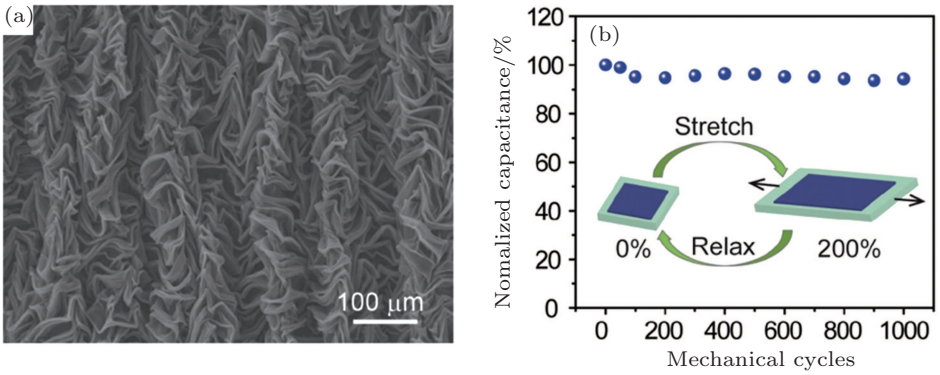


Fig. 7. (a) Herringbone structured crumpled graphene; (b) cycles of stretchable supercapacitors.[37]

Another series of active materials shown in Table 1 is a variety of polymers, including PPy, PEDOT, and PANI. Compared with the conventional inorganic materials in LIBs and supercapacitors, polymers are intrinsically stretchable, so they may have great applications in stretchable devices. Zhao *et al.*[38] fabricated buckled polypyrrole electrodes. The performance of this stretchable supercapacitor is comparable to flat polypyrrole electrodes, retaining 81% of the initial capacity even after being stretched for 1000 cycles with 30% strain. Unfortunately, inorganic materials, especially lithium transition metal oxides, have rarely been used to construct wavy structures so far.

In summary, strong chemical bonding, stable electrolyte substrates, and appropriate materials provide a basis for fabricating a wide range of wavy structures in stretchable devices.

4. Summary and prospects

Flexible electrodes with wavy structure can be significantly more stretchable, and we now know a good bit about designing and fabricating them. But lots of challenges remain to be overcome in developing stretchable electrochemical energy storage devices. (i) Although the wavy structure can improve the deformability of some materials to an extent, the resulting stretchable elastic strain is generally less than 30%–50%. (ii) So far, most wavy-structure materials are still based on the nanocarbon materials. Little research has been published on traditional LIB materials. (iii) Flexible separators, electrolytes, and tabs are needed. A flexible electrochemical energy storage device is composed mainly of flexible electrodes, separators, an electrolyte, and metal tabs. To make the overall device stretchable, all components must be compatible with

the design parameters for stretching without failing in their functions.

Aiming at the above problems, the following new components should be designed and developed.

Stretchable LIBs with wavy structures Inorganic active materials in LIBs and supercapacitors, such as $LiCoO_2$, graphite, and activated carbon, usually have extremely low elastic strain and uniform spherical structures. Repeated or prolonged deformation may cause the active materials to lose electronic contact. On the other hand, traditional LIB materials usually have low electronic conductivity, so obtaining a strong bond between an insulated substrate and an active material is a great challenge.

Elastic materials for electrochemical energy storage Besides the development of traditional LIB materials, developing new active materials with greater deformability may have a significant impact on flexible devices. When we think of such materials, we usually think of the organic based electrode materials developed for LIBs. Indeed, flexible batteries using organic electrodes have inherent advantages, because organic materials are intrinsically flexible and their mechanical and electrochemical properties can be tuned through chemical synthesis.[2] Two strategies have already been pioneered for the fabrication of organic material based batteries with inherent flexibility. One is the use of an electrolyte layer sandwiched between thin layers of polymers that have low conductivity but incorporate redox-active groups. In this strategy, the polymer backbones provide flexibility. The other approach is based on aliphatic redox polymers. These open-shell molecules are called radicals. Such radicals, e.g., nitroxides and galvinoxyls, undergo reversible one-electron redox reactions. These radical polymer batteries can be transformed into completely flexible, foldable, and semi-transparent batteries.[2,49] Although flexible batteries based on organic active materials have obvious advantages over inorganic active materials, the materials must meet many different requirements that sometimes conflict rather sharply.

New wavy structures Although wavy rigid films integrated with elastic substrates are stretchable, the maximum stretchable elastic strain is about 30%–50%. In order to improve stretchability, another strategy is to develop a mesh structure. In such designs, rigid parts bonded with elastic substrates are connected by stretchable interconnects. Stretchable interconnects can move out of the substrate plane, thus this structure can accommodate 100% or higher elastic strain. This mesh-based concept is also called "interconnect island structure." Figure 8 shows the fabrication procedure and the structure. The interconnect island mesh design is obtained on a wafer through a patterned layer of photoresist. The mesh is then transferred to a pre-strained elastomeric substrate. Once the pre-strain is released, the interconnections buckle and move out of the plane, ready to accommodate large applied deformations. This concept was first used in flexible electronics. For example, Kim *et al.*[50] developed a kind of island structure with serpentine interconnections. The wavy structure can even accommodate $\sim 140\%$ elastic strain, which has great potential for applications of stretchable energy storage devices.

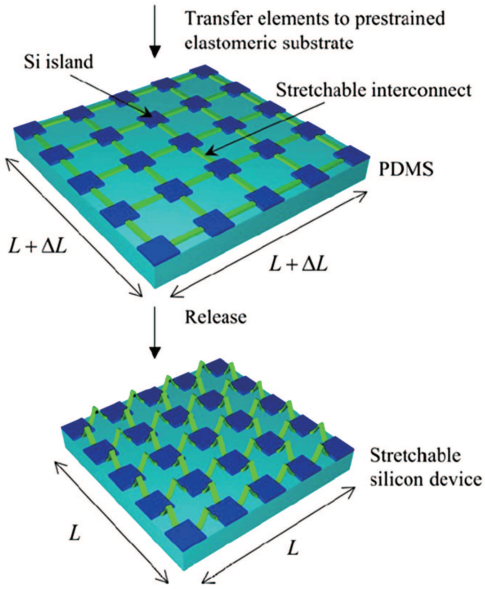


Fig. 8. Fabrication of noncoplanar interconnect-island structure.[51]

Kim *et al.*[52] prepared a stretchable solid-state micro-supercapacitor array using a serpentine wavy structure. The narrow and long serpentine metallic interconnections are encapsulated by a polyimide thin film to ensure that they are within the neutral plane (Fig. 9). This stretchable micro-supercapacitor is stable over stretching up to 30% without degradation.

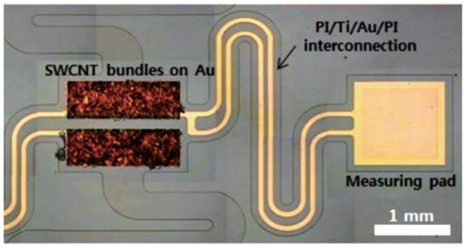


Fig. 9. Wavy structure with serpentine interconnects.[52]

Based on serpentine designs, Xu *et al.*[53] developed stretchable lithium batteries with a self-similar island-bridge structure. This design enables reversible stretchability up to 300%. This stretchable battery uses silicone elastomers as substrates, stretchable electrodes, and polymer electrolyte stacked sequentially. Its design is illustrated in Figs. 10(a) and 10(b). Figures 10(c)–10(e) show the structure of stretchable current collectors in which Cu and Al islands are connected

by S type interconnections, then $LiCoO_2$ and $Li_4Ti_5O_{12}$ active materials are transferred to the Cu and Al islands. During stretching, the S type bridges with self-similar structure undergo larger elastic deformation. Even under 300% elastic strain, the whole structure can still work properly, as shown in Fig. 10(f).

Integrated devices Wavy structure enables electrodes to stretch to some extent. However, in an integrated device, other components, such as the separators, the electrolyte, and the metal tabs of an LIB or supercapacitor should also accommodate stretch strain. Although liquid electrolytes have excellent rate performance, leakage during stretching is a worry and a safety concern. In order to solve this problem, some stretchable gel-polymer electrolytes have been developed and have found potential applications.[54,55] However, many applications need the flexibility of these electrolytes to be improved to enhance their stretchability. Conventional stainless steel or Al-polymer composite films and metal tabs also limit the flexibility of flexible devices. Metal tabs connect the electrode to the outer circuit. As wavy structures usually lie on polymer substrates, ensuring good connection between metal tabs and stretchable tabs is extremely important.

With the development of flexible electronics, stretchable electrochemical energy storage devices have drawn intense attention. Although we have made great progress in the fabrication of flexible electrodes in recent years, obstacles still need to be overcome. Future efforts should be made as follows: (i) develop new intrinsically elastic active materials; (ii) develop new wavy structures to achieve higher flexibility, such as self-similar structures and serpentine structures.

Although there are still many problems to overcome, the ubiquitous potential applications of flexible LIBs with superior electrochemical and mechanical properties in stretchable electrochemical energy storage devices are greatly anticipated for the near future.

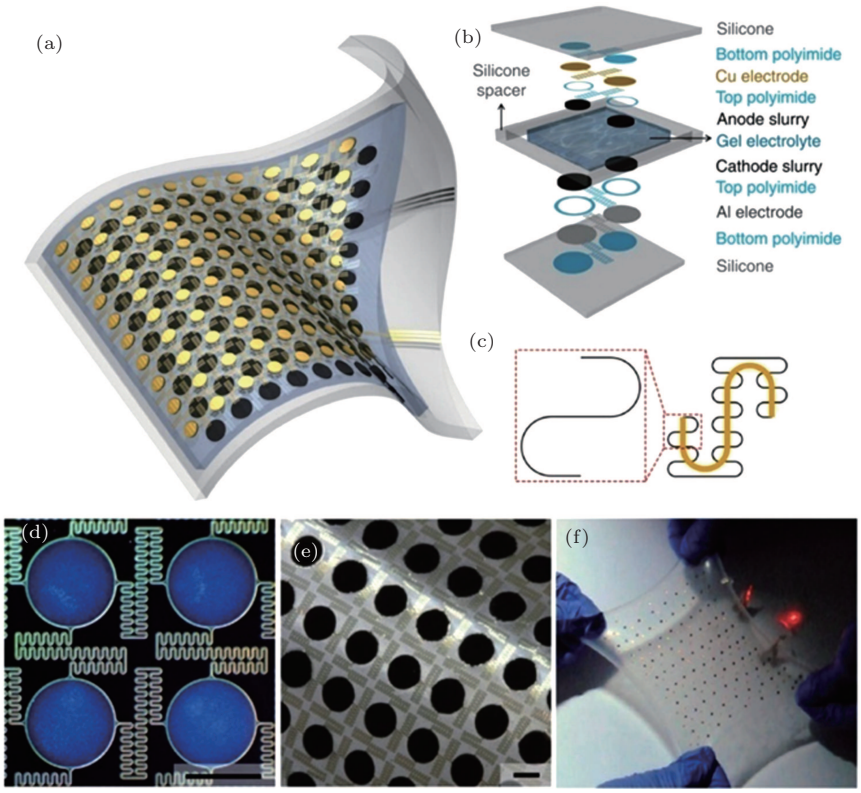


Fig. 10. (a) and (b) Structure of stretchable LIBs; (c) and (d) stretchable current collectors with island-bridge structure; (e) island-bridge electrodes with active materials; (f) illustration of stretchable batteries.[53]

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