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# A mini-review: Emerging All-Solid-State Energy Storage Electrode Materials for Flexible Devices

Yang Yang*

NanoScience Technology Center, Department of Materials Science and Engineering, Energy Conversion and Propulsion Cluster, University of Central Florida, 12424 Research Parkway Suite 423, Orlando, Florida 32826, United States

*E-mail: Yang.Yang@ucf.edu

**Abstract:** New technologies for future electronics such as personal healthcare devices and foldable smartphones require emerging developments in flexible energy storage devices as power sources. Besides the energy and power densities of the energy device, more attention should be paid to safety, reliability, and compatibility within the highly integrated systems because they are almost in 24-hour real-time operation close to the human body. Thereupon, all-solid-state energy devices become the most promising candidates to meet these requirements. In this mini-review, the most recent research progress in the all-solid-state flexible supercapacitors and batteries will be covered. The main focus of this mini-review is to summarize new materials development for all-solid-state flexible energy devices. The potential issues and perspectives regarding all-solid-state flexible energy device technologies will be highlighted.

**Keywords:** all-solid-state; energy storage; flexible; safety; reliability

## 1. Introduction

Energy storage is the critical technology for many defense and commercial applications by either directly being used as power sources for transportations and electronics or being integrated with other energy devices, such as thermoelectrics and piezoelectrics, to use energy in an efficient manner.[1-3] In recent years, flexible energy storage has been taken into special consideration with

increasing demands for wearable devices, including flexible displays, portable electronics, personal healthcare devices, and so forth.[4-6] In terms of wearable electronics, the future will be miniaturized, integrated, and self-powered devices that are assembled in all-solid-state and can be utilized for long-term without safety and reliability issues.[7-9] So far, some energy storage devices, for instance, electrochemical capacitors (or supercapacitors), metal-ion batteries, and most recently rechargeable metal-air batteries, have been recognized to be the most practical and feasible technologies for all-solid-state energy storage.[10-12] However, the main challenges for the current all-solid-state energy storage are still limited by the low volumetric energy density, high internal resistance at the materials interfaces, poor mechanical durability, and controversial environmental concerns.[13-16] To address these concerns, the flowing strategies have been suggested:

i) The electrode materials should have the high areal and volumetric capacity, which represents their abilities to supply high energy within a confined space.[17] More specifically, emerging materials store the energy based on the mechanisms beyond double-layer storage and intercalation chemistry should be designed. In addition, some advanced features should be considered in the electrode materials design such as additive-free and free-standing, which can significantly reduce the content of electrochemically inactive materials in the electrode.[18-22]

ii) The electrode materials should have reduced resistance by using high conductivity materials or conducting components towards high-rate performance and less energy consumption by the internal resistance.[23] Experimentally, doping and hybridizing with other elements may improve the conductivity of electrode materials.[24] Computationally, data-driven simulation and machine-learning methods can be used to predict the material compositions and structures to achieve the optimum electrode conductivity.[25]

iii) The advanced solid-state electrolyte films with high ionic conductivities should be

designed.[26] The ionic conductivities of the electrolyte films are always the pain point for solid-state energy storage. Similar to the electrode materials, doping may solve the low ionic conductivity issue of the solid electrolyte.

iv) Materials engineering at the nanoscale should be used to design new self-organized nanostructures that enable capabilities to release the interfacial stress in all-solid-state devices.[27] Nano-engineering has been demonstrated to be very successful in boosting material performance in renewable energy applications.[28-30] Designing new electrode structures may solve the interfacial resistance and stability issues of the solid-state devices.

v) Environmentally benign and non-toxic materials should be utilized.[31] Both electrode materials and solid electrolytes should be very safe and non-toxic in order to be used for flexible and personal devices. New electrode materials without metal dissolving and leaking should be considered for material design.

The detailed and specific reviews on the electrode materials, solid-state electrolyte, and energy storage devices have been comprehensively discussed elsewhere.[32-38] In this mini-review, therefore, recent advances in addressing the safety and reliability considerations of the all-solid-state energy storage devices for wearable devices will be outlined (**Scheme 1**).

## 2. All-Solid-State Supercapacitors

Supercapacitors deliver fast dynamic response, high power density, and long cyclability through non-Faradaic and Faradaic processes in electric double-layer capacitors (EDLCs) and pseudocapacitors, respectively.[39] The recent technological progress in the new nanostructured materials development such as nano-carbons, other carbonaceous materials, and thin-film materials, enables the all-solid-state supercapacitors to be reliable and environmentally benign for wearable devices.[40]

### 2.1. Electrical double-layer capacitors

Non-Faradaic EDLCs store energy in an ionic double-layer (Helmholtz layer) built upon the accumulation and electrostatic adsorption of electrolytic ions at the electrode/electrolyte interfaces, leading to extremely high power densities.[41] The higher power density usually refers to a faster charging rate. On the other hand, the strong dependence of the double-layered charge storage on the surface areas of the electrodes limits the maximum possible number of the adsorbed ions at the EDLCs interfaces, consequently resulting in low energy densities.[42] This makes the EDLCs store insufficient energy for long-term utilization. A general strategy to improve the energy densities of EDLCs is to tremendously increase the electrode/electrolyte interfaces by using high surface conducting materials.[43] In this perspective, nano-carbon materials, including carbon nanotubes (CNTs), graphene, reduced graphene oxide (rGO), nanoporous carbon fibers, and other carbon materials with hierarchically nanoporous structures become the core competencies of all-solid-state EDLCs due to their good electrical conductivity, supreme mechanical strength, and highly engineerable surface area.[44-48]

Creating nanopores in the carbon-based EDLCs has been widely used as the most efficient approach to improve energy densities. Taking graphene as an example, in order to make the best use of its large theoretical surface area (2630 $m^2 g^{-1}$) and extraordinary electron mobility, different porous structures such as foams, aerogels, and sponges have been designed to overcome the aggregation problem.[49-51] But these graphene architectures are of no help in creating additional active sites to increase the charge storage capacity. In addition to using porous architectures, directly creating nanopores in the graphene has been suggested to be a fascinating approach to form hierarchically porous structures, leading to the dramatically improved capacitance.[52] For instance, by integrating macropores, mesopores, and micropores into the bamboo-like carbon

fibers with a hierarchically porous structure, excellent reliability and outstanding capacitance were achieved.[53] The usage of hierarchically porous carbons in the EDLCs for wearable electronics is emerging but still controversial. This is because carbon materials usually have low densities, which require high materials loading in limited space in order to achieve sufficiently high capacitance, therefore, resulting in the structural collapse.

Polyvinyl alcohol (PVA) gel has been widely used as a porous matrix to mix with ionically conducting agents such as phosphoric acid, KOH, other salts, and ionic liquids, forming solid polymer electrolyte for the all-solid-state EDLCs. This due to the attractive mechanical and electrical merits of PVA, including high stretchability, good strength, and controllable thickness and porosity.[54-56] The most important feature of using PVA gel electrolyte is due to the reduced probability of electrolyte leakage, which enables the wearable EDLCs tailorable (being cut) and safe at the device level.[57] Taking into account the charge is stored at the surface or subsurface of EDLCs electrodes, the following concerns are still unsolved in the gel electrolyte based all-solid-state EDLCs: i) Since using high surface area nanoporous electrodes are necessary for the high capacitance EDLCs, how to completely fill the nanoscale pores with the gel and form a seamless interface? ii) How to maintain sufficient strength to resist intense mechanical impact in the gel electrolyte with weak molecular interactions? And these concerns may become more serious when the ceramic electrolyte is used because of the sluggish ion mobility across the poorly contacted electrode/electrolyte interfaces.[58-60] Most recently, Braun et al reported a bottom-up method to completely infill gel electrolytes into porous electrodes (Figure 1a).[61] As a result, a 500 μm thick all-solid-state supercapacitor electrode composed of CNTs completely infilled with a PVA gel electrolyte was fabricated (Figure 1b). Under the rolling-up test, the CNTs-based electrode did not show any microcracks, indicating exceptional mechanical property (Figure 1c). The excellent

mechanical properties enable the CNTs-based electrode a 95% capacitance retention after 5000 bending cycles (Figure 1d). The areal capacitance of the 500 μm thick supercapacitor electrode delivered an outstanding capacitance of 2662 mF $cm^{-2}$ (Figure 1e, f), which is superior to the current flexible supercapacitors (Figure 1g).

Balancing energy and power densities in energy storage devices is always very challenging. Although recent advances have improved the energy densities of EDLCs, they are still known for providing high power density for high energy consumption in a short period. Therefore, other high energy density energy devices such as pseudocapacitors and batteries have been developed in order to integrate with EDLCs and fill the functional gap (high energy density) in a solid-state device.

### 2.2. Pseudocapacitors

Beyond EDLCs, pseudocapacitors exhibit high energy densities derived from reversible Faradaic redox reactions at the surface and subsurface of the materials, including some conducting polymers (CPs) and transition metal compounds (TMCs).[62-64] Although these CPs such as polyaniline (PANi), poly(3,4-ethylene dioxythiophene) (PEDOT), and polypyrrole (PPy) show great potentials as active materials for pseudocapacitors, they are mostly used as conducting components in TMCs-based electrodes rather than being used alone.[65-67] This is because of their lower capacities than TMCs and low-density (1~2 g $ml^{-1}$) issue similar to carbon materials.[68-69] The poor cycling stability of CPs caused by structural alteration and dissolving in organic electrolytes is another barrier to practical application.[70]

Because of the insufficient flexibility and low conductivity, TMCs are always mixed with conducting materials such as carbons and CPs.[71] In these TMCs-based hybrid electrodes, carbons or CPs serve as conducting frameworks, which only contribute in a minor way to the overall capacitance as compared to TMCs.[72] Thereupon, it is always a trade-off between the capacity and

flexibility in the pseudocapacitors using hybrid electrodes.[73-74] It is necessary but very challenging to develop new techniques that can increase the loading amount of TMCs and meanwhile can maintain the mechanical strength without sacrificing the flexibility of the hybrid electrodes. More recently, some advanced techniques, including growing or loading active materials on 3D metallic current collectors and forming highly porous nanostructured films, have been developed to increase the TMCs loading in the flexible and robust electrodes without using any carbon and CPs additives.[75-78] The self-adjusting capability of these 3D current collectors and porous films enables highly flexible and mechanically robust electrodes for wearable energy storage devices. Our group recently developed a freestanding NiFe oxyfluoride (NiFeOF) holey film (HF) using an electrochemical approach - electrodeposition followed by anodization (Figure 2a-c).[79] The metallic NiFe alloy filaments remained in the NiFeOF HF protected the nanoporous structure of the materials during bending and twisting tests (Figure 2d, e). As a result, the as-prepared NiFeOF HF is freestanding and self-supporting, which can be used as electrodes without reliance on additives. The interconnected holey structure and hierarchical pores provide a high surface area for energy storage (Figure 2f, g). Endowed with the good electrical conductivity and highly porous structure, the NiFeOF holey film delivered a maximum specific capacitance of 670 F $cm^{-3}$ (Figure 2h, i). Additionally, the NiFeOF HF presented exceptional performance stability under bending and long-term cycling conditions (Figure 2j, k), showing supreme reliability for wearable electronic devices.

Although pseudocapacitors exhibit better energy densities than EDLCs and sometimes may show both acceptable energy densities and power densities, they may not really compete with EDLCs and batteries in terms of high power and energy, respectively.

## 3. Flexible Battery

Rechargeable batteries have been well investigated because of their capabilities to provide high energy density to power electronic devices for long-term utilization.[80] Metal-ion batteries, especially Li-ion batteries (LIBs), have been widely investigated for flexible batteries due to their abilities to be built in an all-solid-state construction.[81] Although the energy storage mechanisms between LIBs and supercapacitors are significantly different, the basic concepts to develop flexible batteries are similar.[82] To enhance the flexibility and conductivity of the battery electrodes, conducting additives such as carbon and carbonaceous materials are used to form composites with TMCs-based active materials.[83] However, taking into account the nonaqueous electrolytes used in most rechargeable batteries, potential environmental and safety issues should be concerned to develop a human-compatible wearable device.[84]

### 3.1. Li-ion batteries

The commercial and most typical LIBs are produced using layered materials as electrodes in which Li-ion intercalation/extraction processes are involved during discharge/charge cycling.[85] Li-intercalation enables small volume expansion of the active materials which ensures stable performance during long-term utilization, nevertheless, less energy storage capacity is achieved.[86] Thereafter, novel electrode materials such as transition-metal based multi-valence materials based on other energy storage mechanisms such as alloying and conversion reactions have been developed to deliver much higher capacities than Li-intercalation electrodes, but the huge volume change becomes the major barrier to flexible batteries.[87] To address this issue, mechanically robust additives and self-adjusting nanostructures have been developed.[88-90] Similar to the flexible SCs, carbon materials and CPs are commonly used to form a flexible and high conductivity network to load electrode materials for flexible LIBs.[79] Mesoporous $NiCo_2O_4$ nanowire arrays coated by carbon textiles have been demonstrated to facilitate the electron transport by direct connecting

active materials to the current collectors and provide facile ion diffusion path by forming mesoporous structure. Benefiting from these structural merits, the binder-free $NiCo_2O_4$/carbon textiles anodes exhibit high performance and excellent reliability.[91] A ploypyrrole@porous silicon hollow spheres (PPy@PHSi) composite exhibited excellent structural stability and electrochemical performance (high rate capability and outstanding cyclability) for flexible LIBs, owing to the synergism between the porous structure and the PPy coating. The porous structure of the shell buffered the volume change and reduced the internal stress, therefore facilitating the $Li^+$ diffusion in the porous electrodes. In addition, the PPy coating significantly enhanced the electrode conductivity and stabilized the structure.[92] Mg-modified $LiMnPO_4$ nanofibers were mixed with conducting carbon matrix in order to enhance the electrode conductivity, structural integrity, and flexibility. Therefore, a high capacity of 107 mAh $g^{-1}$ was achieved at 5C, representing a superior rate performance for $LiMnPO_4$-based cathodes.[93] Flexible LIBs full cells composed of $Mn_2O_3$ and $LiMn_2O_4$ nanowires as anodes and cathodes, respectively, have been developed without using any carbon supporting materials. The structure of the one-dimensional nanowire provides short $Li^+$ transport path and volume flexibility during lithiation, leading to high rate performance.[94] Even though various advanced materials and new techniques have been conceived to fabricate flexible LIBs, it is still very challenging to achieve a balance between device flexibility (mechanical property) and LIBs performance (electrochemical properties such as power and energy densities) because of the electrochemically inactive components such as conducting additives and binders commonly used in the current flexible LIBs.

Safety issues related to the organic electrolyte leakage, unsatisfactory package to withstand harsh utilization environments, and battery failure originated from either thermal runaway or metal dendrite growth, are the chief concerns in view of practical applications of the flexible LIBs in

wearable and human-compatible electronic devices.[95] To address these battery safety risks, ceramic and novel polymer separators associated with thermal shutdown functions are of special importance in improving the safety and reliability of the flexible LIBs.[96] A thermostable ceramic $SiO_2$-grafted PE separator prepared by electron beam irradiation shown a shrinkage ratio of only 20% even at 180 °C.[97] That separator also displayed an improved ionic conductivity because of the good wettability and electrochemical stability. Conventionally, most of the polymer separators are unstable at 120 °C and above when used in LIBs. To enhance thermal stability, a pure aluminum oxide nanowire-based membrane without any organic additives was developed as a bendable ceramic separator. At bother room temperature and 120 °C, the LIBs fabricated with ceramic separator shown a higher rate-performance and longer cyclability as compared to the conventional polymer separator.[98] Recently, ceramic nanowire fillers have been demonstrated to form ionically conducting networks in the polymer-based solid electrolyte. Dendrite growth threatens the safety of LIBs by piercing the separator and making the cell short. To address this issue, an aramid-PEO nanofibers composite was recently demonstrated to show suppressed dendrite growth, high modulus, and high ionic conductivity. The small pores in the membranes were proved to eliminate the possibility of dendrite growth.

One of the most promising approaches to solve the safety issues in flexible LIBs is to utilize ionic liquids (ILs) in the solid electrolytes due to their unique merits such as low melting point, almost no vapor pressure (non-volatile), high-temperature stability (non-flammable), and wide electrochemical stability window.[99] When used in the flexible LIBs, ILs-based solid electrolytes do not release any toxic compounds such as HF if the cells are damaged and exposed to the atmosphere.[100] Yassar et al recently reported an all‐3D‐printed LIBs using the ILs-based solid electrolyte (Figure 3a-f).[101] By adding nanosized ceramic fillers to the solid electrolyte, a

continuous, thin, and dense layer was obtained between the porous electrolyte and the electrode. This is helpful to effectively reduce the interfacial resistance of the all-solid-state LIBs. As a result, the ionic conductivity of 0.78 $\times 10^{-3}$ S $cm^{-1}$ was achieved using the 3D printed solid electrolyte, leading to superior capacity and rate performance to the traditionally casted flexible LIBs (Figure 3g-i).

LIBs surpass supercapacitors (EDLCs and pseudocapacitors) in terms of energy density, however, they have the most serious safety and reliability concerns because of the metal dissolving/leaking and electrode material decomposition during improper usage such as over-charging/over-discharging.

### 3.2. Other metal-ion batteries

Beyond LIBs, other flexible metal-ion batteries such as Na-ion, Mg-ion, and Al-ion batteries have been developed in recent years. Besides experiencing similar challenges to flexible LIBs, other flexible batteries face problems in terms of sluggish metal ions diffusion in the electrodes and limited options for the electrode materials and electrolytes. A universal strategy to address these issues is to develop 3D electrodes with open channels in order to achieve the facilitated metal ions/clusters extraction and insertion from host materials to the electrolyte. However, the development of 3D electrodes for flexible Na-ion batteries is still hampered by the intricate production methods and the relatively high cost of building blocks for the 3D structures such as graphene and CNTs. Wu et al designed a simple and low-cost electrospinning technique to wrap large-sized $Na_3V_2(PO_4)_3$ with the hierarchically 3D electronic channels for flexible Na-ion batteries.[102] Such flexible electrodes exhibited outstanding electrolyte wettability, ultrafast electrical conductivity, and high $Na^+$ ion diffusion coefficients, leading to a high reversible capacity of 116 mAh $g^{-1}$ at 0.1 C. Even at a high rate of 30 C, the discharge capacity of 63 mAh

$g^{-1}$ remained. The polymer-based solid electrolyte can boost the development of high safety and flexible Mg-ion batteries because of the enormous merits, including greatly improved safety, high energy density, and structural flexibility. Recently, Cui et al developed an *in situ* crosslinking reaction method to fabricated a novel polytetrahydrofuran-borate-based gel electrolyte coupling with glass fiber (Figure 4a).[103] That gel electrolyte exhibited reversible Mg plating/stripping performance, high $Mg^{2+}$ ionic conductivity, and remarkable $Mg^{2+}$ ion transfer number (Figure 4b, c). The $Mo_6S_8$/Mg batteries assembled with that gel electrolyte delivered unprecedented electrochemical properties at a wide temperature range (−20 °C to 60 °C, Figure 4d, e) and showed well-addressed safety issues without suffering from internal short-circuit failure during the cutting test (Figure f-i). Among all the metal-ion batteries beyond Li-ion, Al-ion batteries provide a three-electron transfer during the $Al^{3+}$/Al redox reactions, as a result delivering a maximum gravimetric capacity of 2980 mAh $g^{-1}$. In addition, the price of Al is sufficiently low and stable in the open air under ambient conditions for large-scale manufacturing, which can significantly reduce the production cost of rechargeable batteries. However, the three-electron transfer process involved in the charge/discharge reactions, as well as the strong bonding between $Al^{3+}$ and the host materials, makes Al-ion batteries slow in reaction kinetics. Most recently, our group designed a self-supported tin sulfide (SnS) porous film (PF), which was used as a flexible 3D cathode in the Al-ion batteries, delivering a high specific capacity of 406 mAh $g^{-1}$.[24] A capacity decay rate of 0.03% per cycle is achieved, indicating good stability. That self-supported SnS film showed outstanding electrochemical performance and stability during dynamic and static bending tests. The porous structure of SnS is beneficial for minimizing the volume expansion during charge/discharge, leading to improved structural stability when used as flexible 3D electrodes.

Although recent research progress has improved the kinetics for other metal-ion storage in the electrode materials, more research efforts on enhancing the Columbic efficiency and further increasing the power/energy densities of the materials are still required.

### 3.3. Metal-air batteries

Metal-air batteries (MABs) store the energy by the surface catalytic oxygen reduction and evolution reactions (ORR/OER) on the cathode side and redox reactions on the metal anode side.[104-106] In principle, MABs deliver a much larger capacity to maintain a high power density than that of LIBs. For the detailed background of the charging/discharging mechanism please refer to the prior comprehensive review papers.[37, 107-108] In order to activate the catalytic reactions occurring on the air-breath cathodes, high surface area carbon-based bifunctional catalysts are preferred. Using a facile $H_2$ etching approach, Zhang et al prepared a coaxial cable-like structure composed of carbon fiber skeleton and nanostructured porous and defect-rich graphene skin.[109] By introducing more heteroatoms and defects as active sites, the core-shell nanocarbons exhibited excellent OER/ORR activities and reliability under bending tests. The metal anodes play the central roles in determining the MABs energy density and cycle life because of metal (e.g. Al, Zn, Fe, and Mg) corrosion and the irreversible formation of discharge products on the electrode surfaces. More specifically, Zn anodes experience the inhomogeneous deposition and the formation of dendrites when charging, leading to a quick loss of cyclability and potential safety issues caused by the internal short circuits. Fe anodes suffer from the surface passivation by iron hydroxide formed during the discharge process. Hence, increasing interest has been devoted to developing stable anode materials that are resistant to surface passivation and corrosion.[110] Porous metals or alloys with 3D structures have been mostly used to suppress the metal passivation and dendrite formation by eliminating the electrical field inhomogeneity during charging. However,

relevant research progress in 3D metal anodes for flexible MABs is still very limited. Taking Zn-air batteries as an example, Zn anodes are most commonly fabricated by coating Zn particles slurries on the current collectors or directly using Zn foils.[111] Besides surface passivation by the discharge product and internal short-circuit failure, these Zn anodes possess insufficiently mechanical property, leading to fatigue failure, mechanical rupture, and eventually losing the electrical contact under external deformation. Lee et al developed a new class of flexible Zn-air batteries using a multifunctional heteronanomat (HM) architecture to address these issues. The HM framework-supported electrodes were fabricated by a one-pot concurrent electro-spraying and electro-spinning process (Figure 5a), forming a 3D bicontinuous ion/electron transport channels in the electrodes (Figure 5b, c). Benefiting from that unique structure, the HM-structured electrodes showed excellent electrical properties under deformation tests (Figure 5d, e). In addition, when assembled into flexible Zn-air battery cell, considerably improved mechanical property and electrochemical rechargeability were achieved.[112]

MABs are the most promising energy devices that can be used to complement the traditional energy storage devices such as supercapacitors and metal-ion batteries because of their high energy densities and power densities. From the perspective of practical application, reducing the materials cost and designing cell configuration should be focused on future research in order to avoid the electrode materials dead and electrolyte leakage.

## 4. Conclusions and Outlook

Flexible electronic devices powered by bendable, foldable, and even cuttable energy devices are of significance for both defense and commercial utilizations in the future. Safety should be placed in a priority position when developing flexible energy devices. Flexible supercapacitors are usually safe and provide high power but low energy, which can not be used as power sources alone

for electronic devices. Therefore, developing safe flexible batteries become increasingly important. Making the energy devices all-solid-state could be a promising solution to the safety issue for flexible batteries. ″All-solid-state″ does not necessarily mean ″rigid″ or ″brittle″. Using 3D porous electrodes or developing advanced thin-film technology have been demonstrated to be very effective strategies for improving the flexibility of the device and meanwhile achieving improved performance. Despite the increasing interests in flexible energy storage in recent years, there are many challenges and opportunities to be explored:

1. *Integration with other energy solutions*: The future flexible electronics should be minimized, foldable, low energy consumption, and all-integrated. In order to provide continuous energy supply, integrating with other energy sources such as solar or thermal energy could be a solution to the low energy density of the state-of-the-art electrochemical energy storage devices. To this end, thin-film solar cells and thermoelectric devices could be used to generate electricity from the external energy sources (sunlight, environment temperature change, etc), which can provide energy to continuously charge the flexible batteries or supercapacitors during day time. The integration of multiple components into a single device is highly demanding for flexible electronics, which requires the involvement of multiple disciplines in the device design such as electrical engineering, industrial engineering, and so forth.

2. *Developing all bio-compatible materials for the energy storage devices*: A special priority should be given to the development of bio-compatible materials for flexible energy devices. Besides safety concerns, the bio-compatibility should be paid more attention because all flexible devices would be used in the pocket, on the skin, or implant in the human body. Therefore, soft materials, including polymers, gels, and soft biological materials could be considered in terms of

bio-compatibility. However, it is always a big challenge to make a balance between energy density and safety when using "all-organic" soft materials in energy devices.

3. *Developing new nanomanufacturing techniques for energy device fabrication*: Inspired by the device design in the semiconductor industry, designing 3D interdigitated microstructures could be an effective way to address the mechanical and interfacial issues of the flexible energy devices. In order to build seamless interfaces between anode/solid-state-electrolyte and solid-state-electrolyte/cathode, cleanroom-based techniques such as patterning and lithography should be used for 3D interdigitated energy devices. And more importantly, new manufacturing processes such as additive manufacturing (3D and 4D printing) at the nanoscale could be introduced for the fabrication of 3D energy devices.

4. *Developing new energy harvesting devices*: Instead of electrochemical energy storage, new and emerging energy harvesting devices should be considered when designing flexible energy sources. If the flexible electronic devices are used on the skin, there would be an opportunity to harvest the chemical energy from sweat or mechanical energy from vascular pulsation. Microstructured fuel cells and piezoelectric devices would play roles in converting other energy sources from the human body to electricity, which could power the flexible electronics if the energy consumption for the devices is not high.

5. *Integrating data-driven prediction and machine-learning methods into materials design:* Materials design always involves a huge amount of experimental testing in order to identify an ideal composition or structure for the target performance. However, traditional trial-and-error methods are not efficient for new materials design. The emerging data-driven prediction and machine-learning methods should be integrated into the experimental tests in order to predict the

optimum material compositions and structures for the boosted performance toward solid-state energy storage.

6. *Advanced in-situ/operando characterizations:* Advanced in-situ/operando characterizations such as in-situ X-ray techniques (XRD, XAS, and etc) and in-situ microscopy (TEM, SEM, optical microscope, and etc) are very helpful to identify the material growth mechanisms in the manufacturing process and material failure mechanisms in the solid-state energy devices. Developing new in-situ/operando techniques or integrating in-situ/operando characterizations into the materials design should be very crucial for the solid-state devices.

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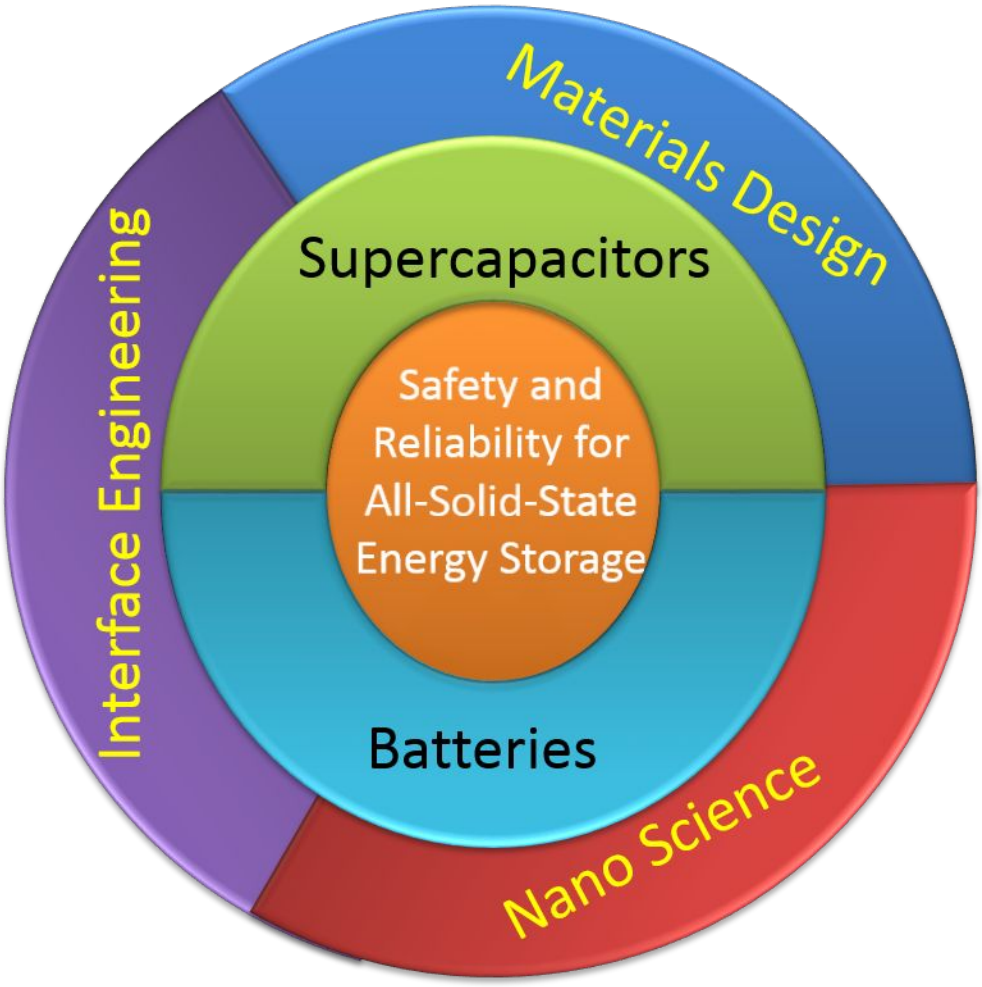


**Scheme 1.** Illustration for the significance and methods to improve the safety and reliability for the all-solid-state energy storage devices such as flexible supercapacitors and batteries by the means of materials design, interface engineering, and nano science.

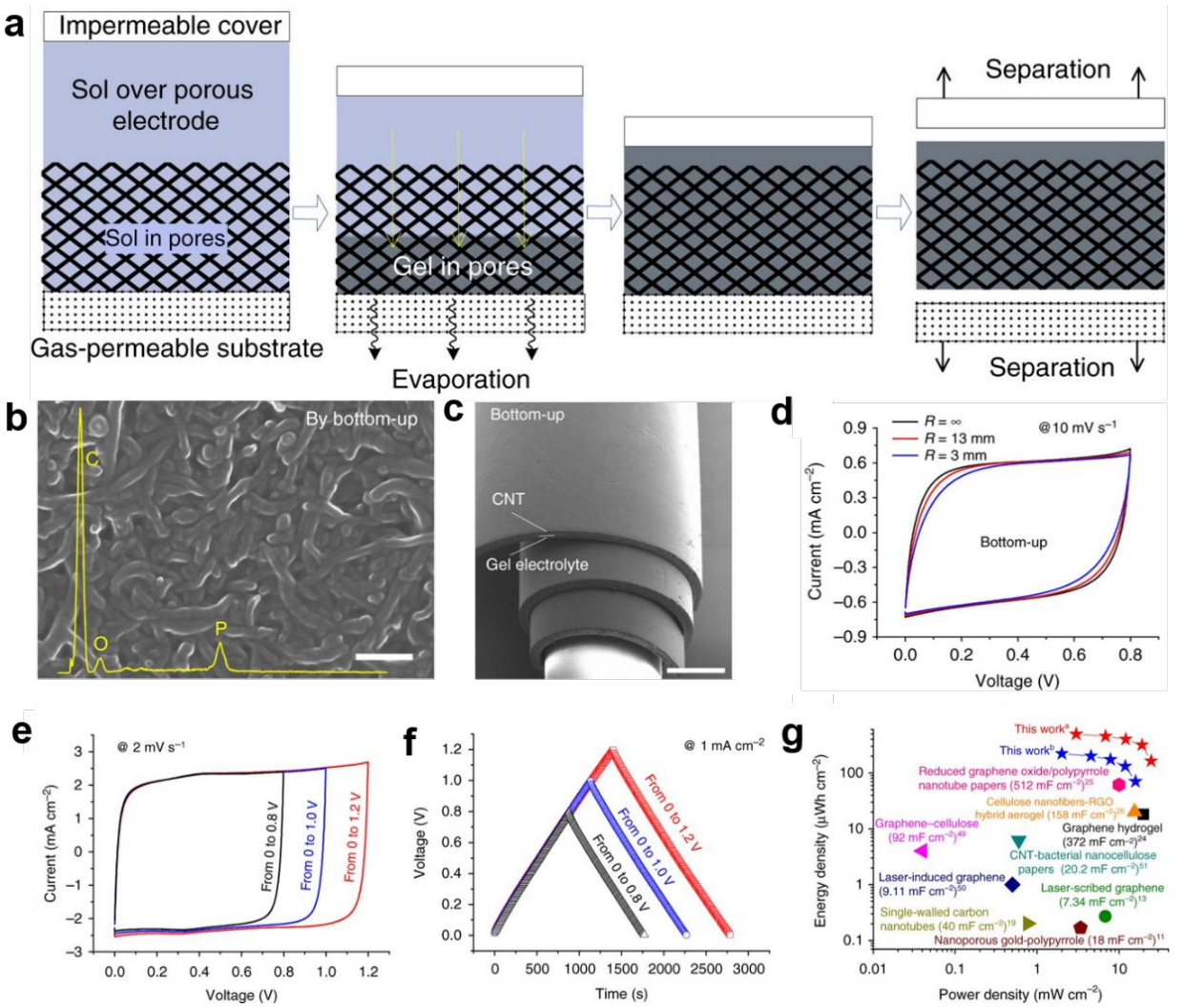


**Figure 1.** (a) Schematic illustration for the bottom-up infilling method. Left to right: sol casting on the porous electrode; the gel formation; a freestanding gel-filled electrode after substrate removal. (b) SEM image of the CNTs-based electrodes infilled with gel electrolyte. Scale bar is 200 nm. (c) The lack of microcracks in the 150 μm thick CNTs-based electrodes infilled with gel electrolyte tested by rolling-up over a glass tube with a radius of 0.5 mm. (d) Electrochemical performance of the CNTs-based electrodes supercapacitor. (e) CV and (f) GCD curves over different potential windows for the 500 μm thick CNTs-based electrodes. (g) Areal Ragone plot.

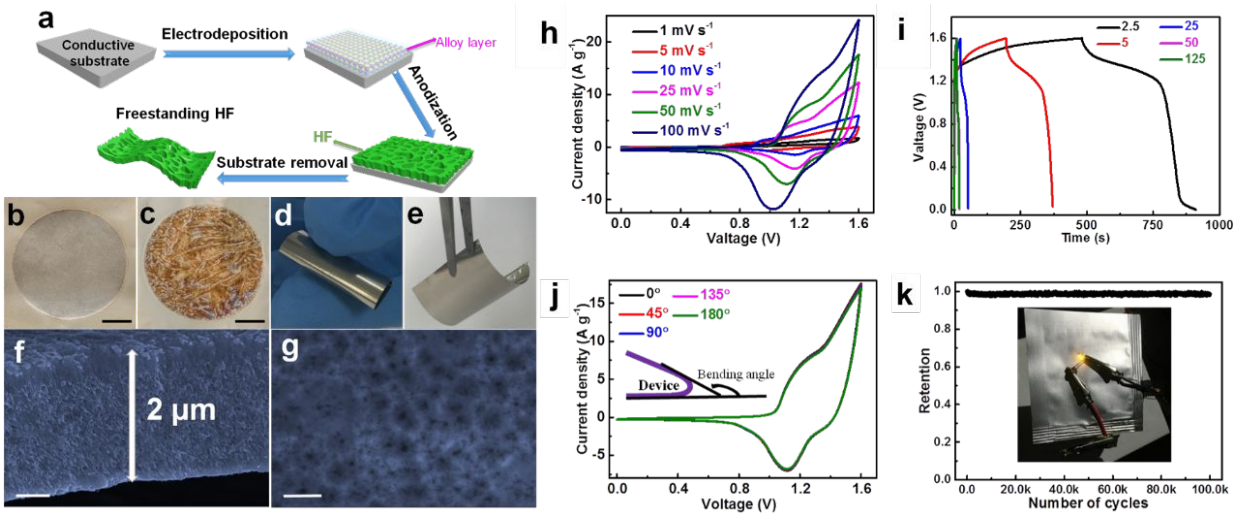


**Figure 2.** (a) Schematic illustration for the electrochemical fabrication of NiFeOF holey layer (HF). (b, c) Photos of the electrodeposited NiFe alloy and the anodized NiFeOF HF, respectively. The scale bars are 0.25 inch. (d, e) Excellent flexibility and mechanical robust feature of the freestanding HF. (f, g) Cross-sectional and top−view SEM images of HF. The scale bars in (f) and (g) denote 500 and 200 nm, respectively. (h) CV curves. (i) Charge/discharge profiles. (j) CV curves with different binding angles. (k) Cycling performance.

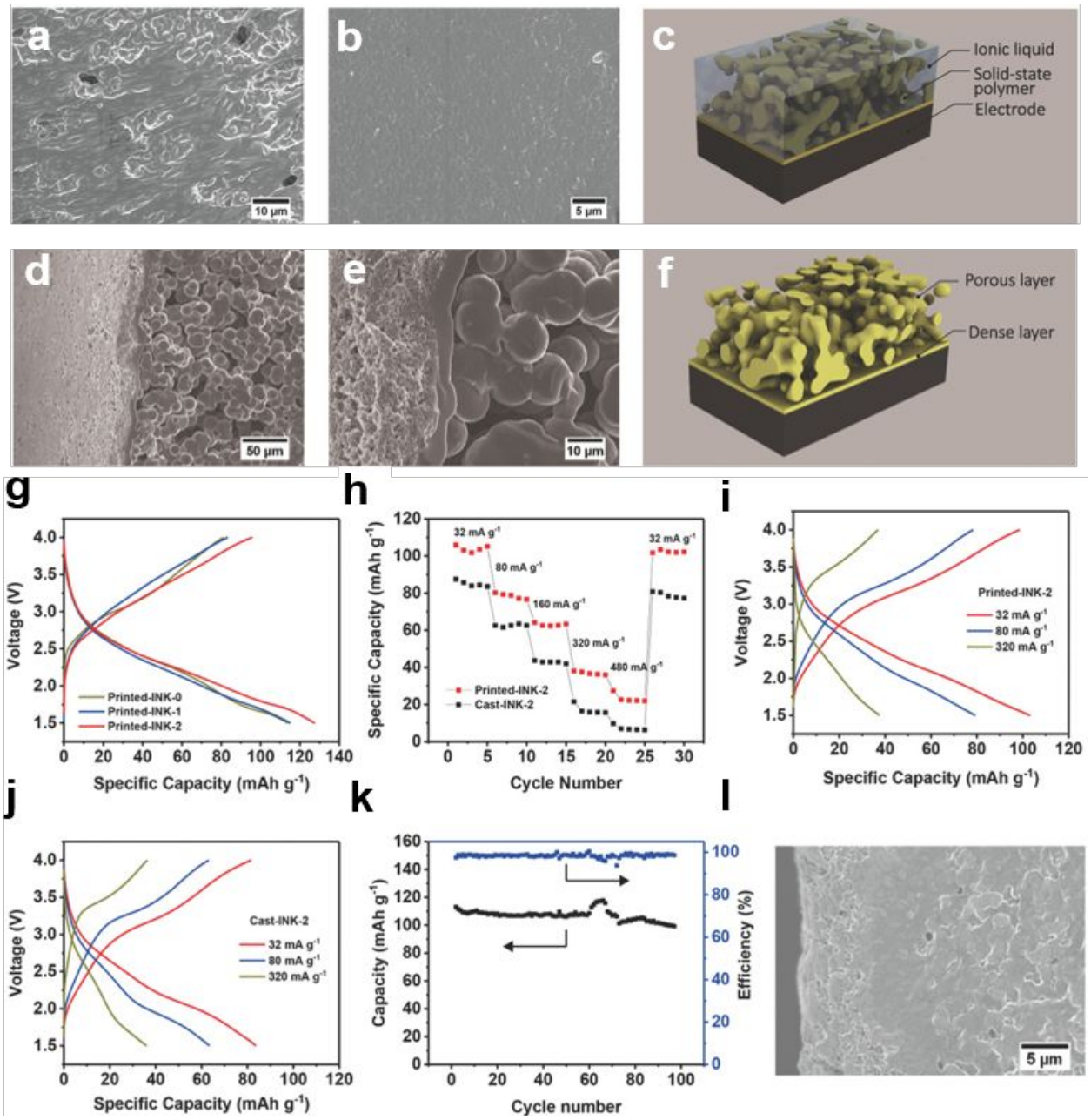


**Figure 3.** (a, b) Cross-sectional and surface SEM images of the 3D printed electrolyte, respectively. (c) Schematic of the 3D printed solid electrolyte. (d) Cross-sectional SEM image of the 3D printed electrolyte after washing out the ionic liquid. (e) SEM image of the dense layer between the porous layer and the electrode. (f) Schematic of the bilayer structure of the 3D printed solid electrolyte. (g) First cycle charge-discharge profiles. (h) Rate profile. (i) Voltage profile of the 3D printed LIBs cell. (j) Voltage profile of the casted LIBs cell. (k) Cycling performance. (l) Cross-sectional SEM image of the 3D printed electrolyte after 100 cycles.

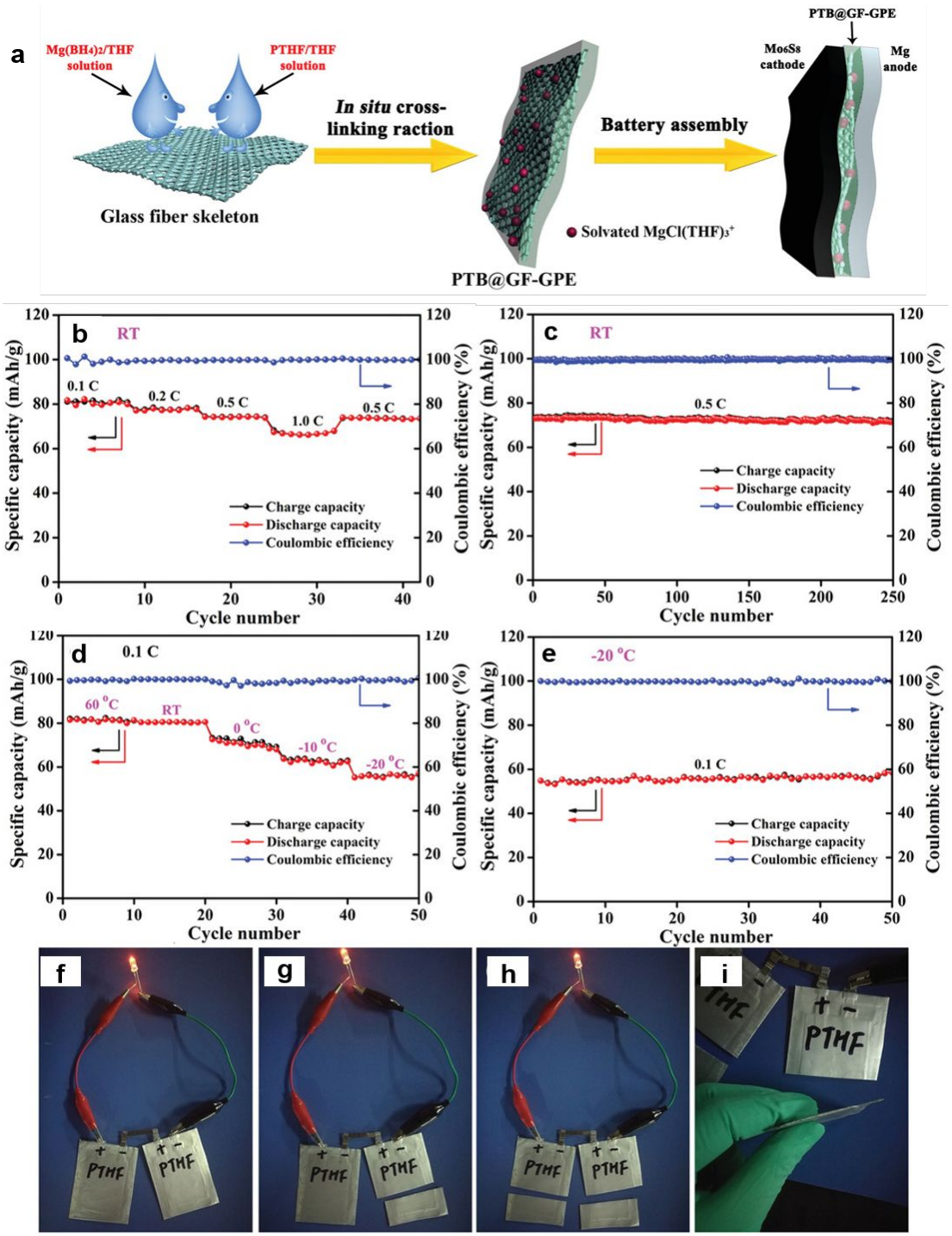


**Figure 4.** (a) Schematic illustration of the preparation of Mo6S8//PTB@GF-GPE//Mg flexible Mg-ion battery cells. (b) C-rate performance at room temperature (RT). (c) The RT cyclic stability at 0.5 C. (d) Temperature-dependent performance at 0.1 C. (e) The cyclic stability at 0.1 C and at -20 °C. (f-i) Flexible Mg-ion batteries under the cutting tests.

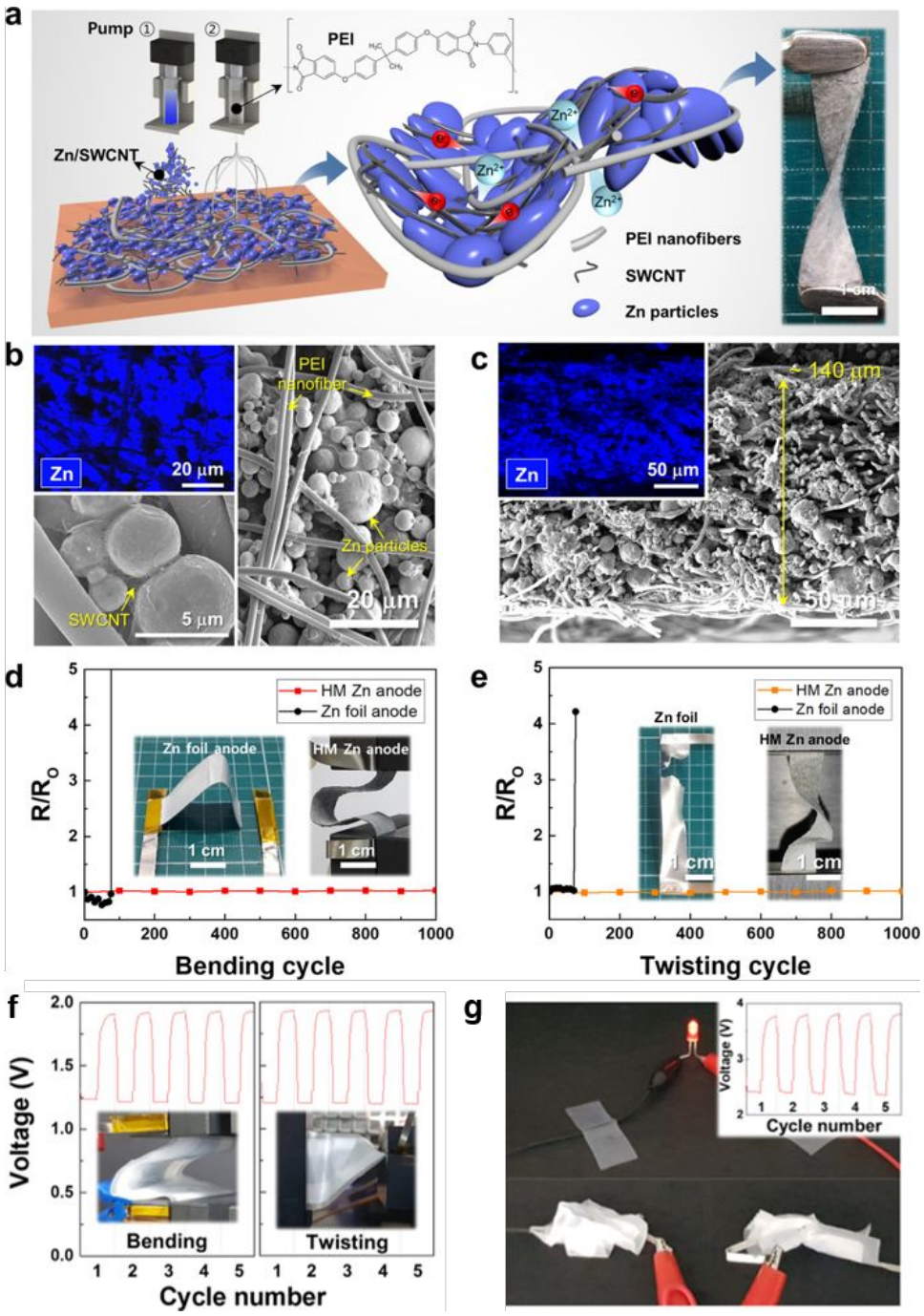


**Figure 5.** (a) Schematic illustration of the electrospraying/electrospinning-assisted fabrication of Zn anode. (b, c) Top-view and cross-sectional SEM images of Zn anode, respectively. The insets are the EDS mapping of Zn. (d, e) The electrical resistance of Zn anode as functions of bending a nd twisting, respectively. (f) Galvanostatic discharge/charge cycling during the bending and twist ing tests. (g) The operation of LED powered by flexible Zn-air batteries. The inset is the galvano

static discharge/charge cycling behavior of the flexible Zn-air batteries.

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