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Permeable Superelastic Liquid Metal Fiber Mat Enables Biocompatible and Monolithic Stretchable Electronics

Zhijun Ma ^{1,2}, Qiyao Huang ¹, Qi Xu ², Qiuna Zhuang ¹, Xin Zhao ³, Yuhe Yang ³, Hua Qiu ⁴,
Zhilu Yang ⁴, Cong Wang ⁵, Yang Chai ⁵, Zijian Zheng ^{1*}

¹ Laboratory for Advanced Interfacial Materials and Devices, Research Center for Smart Wearable Technology, Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong SAR, China.

² State Key Laboratory of Luminescent Materials & Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, Guangdong Engineering Technology Research and Development Center of Special Optical Fiber Materials and Devices, School of Materials Science and Engineering, South China University of Technology, Guangzhou, China.

³ Department of Biomedical Engineering, The Hong Kong Polytechnic University, Hong Kong SAR, China.

⁴ Key Lab of Advanced Technology of Materials of Education Ministry, School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, 610031, China.

⁵ Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR, China.

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Abstract

Electronic devices and systems with high stretchability are essential in the fields of wearable electronics, on-skin electronics, soft robotics, and bioelectronics. Stretchable electronic devices conventionally built with elastomeric thin films show a lack of permeability, which not only impedes wearing comfort and creates skin inflammation over long-term wearing, but also limits the design form factors of device integration in the vertical direction. Here we report a new type of stretchable conductor, namely liquid metal fiber mat (LMFM), which is fabricated by simple coating or printing of liquid metal on electrospun elastomeric fiber mat. Liquid metal hanging among the elastomeric fibers self-organizes into the laterally mesh-like and vertically buckled structure, which simultaneously offers high permeability, stretchability, conductivity, and electrical stability. Besides, LMFM shows smart adaptiveness to omnidirectional stretching over 1800% strain and good biocompatibility. We demonstrate the use of LMFM as the building block to realize highly permeable and multifunctional monolithic stretchable electronics.

Introduction

Electronic devices and systems with high stretchability are essential in the fields of wearable electronics, on-skin electronics, soft robotics, and bioelectronics¹⁻³. High-performance stretchable conductors are critical cornerstones to offer the stretchability. Recent studies have shown that structuring conductive materials including metal, carbon nanotubes, graphene, and their composites into transformable geometries such as buckle, serpentine, and spring can achieve high stretchability and durability while maintaining high conductivity of the materials. Applying these stretchable conductors as electrodes and current collectors of devices, or as interconnects bridging different active components has enabled a wide variety of stretchable electronics for health monitoring, medical diagnostic and treatment, smart actuation, energy conversion and storage, and Internet of Things⁴⁻⁹. With three-dimensional (3D) multilayer designs, 3D-stacked stretchable electronic systems with a high density of functions were also reported very recently¹⁰⁻¹⁵.

Nevertheless, the majority of stretchable electronics nowadays are fabricated with impermeable elastic thin films², which create serious health concerns in the long-term wearing¹⁶. Healthy skin requires microenvironment that provides sufficient permeability to air, moisture, and liquid¹⁷. Even under indoor sedentary conditions, the human body has a requirement to lose water from the skin by "insensible perspiration" at an evaporation rate of $\sim 600 \text{ g/m}^2 \text{ day}$ for thermoregulation¹⁸. Covering the skin with materials that display inadequate moisture permeability will result in uncomfortable sensations, such as dampness and clamminess.¹⁹ Skin irritation is also closely related to the permeability of skin-contacted materials.²⁰⁻²² Skin occlusion created by covering tape, gloves, impermeable dressings or

transdermal devices can lead to a subsequent skin irritation within hours to days^{23,24}. Therefore, long-term wearing of impermeable elastic electronics, especially those directly attached to skins, not only leads to discomfort but also results in allergy and inflammation.

On the other hand, low permeability also limits the advanced functionality of stretchable electronics. In many health-monitoring applications, permeability to analytes (commonly in the form of gas, moisture, and liquid) is critical to ensure rapid, sensitive, and accurate detection of the physiological signals^{2,25,26}. This is especially true for 3D-stacked stretchable systems, in which analytes need to travel through several layers of materials to reach the sensing layer of the device. To date, there is a lack of permeable conductor that can provide high stretchability, stability, and conductivity for the fabrication of 3D stacked stretchable electronics.

Recently, gallium-based room-temperature liquid metal has been widely reported for the fabrication of stretchable conductors through various strategies, which include sealing liquid metal into patterned elastic channels^{27,28}, dispersing micro- and nano-droplets of liquid metal in an elastomeric matrix²⁹⁻³² and coating liquid metal on encapsulated elastomeric sponge^{33,34}. These developments have led to high-performance stretchable conductors showing high conductivity, high stretchability, and in some examples self-healing ability^{35,36}. However, none of these materials were permeable. The permeability of stretchable electronics has been largely overlooked in the past.

Here, we report a new type of highly permeable superelastic conductor named liquid metal fiber mat (LMFM), which enables the fabrication of biocompatible and multifunctional monolithic stretchable electronics. LMFM is fabricated by coating or printing of liquid metal on an electrospun elastomeric fiber mat, followed by a simple mechanical activation process,

in which the liquid metal self-organizes into a laterally porous and vertically buckled film hanging among the fibers. LMFM possesses excellent permeability to air, moisture, and liquid, and retains superelasticity (over 1,800% strain) and ultrahigh conductivity (up to 1,800,000 S/m) over 10,000 cycles of tensile test. In vivo and in vitro biocompatibility tests show excellent biocompatibility of LMFM when it is directly applied to the skin. We show facile fabrication and encapsulation of many kinds of permeable stretchable electronics with LMFM. Importantly, we demonstrate the fabrication of permeable monolithic stretchable electronics by continuous fabrication of multilayer LMFM, which provides multifunction with electrocardiography (ECG) sensor, sweat sensor, and heater in a vertical stack.

Fabrication of LMFM

As illustrated in Figure 1a, LMFMs are fabricated by three simple steps including 1) electrospinning of the superelastic fiber mat, 2) coating of liquid metal on the stretchable mat, and 3) activation of permeability through pre-stretch. As a proof-of-concept, poly(styrene-butadiene-styrene) (SBS) and eutectic gallium-indium alloy (EGaIn) were chosen as the elastomer and the liquid metal. We fabricated a LMFM sample with 320 μm thick SBS mat and 0.8 mg/cm^2 mass loading of EGaIn. The average diameter of SBS microfibers was 2.7 μm (Figure 1b) and the breaking strain of the SBS mat was 2,300% (Figure 1e). This freshly prepared EGaIn-coated SBS mat showed a shiny metal-like surface with little permeability (Figure 1c). To activate the permeability, the substrate was repeatedly stretched to a strain of 1,800% for 12 cycles, during which the shiny surface became dim and the planner EGaIn was transformed into mesh-like porous structure hanged among the SBS microfibers (Figure 1d).

The sample after activation is denoted as 0.8EGaIn-SBS (the value “0.8” indicates the loading amount of EGaIn, namely, 0.8 mg/cm²).

The porous SBS microfibers and the mesh-like EGaIn provided excellent permeability (Figure 1f). The air permeability of 0.8EGaIn-SBS (79.5 mm/s) was much higher than commercially available nylon cloth (11.8 mm/s) and medical patch (7.0 mm/s). In sharp contrast, the air permeability of Ecoflex and polydimethylsiloxane (PDMS) (360 μm thick), which are the most commonly used elastomeric materials in stretchable electronics, was zero. As shown in Figure 1f, the moisture permeability of 0.8EGaIn-SBS (724 g/m²·day) was also higher than that of the nylon cloth (621 g/m²·day) and 22 folds higher than that of the medical patch (31 g/m²·day), which satisfies the insensible perspiration of the human body as discussed above. In contrast, the moisture permeability of PDMS and Ecoflex films were below 50 g/m²·day. At this point, 0.8EGaIn-SBS is hydrophobic, namely, it is permeable to air and moisture but waterproof. Treating 0.8EGaIn-SBS with oxygen plasma rendered the sample hydrophilic; the water contact angle of 0.8EGaIn-SBS reduced from 88.5° to zero after the plasma treatment. Water, artificial sweat, and alcohol could immediately penetrate the hydrophilic 0.8EGaIn-SBS once dropped onto the surface (Figure 1g).

The Young's modulus of 0.8EGaIn-SBS was ~0.1 MPa, which was much softer than a compact SBS film (~0.8 MPa, Supplementary Figure 1) and was very similar to the modulus of human skin^{37,38}. 0.8EGaIn-SBS was highly conductive and stable during stretching. The initial conductivity (at 0% strain) of the 0.8EGaIn-SBS was ~10,000 S/m. Its resistance only increased by 4.1% when stretched to 1,800% strain (Figure 1h), corresponding to a quality factor (Q value, the strain of material divided by resistance change of material³⁹) of 441, which

is the highest among reported values of highly stretchable conductors^{31,39,40}. The ultrahigh Q value is critical to retain the electrical stability of stretchable electronic devices at large deformations. As a proof-of-concept, one piece of 0.8EGaIn-SBS (inset in Figure 1h) was used as an interconnect between an audio source and a loudspeaker to transmit an audio signal (Supplementary Figure 2a). The transmitted waveforms and amplitudes of the audio signal were almost identical at 0% and 1,000% strains of 0.8EGaIn-SBS (Supplementary Figure 2b).

Mechanism of superelasticity

The ultra-high stretchability and electrical stability of the EGaIn-SBS were mainly ascribed to the formation of the laterally mesh-like and vertically wrinkled structure of the liquid metal, which was self-formed in the pre-stretching activation step (Figure 2). It is known that a thin solid layer of oxide (Ga_2O_3) with a thickness of ~ 3 nm will form instantly on the surface of EGaIn upon exposure to air^{35,41,42}. In the activation process, when the substrate was stretched to 1,800% strain, the compact EGaIn film broke up into mesh-like structure and new oxides were formed because of the increase in the total surface of EGaIn (Figure 2a). The oxide layer is much harder than the liquid metal, so that when the substrate returned slowly to 0% strain, EGaIn buckled as a consequence of the mechanical competition between the harder upper oxide layer and the softer underlying substrate (Figure 2a)⁴³. The formation of meshes and buckles began immediately at the first pre-stretch cycle and intensified as the numbers of pre-stretch cycles increased (Supplementary Figure 3a-d). Along with the repeating activation process, the electrical resistance of 0.8EGaIn-SBS increased slowly. We found that the change of resistance and the Q value in each cycle reached a stable stage after 12 pre-stretch cycles

(Supplementary Figure 3e), indicating that the wrinkled mesh-like structure reached a reversible state (Figure 2b).

After activation, the lateral meshes changed gradually from circular to ribbon-like shape when stretched, and returned to circular shape when the load was released (Figure 2b). This transformation is similar to the serpentine design of stretchable conductors reported in many stretchable electronics². Meanwhile, the vertical buckles of EGaIn became flatten when the substrate was stretched, which is similar to that of an accordion (Figure 2b). The highly reversible transformation of the lateral meshes and vertical buckles both contributed to the high Q value at high strains. The spontaneous formation of highly stretchable and permeable structure in the ambient environment is an obvious advantage of EGaIn-SBS when compared with those highly stretchable conductors fabricated by complicated lithographic processes^{44,45}.

Stable and self-adaptive superelasticity

The activated EGaIn-SBS acquired long-cycle stability upon deformations, as a result of the reversible transformation of the porous structures and buckles. For example, after more than 100 cycles of stretching to 1,000% and 1,800%, the electrical resistances of 0.8EGaIn-SBS only increased by 18% and 36%, respectively (red and black curves in Figure 3a). The increase of resistance after repeating high-strain stretching was majorly attributed to the physical breakage of SBS fibers (Supplementary Figure 4). When the tensile strain was limited to 100%, 0.8EGaIn-SBS could bear more than 25,000 cycles with less than 30% change of the electrical resistance (cyan curve in Figure 3a). Considering that strains induced by typical motions of the human body are less than 55%⁴⁶, the superelastic EGaIn-SBS satisfies different

kinds of wearable applications.

By increasing the mass loading of EGaIn from 0.8 to 5.0 mg/cm², we could easily enhance the conductivity of EGaIn-SBS from 10,000 to 1,800,000 S/m (Supplementary Table 1). Such an activation process exhibits good reproducibility (Supplementary Figure 5-9). We found a tradeoff between the conductivity and the Q value: the Q value decreased with the increase of conductivity (Figure 3b). The tradeoff can be qualitatively investigated with a simplified model of EGaIn-SBS. The whole conductor consists of both reversible part (vertical wrinkle or planar mesh-like structure) that can exhibit negligible resistance change by accommodating the strain, and unavoidably irreversible part whose resistance increases with the increase of the strain. For simplicity, we could consider one segment of EGaIn-SBS with both reversible (L_{rev}) and irreversible (L_{irrev}) parts, as schematically illustrated in Supplementary Figure 9a. The Q value of the conductor can then be calculated as:

$$Q = \frac{\varepsilon}{a(\varepsilon^2 + 2\varepsilon)} = \frac{1}{a(\varepsilon + 2)} \quad (1)$$

where ε is the strain and a is the ratio of the irreversible part in the conductor (see Method for the detailed elaboration of the equation). As shown in the cross-sectional SEM images of EGaIn-SBS (Supplementary Figures 9b-d), the ratio of the wrinkled part ($1-a$) was greatly reduced when the mass loading of EGaIn increased. According to Equation (1), even though the increase of mass loading enhances the conductivity, it decreases the Q value.

The high permeability of EGaIn-SBS was maintained even with very high mass loading of EGaIn. As shown in Supplementary Figure 10, the air permeability decreased from 79.5 to 19.1 mm/s and the moisture permeability decreased from 724 to 520 g/m² day, when the mass loading of EGaIn increased from 0.8 mg/cm² to 5 mg/cm². Considering that permeability is

closely related to the porosity of fibrous materials⁴⁷, such phenomena can be attributed to the high porosity (~72%) of EGaIn-SBS mats at different mass loadings of EGaIn (Supplementary Table 1).

Importantly, EGaIn-SBS possessed smart self-adaptability: the orientation of wrinkles could reconstruct according to the change of tensile direction owing to the isotropic stretchability of the SBS mat and EGaIn. When the stretching direction of EGaIn-SBS was changed, the original buckles were broken and new Ga₂O₃ formed. Following the same activation process, new buckles would form along the reoriented direction (Figure 3c). As a proof-of-concept, we rotated the tensile direction of 2.0EGaIn-SBS by 45° and then stretched to 1,800% strain for 10 cycles. This reorientation was repeated four times. As shown in Figure 3d, the direction of buckles also reoriented accordingly to follow the tensile direction. The corresponding cycled change of resistance was also an evidence of the regeneration of the porous buckled structures of EGaIn in each of the reorientation step. Such a smart self-adaptability enabled omnidirectional stretchability and stability without the need for any specific design. As such, EGaIn-SBS is particularly superior in applications where complex deformation frequently happens. It also enables great design flexibility where multiple stretchable devices with different stretching directions are needed at the same time.

Biocompatibility of LMF

Biocompatibility is of paramount importance for wearable and on-skin applications. EGaIn-SBS and SBS were affirmed to possess low cytotoxicity in the *in vitro* study by using L-929 cells as the model cell. Bright-field and fluorescent live/dead staining images showed a

regular cell morphology and scarce dead cells in all groups except for the positive control group which presented severe dead cells. Quantification of the live/dead stained cells presented high cell viability of near 95% after 24 h with no significant difference among all tested groups. The absorption at 570 nm in MTT assay (proportional to the number of cells) of all groups remarkably increased with incubation time from day 1 to day 3 with a similar trend indicating that there was no significant evidence of the toxicity of the EGaIn-SBS and SBS. (Figure 4a-c).

In vivo animal experiments on the rabbit skin further demonstrated that neither SBS mat nor EGaIn-SBS mat caused obvious irritation (i.e., no erythema and oedema on the skin) during the observation period (24, 48 and 72 hours, Supplementary Figure 11), indicating that our SBS and EGaIn-SBS mats are skin-friendly. Slight erythema was observed for the non-permeable EGaIn-SBS film (mass loading also 2.0 mg/cm²) one day after the test although the erythema disappeared two days later.

In addition, we carried out on-skin tests to prove the importance of permeability for long-term wearability (Figure 4d). Six samples, including SBS mat, 2.0EGaIn-SBS mat, non-permeable 2.0EGaIn-SBS film, non-permeable SBS film, Ecoflex film, and PDMS film, were attached on the forearms of one volunteer for one week of wearing. As shown in Figure 4d, neither SBS mat nor 2.0EGaIn-SBS mat caused any negative effect on the skin after one week of attaching. In contrast, all the non-permeable samples caused obvious skin erythema.

Printing of monolithic stretchable electronics

The additive manufacturing principle and the self-adaptive superelasticity of EGaIn-SBS

provide an excellent platform for the fabrication of stretchable electronics via printing. As a proof-of-concept, we printed a wide variety of EGaIn patterns on SBS mats by stencil printing (Figure 5a-b). After mounting commercially available LED chips onto the EGaIn, the second layer of SBS mat serving as an encapsulating layer was then electrospun on top. The encapsulated LED array was resilient to different degrees of stretching and twisting (strain=500% and twisting degree=720°) and could still function underwater (Figure 5c). No obvious change in the performance of the LED array and no leakage of liquid metal were observed even after washing the encapsulated device for 120 min (Figure 5d-e, Supplementary Video 1).

By repeating the electrospinning and printing processes, we fabricated vertically stacked multilayer electrical circuits that incorporated into one monolithic elastic mat (Figure 6a), which maintained the high permeability even reached a large thickness of ~2 mm (Supplementary Video 2). As shown in Supplementary Figures 12a and 12b, the air and moisture permeabilities of the monolithic elastic were higher than 8.0 mm/s and 600 g/m² day, which are similar to the commercial nylon cloth and satisfy the insensible perspiration of the human body. The monolithic stretchable mat could also become highly permeable to liquid after plasma treatment (Supplementary Figures 12c and 12d).

The permeable stacked architecture promises a new type of monolithic stretchable electronics with excellent wearing comfort and multifunctionality that are difficult to realize with conventional elastic thin films. As a proof-of-concept, we fabricated one 100 mm × 60 mm monolithic stretchable electronic mat, which contained three layers of printed EGaIn electrodes with a total thickness of ~1 mm (Figure 6b). The three-layer EGaIn electrodes functioned as an ECG sensor (top layer), a sweat sensor (middle layer), and an electrothermal

heater (bottom layer). Such a vertically stacked multilayer architecture is expected to provide multi-channel monitoring of human physiological states and electrothermal therapy. The top layer, which was in direct contact with human skin, could collect reliable low-noise ECG signals at both stretched and compressed states as a result of the superelasticity of EGaIn-SBS (Figure 6c). In contrast, the commercial ECG patch could only work when the skin was lied flat. The interdigitated electrode pair on the middle layer was a capacitor for monitoring the volume change of sweat which penetrated through the first ECG layer from the epidermal of human skin. The capacitance increased as a function of the received volume of sweat, which indicated the sweating rate (Figure 6d). In addition, it also monitored the ion concentration, e.g., NaCl, in sweat at different stretched states of the skin (Figure 6e). On the bottom layer, the electrothermal heater could respond rapidly and sensitively to the applied voltage. For example, the surface temperature could be adjusted step-wisely from 30 °C to 95 °C with an increment of applied voltage at 0.08 V per step from zero to 0.48 V (Figure 6f). This performance suggested the precise control of output temperature at very low power. At a steady applied voltage of 0.15 V, its output temperature only changed by 15% (from 34.4 °C to 40.1 °C) when the device was stretched to 100% strain (Figure 6g). The heater also demonstrated stable cycling performance as shown in Figure 6h.

Discussions

At this moment, we found that EGaIn-SBS underwent oxidation at a very slow speed. After 30 days of storage in the air, the electrical resistance of a 2.0EGaIn-SBS went up by 61% (Supplementary Figure 13a-c). EGaIn-SBS could sustain 10 cycles of rubbing and peeling tests.

The electrical resistance of 2.0EGaIn-SBS increased by 50% when it was rubbed against printing paper and human skin (Supplementary Figure 13d). The electrical resistance increased from 1.4 to 4.9 Ω after 10 times of peeling (Supplementary Figure 13e). Indeed, the slow deterioration of EGaIn may cause some stability issues for devices that require long-term usage with ultrahigh sensitivity. Encapsulating the LMFM with an additional layer of SBS fiber mat could significantly enhance the stability. No change of electrical resistance was observed in the rubbing test for the encapsulated sample (Supplementary Figure 13d). The oxidation could also be mitigated: the electrical resistance only increased by 39% after encapsulation (Supplementary Figure 13a).

In summary, LMFM is a new type of stretchable conductors that are easily prepared by coating or printing of liquid metal onto elastic electrospun fiber mats. With a simple pre-stretch process, liquid metal self-organizes into a laterally porous and vertically buckled mesh that hanged among the elastic fibers. In comparison to other state-of-the-art liquid-metal-based stretchable conductors (Supplementary Table 2), LMFM is the only materials strategy to date that can simultaneously achieve ultrahigh conductivity, ultrahigh Q value, ultrahigh strain, high biocompatibility, and high permeability. With the unique advantages of permeability and omni-superelasticity, we have shown a proof-of-concept three-layer monolithic stretchable electronic mat. In principle, one can realize many more functions by topping up the number of device layers. For example, we fabricated a monolithic mat with five layers of devices with different EGaIn electrodes (Supplementary Figure 14), which still showed high permeability. We further demonstrated the 3D interconnects of the electrical components in different layers via simple punching and subsequent injection of liquid metal (Supplementary Figure 15). We envision

that LMFM will become a versatile and user-friendly platform to fabricate monolithic stretchable electronics that provide high-integration-density, multifunctionality, and long-term wearing ability.

Data availability

The main data supporting the findings of this study are available from the corresponding author upon request. Source data of Fig.1, Fig. 3, Fig. 4, Fig. 5, and Fig. 6 are provided with this paper.

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Author Contribution

Z.J.M. and Z.J.Z. conceived and designed the experiments. Z.J.M and Q.X. performed the experiments. Z.J.M., Q.Y.H., and Q.N.Z performed the materials characterization. Z.J.M. tested the devices' performance. X.Z., Y.H.Y., H.Q and Z.L.Y. performed the *in-vivo* cell and animal experiments. Z.J.M and Q.Y.H. analyzed the data. Y.C. and C.W. conducted the numerical model and calculation for the materials. Z.J.M, Q.Y.H., and Z.J.Z wrote the

manuscript. Z.J.Z. supervised the project. All authors discussed the results and commented on the manuscript.

Competing Interests

The authors declare no competing interests.

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Methods

Electrospinning of SBS mats

Poly(styrene-block-butadiene-block-styrene) (SBS) was dissolved in 1,2-dichloroethane (DCE) by magnetic stirring at the temperature of 50 °C to form a transparent and viscous solution. The mass ratio of SBS to DCE was controlled at 1:5. Then the solution was injected into a 20-mL syringe for the electrospinning. During the electrospinning, the applied voltage, feeding rate of solution, and collecting distance of fibers were set as 12 kV, 5 mL/h, and 15 cm, respectively. The whole electrospinning process was performed at room temperature in the ambient environment. The as-electrospun SBS microfibers were collected on a stainless-steel plate. After collection, the SBS mat was peeled off the stainless-steel plate for the subsequent use.

Fabrication of EGaIn-SBS

Eutectic gallium-indium alloy (Sigma Aldrich, mass ratio of Ga: In=75.5: 24.5, melting point: 15.7 °C, conductivity: 34,000 S/cm, abbreviated as EGaIn) was employed as the conductive agent. EGaIn was coated on the surface of the electrospun SBS mat to prepare the composite mat (EGaIn-coated SBS). To improve permeability and electrical stability, the EGaIn-coated SBS composite mat was activated by repeated pre-stretching at the strain of 1,800% for 12 cycles. The activated sample was denoted as EGaIn-SBS. The areal mass loading of EGaIn was varied in the range from 0.8 mg/cm² to 5.0 mg/cm² to tune the electrical properties of the samples. For the printing of EGaIn circuits on SBS mats, different stencils with designed patterns were prepared as masks. To fabricate a EGaIn circuit on the SBS mat,

the stencil was firstly covered on top of an SBS mat, and then EGaIn was dropped onto the stencil and spread by a squeegee. After removing the stencil mask, SBS mat printed with a designed EGaIn circuit was obtained.

Fabrication and testing of permeable monolithic stretchable electronics

Monolithic stretchable electronics containing multilayers of vertically stacked EGaIn-SBS devices were fabricated by sequential electrospinning and stencil printing. Firstly, an SBS fibrous mat was prepared by the electrospinning approach. Then, the stencil with a designed pattern was covered on the SBS fibrous mat, followed by printing EGaIn (mass loading: ~ 2 mg/cm²) onto the stencil-covered SBS mat. After removing the stencil, the first layer of EGaIn circuit was obtained. The above process was repeated until all the required layers of EGaIn circuits were prepared. An additional layer of SBS mat was electrospun on the surface of the EGaIn circuit to serve as the encapsulation layer for such a monolithic stretchable device.

The monolithic stretchable electronics containing three layers of printed EGaIn electrodes were functioned as an ECG sensor (top layer), a sweat sensor (middle layer), and an electrothermal heater (bottom layer), respectively. Plasma treatment was applied to render the surface hydrophilicity. To connect the printed EGaIn devices and electrode to the external multimeters, strip of SBS (5 cm x 1 mm x 0.1 mm) uniformly brush-coated with EGaIn (mass loading: ~ 0.84 mg/cm²) was attached to each end of the electrodes. Thin copper wires were then wrapped on the other ends of the EGaIn-SBS strips, and connected to external multimeters (Supplementary Figure 16). For the ECG testing, a commercial ECG device (Heal Force PC-80D) with 4 electrode wires was used to collect ECG signals. Three of the electrode wires were

connected to commercial ECG patches and then attached to the human skin of the left legs, right legs, and left wrist, while the 4th electrode wire was connected to the printed EGaIn electrode on the top layer of the monolithic stretchable electronics and then attached to the human skin of the right wrist. 3M tapes were used to fix the edges of the monolithic EGaIn-SBS devices on the skin. The connection of the electrodes to the ECG device is schematically shown in Supplementary Figure 17. To evaluate the sweat sensing performance of the EGaIn electrodes, phosphate-buffered saline (PBS, Gibco, pH=7.4) was used to perform as the artificial sweat. Various volumes of PBS were dripped onto the as-made monolithic stretchable electronics mat, which could induce the capacitance change of the capacitor printed on the middle layer. After reaching a steady-state, the capacitance value was recorded, which could indicate the rate of sweating. The above test was performed at different tensile strain (0%, 50%, 100%) of the mat. NaCl aqueous solutions with different concentrations were used to represent human sweat. For this test, the mat was immersed in the NaCl solution with a specific ion concentration. After reaching a steady-state, the capacitance value was recorded, which could indicate the ion concentration in the sweat. This test was performed at different tensile strains of the mat.

Characterization

The surface morphology of the samples was collected by scanning electron microscopy (SEM, Hitachi TM3000). The mechanical properties of the SBS mat and EGaIn-SBS were tested using an Instron 5599 universal testing system, in which samples were cut into strips with dimensions of 60 mm x 3 mm for the test. The electrical properties of the samples under

different stretching states were investigated by a Keithley 2400 source meter coupled with a computer-controlled stretching motor. In brief, the sample was cut into a small strip with dimensions of 15 mm × 3 mm. Two ends of the strip were then mounted on the motion platform and then stretched by the computer-controlled motor. The resistance changes of the sample at different stretching states were measured by the source meter. Four-terminal method was employed to avoid the significant influence of contact resistance. The connecting parts to the sample were at the two ends of the sample, which were fixed with highly conductive Cu tapes to ensure the good contact. The quality factor, Q value, then can be obtained by following the equation (2):

$$Q = \frac{\frac{L-L_0}{L_0}}{\frac{R-R_0}{R_0}} \quad (2)$$

where L_0 and R_0 are the length and resistance of the EGaIn-SBS mat before stretching, and L and R are the length and resistance of the EGaIn-SBS mat stretching at a specific strain.

The material compositions of EGaIn coating layer on SBS mat were characterized by X-Ray diffraction (XRD, Rigaku SmartLab) and X-Ray photoelectron spectroscopy (XPS, Thermo Scientific Nexsa). The air permeability value (mm/s) of all the samples was tested according to ASTM D737-08 using MO21S air permeability tester (SDL Americ, Inc.). The output airflow rate (unit: mm/s) represents the air permeability of samples. Moisture permeability tests for the samples were performed by using the cup method according to the textile standard E96/E96M-13. Moisture transmission rate (g/m²·day) was determined by measuring the weight loss of the water vapor in a cup with its opening firmly covered by the tested specimen (testing duration: 72 h). Both air resistance and moisture permeability tests

were performed at about 22 °C and 63% relative humidity. Commercial Nylon cloth (Crystal Shine Red, Shuangqian Textile Co., Inc.) and medical patch (MOHRUS Patch, Hisamitsu Pharmaceutical Co., Inc.), PDMS and Ecoflex films with different thickness were also used as the control for comparison. Abrasion test and peeling test of EGaIn-SBS were performed according to ISO 105 and ASTM D903 standards, respectively.

Calculation of Porosity of EGaIn-SBS

The porosity of EGaIn-SBS ($P_{EGaIn-SBS}$) was calculated based on the Archimedes law by using equation (2):

$$P_{EGaIn-SBS} = \left(1 - \frac{V_{true}}{V_{apparent}}\right) \times 100\% \quad (2)$$

where $V_{apparent}$ is the apparent volume and V_{true} is the true volume of EGaIn-SBS mat.

Since the volume of EGaIn-SBS mat is composed of the volume of SBS fiber substrate and the volume of EGaIn, $V_{apparent}$ and V_{true} can be obtained by following equations (3) and (4).

$$V_{apparent} = V_{SBS} + V_{EGaIn} \quad (2)$$

$$V_{true} = V_{SBS(true)} + V_{EGaIn} \quad (3)$$

where V_{SBS} is the apparent volume of the SBS fiber substrate, V_{EGaIn} is the volume of the loaded EGaIn, and $V_{SBS(true)}$ is the true volume of SBS fiber substrate.

The apparent volume of the SBS fiber substrate (V_{SBS}) can be calculated based on the dimension of the sample. The volume of the loaded EGaIn (V_{EGaIn}) can be calculated based on the mass loading of EGaIn on the sample and the density of EGaIn ($6.25 \times 10^3 \text{ g/cm}^3$).

To obtain the true volume of SBS fiber substrate ($V_{SBS(true)}$) in the EGaIn-SBS mat, a piece

of EGaIn-SBS mat with 0.8mg/cm² mass loading of EGaIn (size: 9.6 cm x 4.8 cm x 0.04cm, weight: 0.501 g) was used to measure the true density (ρ) of the tested sample by a density meter. The true density (ρ) was measured as 1.004 g/cm³. Then the true volume of SBS fiber mat substrate ($V_{SBS(true)}$) can be obtained by the equation (4):

$$V_{SBS(true)} = V_{true} - V_{EGaIn} = \frac{m}{\rho} - V_{EGaIn} = \frac{0.501}{1.004} - \frac{0.8 \times 9.6 \times 4.8}{6.25 \times 1000} \approx 0.493(cm^3) \quad (4)$$

where m is the total weight of the tested 0.8EGaIn-SBS sample (0.501 g) and ρ is the true density of the sample (1.004 g/cm³) measured by the density meter. V_{EGaIn} is the volume of the loaded EGaIn, which can be calculated based on the mass loading (0.8 mg/cm²) of EGaIn on the tested sample and the density of EGaIn.

Therefore, with the true volume of SBS fiber substrate ($V_{SBS(true)}$), the porosity of EGaIn-SBS mat with different loadings of EGaIn can be calculated by using equations (1)-(3). The porosity of EGaIn-SBS mat with different mass loading of EGaIn is shown in supplementary Table 1. It should be noted that the dimensions of the EGaIn-SBS mats kept the same in this calculation process, and we assumed that the loading of EGaIn would have the negligible impacts on the thickness of the samples

Calculation of conductivity of EGaIn-SBS

The conductivity (σ) of the EGaIn-SBS mats can be approximately calculated according to the measured electrical resistance (R), the length and width of the EGaIn-SBS mats (L and W , equal to the length and width of EGaIn mesh), and the effective thickness of the EGaIn mesh (T):

$$\sigma = \frac{L}{(W \times T) \times R} \quad (5)$$

where L , W , and R can be directly measured.

The effective thickness of the EGaIn mesh (T) takes account of the mesh-like structure (projection of EGaIn area over the total sample area in a top view, denoted as A_{EGaIn}) and the porosity of the mat ($P_{EGaIn-SBS}$, assuming that EGaIn is filled in all the gaps between the SBS fibers). Therefore, T can be expressed as:

$$T = \frac{M_{areal}}{A_{EGaIn} \times \rho_{EGaIn} \times P_{EGaIn-SBS}} \quad (6)$$

where M_{areal} (0.8, 1.4, 2.0, 2.6 and 5.0 mg/cm²) refers to the areal mass loading of EGaIn on SBS mat, A_{EGaIn} refers to the areal percentage of EGaIn in the EGaIn mesh, and ρ_{EGaIn} (6.25 g/mL) refers to the density of EGaIn used in this work. A_{EGaIn} was measured by software (Adobe Photoshop) according to the SEM images of EGaIn-SBS mats, and $P_{EGaIn-SBS}$ is the porosity of the EGaIn-SBS fiber mat as summarized in Supplementary Table S1.

By replacing T in equation (5) with equation (6), the conductivity of the EGaIn-SBS mats can be calculated as:

$$\sigma = \frac{L \times A_{EGaIn} \times \rho_{EGaIn} \times P_{EGaIn-SBS}}{W \times M_{areal} \times R} \quad (7)$$

Investigation of the cell cytotoxicity of EGaIn-SBS

L-929 cells (ATCC, US) were used to examine the *in vitro* cytotoxicity of the as-prepared SBS and EGaIn-SBS samples following the ISO 10993-5: 2009(E) standard. Briefly, 6×10^4 L-929 cells in 1 mL full Dulbecco's Modified Eagle's Medium (DMEM, Hyclone, Hong Kong) supplemented with 10% fetal bovine serum (FBS, Hyclone, Hong Kong) and 1%

penicillin/streptomycin (PS, Hyclone, Hong Kong) were seeded in a 24 well plate. After 24 h incubation followed by verification of the cell confluency and morphology, we discarded the medium from the culture plate and added 1 mL fresh full medium. Then, 0.2 cm² sterile SBS or 2.0EGaIn-SBS mats were directly added in the 24 well plate to evaluate the cytotoxicity of the materials. The fresh full medium, absorbent gauze (0.2 cm²), 20% DMSO/full medium mixture were used as blank, negative, and positive control. All samples were cultured at 37°C in incubator with 5% CO₂.

After 24 h of incubation, live/dead® and MTT assay were used to quantify the cell viability and proliferation, respectively. Live/Dead assay (Thermo Fisher, Hong Kong) was used to observe live and dead cells in different groups according to the manufacturer protocol. Briefly, after discarding the culture medium, 200 µL phosphate buffer saline (PBS) staining solution with 2 µM calcein AM and 8 µM propidium iodide (PI) was added and incubated for 45 min. After rinsing with PBS, cells were observed using a fluorescent microscope (Zeiss, Germany). For the cell proliferation examination, 500 µL MTT solution was added to each well followed by 2 h incubation. Then, 500 µL dimethylsulfoxide (DMSO) was added to dissolve the formazan. The absorption at 570 nm which reflected the cell metabolic activity was detected using a plate reader (BioTek, US). The cell viability was determined using the absorbance ratio between the tested well and the blank control well.

Animal test

The animal experiment of EGaIn-SBS mat was carried out according to ISO 10993-10:2010(E) standard. All procedures of animal experiments followed all ethical guidelines for experimental animals, and was approved by Southwest Jiaotong University. A total of six New Zealand White Rabbits of 2.0-3.0 kg were used for this study. Four sample patches (2.5×2.5

cm square) were tested on each rabbit. These samples were divided into five groups: group 1: negative control (thin cotton cloth), group 2: positive control (thin cotton cloth rinsed with saturated sodium dodecyl sulfonate (SDS) solution), group 3: SBS mat, group 4: 2.0EGaIn-SBS mat, group 5: non-permeable 2.0EGaIn-SBS film (prepared by casting and drying of SBS solution (concentration: 16.7 wt%, with DCE as solvent)). Briefly, backs of the rabbits were shaved 24 h before the application of each sample. Three sample patches of each group were applied onto the skin under a 2.5×2.5 cm gauze pads that were secured with semi-occlusive medical sterile wound dressings (Hynaut, Tsingtao, China). After direct exposure to shaved skin for 24 h, the patches were removed, and the test sites were cleaned using lukewarm water. The skin was observed for any visible change such as erythema at 0 (initial), 24, 48, and 72 h after sample application. The mean erythema scores (MES) were recorded ranging from 0 to 4 (0 = no erythema; 1 = slight erythema; 2 = moderate erythema; 3 = moderate to severe erythema; and, 4 = severe erythema) depending on the degree of erythema.⁴⁸

The skin irritation test of the EGaIn-SBS mat was also carried out on human skin. One volunteer participated in this study. Six samples, including SBS mat, 2.0EGaIn-SBS mat, and non-permeable 2.0EGaIn-SBS film, SBS film, Ecoflex film, and non-permeable PDMS film were attached to the skin of the forearms of one volunteer, which edges were secured with acrylic adhesive (Walker Tape Co. Ltd). After one week of wearing, the covering materials were removed from the skin and the appearance of the skins before and after the test were imaged.

Numerical Model of the EGaIn-SBS

To reveal the tradeoff between the conductivity and the Q value, we constructed a simplified model to investigate their qualitative relationship. After repeating the activation process, most of the parts in our LMFM reached fully reversible states. The whole conductor consists of both reversible part (vertical wrinkle or planar mesh-like structure) that can exhibit negligible resistance change by accommodating the strain, and unavoidably irreversible part whose resistance increases with the increase of the strain. For simplicity, we consider one segment of LMFM with both reversible (L_{rev}) and irreversible (L_{irrev}) parts, as schematically illustrated in Supplementary Figure 9a.

The total length (L) can be written according to Equation (8):

$$L = L_{irrev} + L_{rev} \quad (8)$$

We can define $a = \frac{L_{irrev}}{L}$, $b = \frac{L_{rev}}{L}$, where $a + b = 1$. According to Ohm's law, we can describe the resistance as Equations (9):

$$R_{rev} = \rho \frac{L_{rev}}{S}, \quad R_{irrev} = \rho \frac{L_{irrev}}{S}, \quad R_{total} = R_{rev} + R_{irrev} \quad (9)$$

in which we assume the conductor has a uniform cross-sectional area (S), and ρ is the resistivity of liquid metal. Under uniaxial stretching, the reversible part can accommodate the strain without length change; for the irreversible part, its length and effective cross-sectional area change as following,

$$L_{irrev} \rightarrow L'_{irrev}, \quad S \rightarrow S',$$

Because the liquid metal is fluidic and isotropic, it is not compressible or expandable. Therefore, it is reasonable for us to assume that the effective total volume of liquid metal is unchanged during the stretching process. In this way, we can describe the stretched length, effective cross-sectional area, and the resistance of the stretched part after the uniaxial strain

with the stretch ratio (γ):

$$L'_{irrev} = \gamma L_{irrev} \quad (10)$$

$$S' = \frac{S}{\gamma} \quad (11)$$

$$R'_s = \rho \gamma^2 \frac{L_{irrev}}{S} = \gamma^2 R_{irrev} \quad (12)$$

Thus, the total resistance of the conductor changes as well:

$$R'_{total} = a\gamma^2 R_{irrev} + bR_{rev} = (a\gamma^2 + b) R_{total} \quad (13)$$

The stretch ratio γ can be written as engineering strain (ε) as:

$$\gamma = 1 + \varepsilon \quad (14)$$

and the total resistance after the uniaxial strain (R'_{total}) can be expressed as equation (15):

$$R'_{total} = (a\lambda^2 + b)R_{total} = a(\varepsilon^2 + 2\varepsilon)R_{total} \quad (15)$$

Therefore, the fractional resistance change of stretchable conductor is $a(\varepsilon^2 + 2\varepsilon)$. The quality factor (Q) of the stretchable conductor can be expressed as equation (16):

$$Q = \frac{\varepsilon}{a(\varepsilon^2 + 2\varepsilon)} = \frac{1}{a(\varepsilon + 2)} \quad (16)$$

According to the above equations, we can know that the quality factor of the stretchable factor is determined by not only the engineering strain (ε) but also the ratio of the irreversible part (a) in the conductor.

We then address the qualitative relationship between mass loading and the ratio of the irreversible part (a). Supplementary Figures 9b-d shows cross-sectional SEM images of LMFM with different mass loadings. With the increase of mass loading, the morphology of the conductor is dramatically changed. We can see that the wrinkled part is greatly reduced, thus indicating the ratio of the irreversible part (a) in the whole conductor will increase greatly. We can identify the qualitatively positive relationship between mass loading and the ratio of the

irreversible part (a), but it still lacks reliable experiment skills to determine their quantitative relationship between them. According to Equation (16), the increase of mass loading decreases the quality factor (Q) but enhances the conductivity.

Figure Captions

Figure 1. Permeable and superelastic liquid metal fiber mat (LMFM). **a**, Schematic illustration of a typical fabrication process of LMFM. **b-d**, Digital images and scanning electron microscope (SEM) images of the electrospun SBS mat (**b**), EGaIn-coated SBS mat (loading amount of EGaIn: 0.8 mg/cm^2) (**c**) and permeable 0.8EGaIn-SBS after activation via pre-stretch (**d**). **e**, Stress-strain curves of the electrospun SBS mat and 0.8EGaIn-SBS. **f**, Comparison of air permeability and moisture permeability of the 0.8GaIn-SBS with the commercial nylon cloth, medical patch, PDMS film, and Ecoflex film. **g**, Left: water contact angle measurement for 0.8EGaIn-SBS before and after plasma treatment; right: digital images of a 0.8EGaIn-SBS dripped with artificial sweat (red), water (yellow), and alcohol (blue). **h**, Resistance change of the 0.8EGaIn-SBS as a function of tensile strain (R_s refers to the resistance at the stretching state, R_{s0} refers to the resistance at the zero-strain state). Inset in (**h**) shows digital images of the 0.8EGaIn-SBS at the strain of 0% and 1,000%.

Figure 2. Mechanism of superelasticity of LMFM. **a**, Schematic diagrams showing the pre-stretch activation process for the preparation of permeable EGaIn-SBS mat. **b**, Schematic diagrams, SEM topographical and cross-sectional images showing the detailed structures of 0.8EGaIn-SBS during the stretching.

Figure 3. Stable and self-adaptive superelasticity of LMFM. **a**, Resistance change of the 0.8EGaIn-SBS as a function of stretching cycles at different strains (R refers to the resistance after stretching under the specific stretching strain. R_0 refers to the resistance before stretching).

b, Quality factor (Q) of the EGaIn-SBS with different loading amounts of EGaIn as a function of tensile strain. **c**, Schematic diagram showing the self-adaptability of EGaIn-SBS during the stretching. **d**, Resistance changes of the EGaIn-SBS as a function of stretching cycles (strain: 1,800%) along with the changes of stretching directions (R_s refers to the resistance under the stretching state. R_{s0} refers to the resistance at the released state). Insets in **(d)** are the SEM images showing the adaptiveness of 2.0EGaIn-SBS: buckles reconstructed and reoriented to follow the tensile direction.

Figure 4. Biocompatibility of LMFMs. **A**, Bright-field and fluorescent images of cells cultured in the incubation medium with the control sample, absorbent gauze, SBS mat, 2.0EGaIn-SBS, and 20% DMSO. **B**, Quantification of L-929 cell viability in different incubation groups. **C**, Absorption at 570 nm in MTT assay of different incubation groups after 1, 2 and 3 days of incubation. **D**, Digital images showing the skin irritation results of different materials on the forearms of the volunteer.

Figure 5. Printed and encapsulation of EGaIn-SBS. **a**, Digital images of SBS mats stencil-printed with various EGaIn patterns before (top) and after (bottom) pre-stretch activation (scale bar: 1 cm). **b**, Digital images showing the superelastic patterned EGaIn-SBS. **c**, Digital images of an encapsulated stretchable mat printed with EGaIn interconnects and mounted with LEDs at the released state (left) and the stretching and twisting state (right). The mat was encapsulated by post electrospinning of SBS microfibers on its surface. Inset in **(c)** shows the cross-sectional structure of the encapsulated stretchable mat. **d**, Digital images of the encapsulated stretchable

mat printed with EGaIn interconnects and mounted LEDs underwater. The mat performed well underwater both at the released state (left) and the stretching state (right). **e**, Resistance of the encapsulated stretchable mat as a function of washing time. Insets in (**e**) show that the mat can steadily light the LED array during washing.

Figure 6. Monolithic stretchable electronics. **a**, Schematic illustration showing the fabrication of the vertically stacked monolithic stretchable mat by alternating electrospinning of SBS fibers and stencil printing of EGaIn electrodes. **b**, Digital images of a three-layer monolithic stretchable device and the EGaIn electrode structures in each layer. The top layer (next to the skin) is an ECG sensor, the middle layer is a sweat sensor, and the bottom layer is an electric heater. **c**, ECG signal of the top layer (ECG electrode) of the three-layer monolithic stretchable device. **d**, Capacitance of the middle layer (sweat sensor) of the three-layer monolithic stretchable device at different strains in response to the different sweat volume (phosphate-buffered saline (PBS) was used to perform as the sweat). **e**, Capacitance of the middle layer at different strains in response to different concentrations of NaCl solution (NaCl aqueous solution was used to represent the human sweat). **f**, Temperature of the bottom layer (heater) of the three-layer monolithic stretchable device under stepwise voltage from 0.07 V to 0.75 V. **g**, Temperature of the heater as a function of the stretching strain (driving voltage: 0.15 V). **h**, Temperature of the heater under repeated heating cycle operation with a driving voltage of 0.2 V.