Auxetic mechanical metamaterial based stretchable electronics

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**AUXETIC MECHANICAL METAMATERIAL BASED
STRETCHABLE ELECTRONICS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

AUXETIC MECHANICAL METAMATERIAL BASED STRETCHABLE ELECTRONICS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

31 July 2019
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Ying Jiang
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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

30 July 2019

Date

Prof. Chen Xiaodong

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journal in which I am listed as an author.

Chapter 4,5 is published as Y. Jiang, Z. Liu, N. Matsuhisa, D. Qi, W. R. Leow, H. Yang, J. Yu, G. Chen, Y. Liu, C. Wan, Z. Liu and X. Chen. Auxetic mechanical metamaterials to enhance sensitivity of stretchable strain sensors. *Advanced Materials* **30**, 1706589 (2018). DOI: 10.1002/adma.201706589.

The contributions of the co-authors are as follows:

- Prof. Chen provided the initial project direction and edited the manuscript drafts.
- Prof. Liu assisted in all the finite element simulation and analysis, and revised the manuscript drafts.
- Specific experiment procedure, characterization including microscopy, voltage distribution simulation, microcrack model and demonstration was conducted by me.
- Dr. Liu assisted in whole experiment including experiment design, sample characterization, and results discussion.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Matsuhisa, Dr. Qi, Dr. Leow, Dr. Yang and Dr. Liu.
- Dr. Yu, Ms. Chen and Dr. Wan assisted in data analysis and 3D graph drawing.

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The contributions of the co-authors are as follows:

- Prof. Chen suggested the project direction and edited the manuscript drafts.
- Dr. Liu contributed to theoretical model, logic structure and all contents in the article.
- Dr. Wang assisted in deriving theoretical models.

- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Liu and Dr. Wang.

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Abstract

Stretchable electronics have attracted tremendous attention in recent years, driven by the high demands of human-machine interfaces including wearable healthcare platform, implantable bioelectronics, soft robotics and so on. Compared to conventional silicon-based, rigid electronics, such stretchable electronics with similar mechanical properties to the soft, stretchable and curvilinear biological tissues reduced the mechanical mismatch, elevating signal fidelity in healthcare signal monitoring. Among stretchable electronics, stretchable strain sensors and stretchable electrodes are the most vital components, where the former transduce mechanical stimuli into readable electrical signals, and the latter electrically connects components and detect electrophysiological indicators. However, there is still big challenges to achieve high sensitivity, stretchability, cyclic durability, conformality via simple fabrication procedures in stretchable strain sensors and electrodes. Here a conceptually novel strategy is proposed to solve such challenges: Auxetic mechanical metamaterial employment. The design principle is that, the electrical performance of stretchable electronics is determined via the microscopic morphology of active layer, where can be regulated via mechanical design and the resulting strain distribution. Therefore, it is hypothesized that auxetic mechanical metamaterials with unique, extraordinary mechanical properties can rationally regulate heterogeneous strain distribution in stretchable electronics, thus achieving high electrical and mechanical performance under applied strain.

In detail, the strategy of auxetic mechanical metamaterial was firstly employed in stretchable strain sensors. For conventional flat film-based strain sensors, the transverse Poisson's compression counteracts the longitudinal stretching, leads to intrinsic inadequate sensitivity for practical application. Here the auxetic metamaterials with bi-axial expansion trend are incorporated into stretchable strain sensors, largely enhancing the gauge factor from ~ 24 to ~ 835 as a 24-fold improvement. The stretchability of such auxetic strain sensors can reach $\sim 100\%$ with good cyclic durability of $>2,000$ cycles. As a proof of concept, human radial pulse wave was detected with high signal-to-noise ratio and abundant medical details, experimentally proving the effectiveness of this strategy.

Next, theoretical models are established to investigate the underlying mechanism in between experimental phenomenon for auxetic metamaterial strain sensors. Finite element analysis was employed to investigate the strain distribution and microcrack length in presence of auxetic structures. Voltage drop model explains why such elongated microcracks enhance the sensitivity, consistent with experimental results. To wrap the whole process, an overall model based on elongated microcracks and heterogeneous strain distribution was established for complete theoretical system, beneficial for scientific foundation as well as practical device optimization.

Furthermore, three-dimensional auxetic foam was employed to fabricate high performance stretchable electrodes with both electrical and mechanical stretchability. Such auxetic polyurethane foam via simple, thermal-compression fabrication process exhibits tri-axial negative structural Poisson's ratio of -0.3 at 40% strain, leading to expansion in thickness directions upon longitudinal stretching. Such auxeticity can be rationally tuned via fabrication parameters, and elevates both mechanical (150% to 190%) and electrical stretchability (20% to 150%).

The above results show that the strategy of employing auxetic metamaterials is effective to fabricate high performance stretchable strain sensors and stretchable electrodes, which can be further utilized for other stretchable electronics. This pioneering work brings the whole mechanical metamaterial field into the view of stretchable electronics. The functionalities of stretchable electronics are heavily dependent on mechanical properties under deformation, thus metamaterials with superior mechanical behaviors could inject vitality and build momentum to this field.

Lay Summary

Stretchable electronics with capability to endure mechanical deformation such as stretching, bending and twisting show promising prospect in human-machine interface. This is because the surface of our biological tissues is soft, stretchable and curvilinear, causing mechanical mismatch with conventional, rigid electronics. Currently, the challenge in stretchable strain sensors and stretchable electrodes lies in sensitivity and maintenance of electrical properties under applied strain. Therefore, this thesis employed new strategy to fabricate stretchable strain sensors and electronics with high performance, verified by both experimental results and theoretical modeling.

Firstly, to collect mechanical strain signals from human body with high fidelity, it is in great request to develop highly sensitive stretchable strain sensors. In this regards, a novel strategy of employing auxetic metamaterials is proposed, which is proved to effectively elevate the performance of stretchable strain sensors. Human pulse wave detection using such auxetic strain sensors proves the improvement in signal fidelity and medical details.

Secondly, theoretical model was established to investigate the mechanism under experimental phenomenon, explaining the sensitivity enhancement due to auxetic metamaterial employment. In this regard, finite element analysis and mathematical model are employed to build an overall model, which not only scientifically explains the fundamental mechanism, but also significant to guide further device optimization.

Finally, this strategy of auxetic metamaterial employment was extended to three-dimensional, and on this basis highly stretchable electrodes are fabricated. Such auxetic polymer foam via simple thermal-compression fabrication exhibits transverse expansion when stretching longitudinally, thus exhibiting largely enhanced mechanical and electrical stretchability.

The stretchable strain sensors and stretchable electrodes employing auxetic mechanical metamaterials exhibits high performance for practical applications in healthcare

monitoring as well as biomedical fundamental research. Based on this strategy, many other stretchable electronics with metamaterials could be further developed to achieve more novel functionalities.

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Dr. Wan Changjin, Dr. Liu Zhihua, Dr. Cui Zequn, Dr. Li Zhuyun, Dr. Ji Shaobo, Dr. Wang Changxian, Dr. Zhang Feilong, Dr. Lv Zhisheng, Ms. Chen Geng, Ms. Guo Xintong, Ms. Luo Yifei, Ms. Cui Yajing, Ms. Wang Ting, Mr. Li Wenlong, and Ms. Yi Junqi. And visiting professors: QianYan, Xu Huifang, Qiu Jun, Liu Xijian. Besides, many thanks to technicians and staff in MSE, including but not limit to Wilson, Zili, Patrick, and Dr. Derrick.

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Figure 4.1 Stretchable strain sensors based on auxetic mechanical metamaterials. (a) Conventional thin film structure and (b) auxetic metamaterial structure with 4-unit array, with corresponding deformation under 15% tensile strain from FEA simulation. (c). Normalized displacement in transverse direction ($D_{\perp}$) under longitudinal tensile strain. Negative and positive $D_{\perp}$ represents transverse Poisson compression and transverse auxetic expansion respectively. (d). Illustration diagram of stretchable strain sensors based on auxetic metamaterials, which is composed of: auxetic frame, thin film and conductive SWCNT network.

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Abbreviations

IoTs	Internet of things
GO	Graphene oxide
CB	Carbon black
PVA	Polyvinyl alcohol
PDMS	Poly(dimethylsiloxane)
PPy	Polypyrrole
3DGF	Three-dimensional graphene foam
EMG	Electromyography
EEG	Electroencephalography
ECG	Electrocardiography
ECoG	Electrocorticography
CNT	Carbon nanotube
SWCNT	Single Walled Carbon Nanotube
SEM	Scanning Electron Microscopy
GF	Gauge factor
SNR	Signal-to-noise ratio
MEA	Microelectrode array
2D	Two dimensional
3D	Three dimensional

Chapter 1

Introduction

Conventional electronics are fabricated through silicon-based materials, presenting rigid appearance and mechanical mismatch with soft, stretchable and curvilinear surfaces of biological tissues. Therefore, stretchable electronics has attracted tremendous attention in recent years. Among various stretchable electronics, stretchable strain sensors and stretchable electrodes are most important components for human-machine interfaces such as wearable healthcare platform, implantable bioelectronics, soft robotics. However, the challenges of sensitivity and stretchability still exist in stretchable strain sensors and stretchable electrodes, limiting their practical application. In this thesis, a novel strategy - auxetic mechanical metamaterials employment has been proposed in order to solve these challenges. The innovation in virtue of unique mechanical properties of auxetic metamaterials regulates strain distribution and microcracks, thus can enhance sensitivity and stretchability via optimized design.

1.1 Hypothesis

Stretchable electronics such as stretchable strain sensors and stretchable electrodes, play a crucial role for human-machine interfaces such as wearable healthcare platform, implantable bioelectronics, transient surgical tools, soft robotics with artificial skins and so on. This is because the conventional, silicon-based electronics are rigid, which causes mechanical mismatch with the soft, stretchable human tissues, leading to low fidelity in signal collection, as well as discomfort or even irritation. Therefore, stretchable electronics with similar mechanical properties as biological tissues has been developed in recent years.^[1-5]

Among the various types of stretchable electronics, stretchable strain sensors and stretchable electrodes possess a pivotal role in health monitoring. In case of stretchable strain sensors, they transduce mechanical strain stimuli from human body into readable electrical signals for further data analysis, which can reflect the corresponding healthcare information. For example, mechanical strain in vocal cord phonation (~15%) can be used for respiratory disease detection or subvocal language recognition. In case of stretchable electrodes, it can serve as monitoring device for physiological signals, interconnects in between circuit components, current collection for stretchable battery/supercapacitor, conductive layer for transistors in logic circuits and so on, making it the basic element in stretchable electronics system.

Therefore, this thesis focuses on stretchable strain sensors and stretchable electrodes. Although tremendous efforts have been devoted in this field with great progress, the challenges of sensitivity and stretchability still exist as the major problem towards practical applications. Such challenges are originated from the requirement of practical applications: high sensitivity of stretchable strain sensors ensures high fidelity of mechanical strain signals from human body with abundant medical details, and high stretchability of stretchable electrodes guarantee the maintenance of electrical conductivity upon applied strain.

In fact, such current challenges of sensitivity and stretchability has internal trade-off relationship. To understand this trade-off relationship, we can first consider the extreme case: brittle conductive material. It has the highest gauge factor because it does not possess stretchability. Even under very small strain (e.g. $\sim 1\%$ for gold), the whole thin film would be torn totally with an irreversible fracture, leading to ultrahigh sensitivity to strain. In practical stretchable strain sensors/electrodes, the balance in between sensitivity and stretchability are usually tuned by the thickness of conductive active materials.^[6] In case of thick active material film, the electrical and mechanical performance under strain will be like in the case of brittle conductive material, with low stretchability and high sensitivity. On the contrary, for thin active material film, the stretchability will be larger because the cracks cannot cut throughout the whole device, thus obtaining high stretchability and low sensitivity. Practically, this trade-off effect in between sensitivity and stretchability can also be observed by comparing different research work.^[7] Therefore, there is an intrinsic challenge to achieve both sensitivity and stretchability for stretchable strain sensors, which is one of the targets for this thesis.

Besides, other performance parameters including cyclic durability, linearity, adhesion, defects sensitivity play an important role in practical applications. In next chapter, the quantitative definition and importance of sensitivity, stretchability and other parameters will be discussed, as well as their role in practical applications.

The main design target of this thesis is to solve the challenges of stretchable strain sensors and electrodes, bridging the gap between current development status and practical applications. Generally, for a composite system of brittle conductive active materials and stretchable elastomer, the strain distribution and strain-induced microcracks on active materials determines the electrical performance of the whole device. Previous research focused on material design to obtain optimized combination of conductive materials and stretchable elastomers.^[7-10] However, the mechanics point of view should be taken into accounts, when regulation on mechanical properties tremendously influence the strain distribution and thus electrical performance.

Therefore, our hypothesis is to rationally design and utilize unique mechanical properties in stretchable electronics, which tunes the strain distribution upon applied strain, in order to obtain desired electrical performance. Following this train of thought, auxetic mechanical metamaterials are promising candidate for stretchable electronics, since it has unique and extraordinary mechanical properties different with natural materials.^[11-14] This strategy combining auxetic mechanical metamaterials and stretchable electronics provides a conceptually new platform for rationally designed stretchable electronics.

1.2 Objectives and Scope

The objective of this thesis is to fabricate stretchable strain sensors and stretchable electrodes with high performance including high sensitivity, electrical and mechanical stretchability, cyclic durability, signal-to-noise ratio in healthcare monitoring and so on. To fulfill the objective, the scope of this thesis is listed below:

1. Developing stretchable strain sensors with high sensitivity, stretchability and cyclic durability, based on regulation via auxetic mechanical metamaterials.
2. Developing theoretical models to investigate the underlying mechanism, explaining the regulation role of auxetic mechanical metamaterials in stretchable strain sensors.
3. Developing three-dimensional auxetic foam based stretchable electrodes, where triaxial expansion upon applied strain enhance both electrical and mechanical stretchability.

1.3 Dissertation Overview

The thesis addresses how to fabricate stretchable strain sensors and stretchable electrodes, based on proposed new strategy: employing auxetic mechanical metamaterials. Such strategy rationally regulates the mechanical deformation and microscopic morphology, thus achieving desired electrical performance under applied strain. Different methods

based on this new strategy were proposed to prove its effectiveness, including both experimental results and theoretical analysis.

Chapter 1 provides the background and elucidates the importance of achieving high performance stretchable strain sensors and stretchable electrodes, with current challenges of sensitivity and stretchability. The rationale, goals and scope of this thesis is also elucidated.

Chapter 2 reviews the literature concerning the current status of stretchable electronics, especially for stretchable strain sensors and electrodes. The state-of-the-art strategies to achieve stretchability was summarized, together with the features and drawbacks discussion. The current performance and challenges of stretchable strain sensors and electrodes are also presented, as well as the introduction and development in auxetic mechanical metamaterials.

Chapter 3 discusses the methods to material synthesis, device characterization, theoretical simulation for auxetic metamaterial based stretchable electronics. The principles underlying characterization methods are also discussed.

Chapter 4 elaborates a novel strategy, auxetic mechanical metamaterial employment, to fabricate highly sensitive stretchable strain sensors. The auxetic structures lead to bi-axial expansion upon applied strain, in contrast with conventional transverse Poisson compression in flat thin film. This mechanical design enables further active material separation under strain, resulting in largely enhanced sensitivity of stretchable strain sensors, together with high stretchability, cyclic durability and so on.

Chapter 5 investigates the underlying mechanism of the high performance in stretchable strain sensors with auxetic metamaterials, through theoretical modeling based on experimental results. Finite element analysis and voltage drop model explains the inner connection in between experimental phenomenon. In all, an overall model based on elongated microcracks and heterogeneous strain distribution was established, enabling

scientific foundation understanding and practical device optimization.

Chapter 6 employs three-dimensional auxetic foam as the substrate for stretchable electrodes to increase electrical and mechanical stretchability. The three-dimensional foam endures expansion in thickness direction upon stretching, thus can be employed to enhance both the electrical and mechanical stretchability of stretchable electrodes as well as conformality, in virtue of the maintained electron pathway and conductivity.

Chapter 7 concludes the whole thesis, and presents some preliminary results which are not shown in the main chapters, as well as discussion of challenges and futures in stretchable electronics.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Proposing new strategy/concept, auxetic mechanical metamaterials, to develop high performance stretchable strain sensors with high sensitivity, stretchability, cyclic durability and so on. This pioneering work innovatively regulates strain distribution and electrical performance via mechanical metamaterials, and more methods could be proposed following this strategy.
2. Investigating the theoretical mechanism underlying this novel strategy of auxetic mechanical metamaterial employment, establishing inner linkages in between the phenomenal, experimental results, beneficial for both scientific foundation understanding and practical customization and optimization.
3. Developing three-dimensional auxetic foam structures for fabricating stretchable electrodes with high electrical and mechanical stretchability, customizable auxeticity, controlled deformation and so on, providing a new design platform to improve performance of stretchable electrodes.

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Chapter 2

Literature Review

In this chapter, the state-of-art strategies to endow originally rigid silicon-based electronics with stretchability is presented, including ultrathin substrate, microcrack design, buckling strategy and so on. Based on these strategies, stretchable strain sensors and stretchable electrodes have been developed for human-machine interfaces such as wearable healthcare platform, implantable bioelectronics, soft robotics and so on. However, challenges such as sensitivity, stretchability, conformality, linearity still remain, hindering the practical industrial application. In order to address these issues, here we proposed employment of auxetic mechanical metamaterials for stretchable electronics. Auxetic mechanical metamaterials possess unique and extraordinary mechanical properties, which is suitable for mechanical design of stretchable electronics, especially in microscopic point of view. The history and development trend of mechanical metamaterials are presented, to illustrate its mechanical properties and suitability for usage in stretchable electronics.

2.1 Introduction

The explosive development of silicon-based electronics is shaping our lifestyle and future, bringing novel possibilities for us to explore the world and ourselves. Specifically, wearable electronics emerged in recent years endows integration of human body and electronics with various functionalities, providing a new platform to revolutionize existing healthcare industry. Since the wearable electronics precisely meet the strong demand of healthcare, its world market is expected to grow to \$95 billion by 2025, an over 20-fold increasement in 2016. However, although existing wearable electronics has gained their pace and industrial share like Apple, Samsung, Fitbit, Xiaomi and so on, the challenges still exist for seamless and intimate integration with the soft, stretchable human body.

This unmet challenge comes from the mechanical mismatch in between human body and conventional silicon-wafer based electronics. Human body consists of many soft and stretchable tissues with curvilinear surfaces and complex geometries, while the conventional rigid electronics cannot make conformal contact with tissues and hence lose signal fidelity in sensing and stimulation. Also, tissues in human body are moving all the time, which requires the integrated electronics to be deformable together with these tissues. But the conventional electronics based on silicon-wafer is rigid and undeformable, so despite its huge progress in recent years, this main challenge of stretchability still remains a critical problem while taking wearable/implantable electronics into consideration.

Therefore, stretchable electronics with similar mechanical properties as human body attracted tremendous attention in recent years, towards applications of Internet of Things, mobile healthcare, smart cities and so on (Figure 2.1). The components of stretchable electronics include sensing/input, data processing, driving/output and power part, which can be integrated together into a stretchable platform. This platform, in virtue of its soft and stretchable properties, with the advantages in conformally contact with human tissues, is beneficial for wearable or implantable bioelectronics. The whole stretchable platforms can extract and analyze data in real time, change the conventional on-site diagnostics into mobile healthcare, promoting the Internet of Things and smart cities.^[1]

Figure 2.1 An overview of stretchable electronics platform for healthcare monitoring. Stretchable elements such as sensing, processing, driving and powering components are integrated together for smart system, potentially useful for mobile healthcare, Internet of Things, smart cities and so on.^[2] Reproduced with permission. Copyright 2018, Springer Nature.

In this chapter, current methodologies to achieve stretchability are firstly discussed, together with their underlying mechanism, merits and drawbacks. Then the prototypes of stretchable electronics, especially stretchable strain sensors and stretchable electrodes are reviewed, for a better understanding of the current status. After that, since we innovatively employ auxetic mechanical metamaterials to solve the challenges in stretchable electronics, the introduction and development of auxetic metamaterials is reviewed, elucidating their unique mechanical properties. Finally, the description of this work is presented in terms of foundation, strategy, innovation and so on.

2.2 Strategies to Achieve Stretchability

To seamlessly contact with soft, stretchable and curvilinear surface of human tissues, it is an urgent need to change the conventional, silicon wafer-based electronics into stretchable

electronics. The mechanical properties of common body tissues vary in large range (Figure 2.2), where hard tissues like cartilage and bones exhibits high Young's modulus around MPa to GPa, and soft tissues like brain, spinal cords present low Young's modulus as low as several kPa. Apart from softness, the constantly moving organs also requires electronics to deform together with them, demanding the stretchability of electronics. Therefore, both the softness and stretchability of stretchable electronics are required to match that of their biological counterparts. It is critical to review the development and mechanism of the methodologies to achieve stretchability, in order to meet the requirements and solve the current challenge of stretchable electronics.

Figure 2.2 Young's modulus and maximum stretchability of human tissues and commonly used electronic materials. Reproduced with permission.^[3] Copyright 2017, John Wiley & Sons, Inc.

2.2.1 Ultrathin Electronics

To endow electronics with stretchability without sacrificing their electrical properties, tremendous efforts have been devoted in recent years. The firstly developed methodology to achieve flexibility is to fabricate ultrathin electronics by decreasing thickness. In

principle, any materials with sufficiently low thickness is flexible, because the bending strain decreases linearly with thickness. For example, silicon wafer is rigid and hard to break, but silicon nanoribbons or nanomesh can endure a bending radius of 1 cm. Moreover, this ultrathin method can increase the conformal contact between electronics and human tissues. Consider a thick slab laminated on the skin, there must be voids or space left in between the slab and skin because of the curvilinear skin surface, making the electronics difficult to sense or stimulate the tissue. Alternatively, ultrathin flexible electronics whose thickness is less than the roughness of skin can make contact with skin conformally, not only providing high signal fidelity, but also make the electronics imperceptible to human.

Because of these advantages, various development based on ultrathin electronics has been made for flexible electronics, including ultrathin organic transistor,^[4] optoelectronics,^[5] flexible pressure sensors,^[6] organic photovoltaics^[7] and so on (Figure 2.3).^[8] The employment of ultrathin substrate successfully change the conventional rigid electronics to flexible, skin/tissue-mountable electronics.

Figure 2.3 Illustration of an ultrathin plastic electronic foil, with extremely lightweight, and 12*12 active tactile pixel array. Reproduced with permission.^[4] Copyright 2013, Springer Nature.

However, this method via ultrathin substrate can only achieve flexibility or bendability, which cannot fulfill the requirement of high strain endurance for further application. The truly stretchable electronics should not only be flexible, but also can be stretched to certain level of strain, where the strain level depends on specific application. Therefore, more methods to achieve stretchability in electronics has been developed, such as microcrack based strategy, wavy structures, percolation structures and so on.

2.2.2 Microcrack Strategy

For electronics, stretchability is defined as the maximum strain it can endure without totally losing its electrical properties, which refers to electrical conductivity for electrodes. Microcrack-based structure has become the most commonly used strategy to reach such stretchability, because of its advantages such as high stretchability, ease of fabrication and resistance of local damage/strain concentration.^[9-13] Normally, a freestanding metal film can endure tensile strain less than 2%. Even for soft metal such as gold, the strain before breaking the whole film does not exceed ~5%. However, bonding such fragile metal thin film on top of the elastic elastomer substrate can endow stretchability to the whole device, enduring tens of percent of strain without fatigue.

The typical configuration of microcrack-based electronics consists fragile, non-stretchable gold thin film on top of elastomer substrate (Figure 2.4a). Before stretching, the whole film remains intact and the surface roughness is small. Upon 60% nominal strain, the surface of fold film was torn and microcracks were formed. In presence of longitudinal stretching, the microcracks are aligned in vertical direction, but randomly distributed in the whole area. In between the microcracks, nanocracks are often formed, but their influence in stretchability is far less than microcracks. Besides, because of the Poisson effect, the whole film compresses in vertical direction upon transverse strain, leading to transverse wrinkles on the surface, which also influence the electrical conductivity. After releasing the strain, microcracks close again, where conductive islands contact with each other and resume the electrical pathway. This explains the restoration of electrical performance after strain release, making it possible for cyclic loading in such microcrack-based electronics.

Figure 2.4 (a). Stretchable electrode of gold thin film on top of polydimethylsiloxane (PDMS) elastomer substrate, showing the formation of microcracks upon 60% nominal strain. Reproduced with permission.^[14] Copyright 2014, American Chemical Society. (b). Schematic of microcracks showing how tri-branched cracks can accommodate large strain, endowing stretchability in thin film. Reproduced with permission.^[9] Copyright 2006, AIP publishing. (c). Schematic of conduction pathway in microcrack-based electrodes, explaining conductivity change upon applied strain. Reproduced with permission.^[15] Copyright 2014, Springer Nature.

The theoretical explanation of microcrack-based method to increase stretchability was also investigated (Figure 2.4b). The macroscopic experiment of a cut paper with tri-branched cracks shows such suitably patterned crack can accommodate large strain and thus endow a stiff film with stretchability. Finite element model further quantified the strain level in

the stretchable film, with two configurations: in-plane bending and out-of-plane twisting. The former endures large in-plane strain via ligament bending, while the latter accommodate strain via twisting out of plane. Hence the whole thin film can deform elastically under large strain. The model of electrical conductivity under applied strain was also investigated (Figure 2.4c), where microcracks in between metal thin film separate the film into micro-scaled conductive islands. Upon transverse stretching, the distribution of metal islands changed due to both transverse stretching and vertical compression, changing the electron pathway and hence the electrical conductivity. As long as the metal islands stay connected with each other, the electron pathway maintains its continuity, thus the stretchability can be endowed into the whole film.

Figure 2.5 (a). Microcrack-based strain sensors based on single-walled CNTs. Reproduced with permission.^[16] Copyright 2017, American Chemical Society. (b). Microcrack-based stretchable electrodes fabricated by bio-compatible materials, which can accommodate 100% strain. Reproduced with permission.^[17] Copyright 2018, John Wiley & Sons, Inc. (c). Microcrack-based stretchable motion memory device using the strategy of heterogeneous strain distribution, where rigid components and stretchable strain sensors can cooperatively work together, reaching 50% stretchability. Reproduced with permission.^[18] Copyright 2017, John Wiley & Sons, Inc. (d). Microcrack-based stretchable transistor with graphene as stretchable interconnects, achieving stretchability of ~12%. Reproduced with permission.^[19] Copyright 2015, John Wiley & Sons, Inc.

Due to the high stretchability and electrical performance, microcrack-based strategy has been widely used in various types of stretchable electronics. For example, stretchable strain sensors have been developed via CNTs network on top of elastomer substrate (Figure 2.5a). The microcracks appear on conductive film upon strain, and the fragments connection still maintains electrical conductivity, reaching stretchability of 20%. Stretchable electrodes based on bio-compatible silk materials with microcrack gold active layer are also developed, enduring 100% nominal strain (Figure 2.5b). Since stretchable electrodes are critical components and basic element in stretchable electronics, such microcrack-based electrodes can be further employed as conductive interconnects in memory device, or active layer in transistors for logic circuits (Figure 2.5c, d).

Compared to other methods to achieve stretchability, this microcrack-based method possesses superior advantages, because it can accommodate large stretchability. And it is compatible with conventionally 2D fabrication process, so many following fabrication steps towards complex device can be achieved. Besides, it's not susceptible to local damage/strain concentration, because the microcracks are randomly distributed and no intrinsic fragile point/region was induced in fabrication process. However, it is worth to notice that due to its underlying mechanism, microcrack-based electronics will lose stretchability when its width is comparable to the size of microcracks (tens of micrometer). This is still a challenge especially for small-scale applications such as detection of single cell/neuron electrical activity. Nevertheless, microcrack-based methods still remain the most widely used strategy to achieve stretchability in electronics.

2.2.3 Buckling Strategy

Mechanical buckling is another commonly used method to achieve stretchability in electronics.^[20-24] Conventionally, buckling usually generate catastrophic material failure in the structural mechanics systems. However, the controlled buckling of originally rigid materials on compliant substrate enables stretchability without causing material failure. A typical fabrication process for 1D stretchable buckling structure comprises of wavy

geometry of rigid materials on elastomer substrate (Figure 2.6a). The fabrication step involves lamination of rigid elements such as silicon ribbon onto prestretched elastomer substrate. Upon releasing, it forms micrometer-scale, periodic, wave-like geometries, which accommodates strain much higher than in the material itself. Here the peak strain in originally rigid silicon ribbon is dominated by bending terms:

$$\varepsilon_{Si}^{peak} = 2\varepsilon_c \sqrt{\frac{\varepsilon_{pre} - \varepsilon_{applied}}{\varepsilon_c} - 1} \quad (2-1)$$

Where ε_{Si}^{peak} represents the peak strain in silicon, ε_c , ε_{pre} , and $\varepsilon_{applied}$ represents the critical strain for buckling, prestrain level and applied strain, respectively.

Following the same design philosophy, 2D buckling structures that can be stretched in to two dimensions have been developed (Figure 2.6b).^[25,26] A thin, rigid silicon film laminated on top of biaxially stretched elastomer generates herringbone structures with controlled wavy geometries, achieving full 2D stretchability. Similarly, an “bridge-island” structure can be developed by employing silicon ribbon and compliant substrate, which is beneficial for combination of stretchable interconnects (“bridges”) and rigid components (“islands”). This “bridge-island” structure has a higher efficiency for area utilization than herringbone structures from whole thin film.

Controllable, 3D complex microstructures can also be achieved through compressive buckling (Figure 2.6c).^[27,28] This method based on residual stress-induced bending, and through rational design of bonding area via lithography, the geometry of 3D microstructures can be precisely controlled. In this way the whole device can not only achieve designable 3D microstructures, but also endure large deformation.

Figure 2.6 Buckling structures to achieve stretchability. (a). 1D silicon ribbon laminated on prestrained elastomeric substrate for stretchable Si devices. Reproduced with permission.^[21] Copyright 2006, American Association for the Advancement of Science. (b). 2D stretchable Si devices with silicon membranes or ribbons bonded to bi-axially stretched elastomer substrates, which forms herringbone or wavy configuration upon releasing. Reproduced with permission.^[24] Copyright 2010, American Association for the Advancement of Science. (c). 3D stretchable microstructures fabricated by serpentine silicon ribbons partially bonded to pre-stretched elastomer substrate, changing 2D filamentary ribbons into designed 3D geometries. Reproduced with permission.^[27] Copyright 2010, American Association for the Advancement of Science.

This buckling method has been commonly used to achieve stretchability for bioelectronics. However, there is still a grand challenge to use this method for large-scale manufacturing, because it is not compatible with conventional planar fabrication procedure. Besides, the strain concentration still takes place in the turns or corners of the active materials, largely limiting its stretchability. Therefore, alternative approaches including the aforementioned microcrack-based method still possess significant value.

2.2.4 Percolation Strategy

High stretchability of electronics can also be achieved via percolating networks of nano/micromaterials. Different from microcrack-based or buckling methods where active materials are laminated directly on elastomers, the percolation structures consist the randomly distributed conductive network embedded inside the elastomers. Theoretically, as long as the concentration of conductive materials exceeds the critical conductive value, the percolated device would achieve desired electrical performance. Upon stretching, the elastomer endures mechanical deformation together with embedded conductive network. The entangled nano/micromaterials remains conductive until a critical strain, corresponding to the stretchability of the whole device.^[29-35]

Figure 2.7a shows a typical example of carbon percolation network as epidermal sensors, which consist 3D graphene foam and carbon nanotubes (CNTs).^[36] Using Ni foam as template, few-layer graphene was grown by CVD, following by removal of Ni metal to form 3D graphene foam (3DGF). After uniformly coating the 3DGF with CNT network, the silicone elastomer was added to fill the hollow space of the foam, achieving percolation all-carbon conductive network inside the elastomer. Here the percolation network largely enhanced the stretchability (85%), gauge factor (~35) as well as cyclic durability (5000 cycles), successfully change the originally rigid foam into stretchable epidermal sensors.

The theory of strain effect on percolation based stretchable electronics was investigated (Figure 2.7b).^[37] Assuming randomly positioned circular flakes with uniform size distributed in elastomer network, it is experimentally observed that the electrical resistance in form of voltage drop increases upon strain under fixed current. The theoretical 2D percolation model was established to explain such resistance increase, consistent with experimental results (Figure 2.7c).^[34] When small strain is applied, the conduction path of electrons changes from 2D to 3D network because of Poisson's ratio effect in thickness direction, corresponding to large conductivity change. As the strain increase further, the conduction path aligned in transverse direction without breaking, endowing the whole device higher stretchability.

Compared to microcrack-based or buckling methods, the percolation methods exhibit much less cost efficiency, because the more expensive active materials have to be mixed in the whole 3D structures instead of forming a thin film on substrate surface. And it has less superior stretchability because of the easily detached entanglement of conductive network. However, it presents higher adhesion between conductive active materials and elastomer substrates, since the network is embedded inside into elastomer rather than laminating on it. Moreover, the surface roughness of percolated stretchable devices is much smaller, since the roughness of active materials has been eliminated.

Figure 2.7 Percolation strategy to achieve stretchability. (a). Fabrication of percolation-based all-carbon epidermal sensors. Reproduced with permission.^[36] Copyright 2017, John Wiley & Sons, Inc. (b). Voltage drop distribution simulation shows the electrical conductivity change under different strain, consistent with experimental results. Reproduced with permission.^[37] Copyright 2014, Royal society of chemistry. (c). Schematic illustration of nanoparticle network under different strain, showing high resistance change under small strain, and maintenance of conductivity path under large strain, reaching high stretchability. Reproduced with permission.^[34] Copyright 2016, John Wiley & Sons, Inc.

2.2.5 Other Strategies

Besides the aforementioned strategies, origami/kirigami structures are also employed to achieve stretchability in electronics, where “ori” means folding, “kiru” means cutting and “kami” means paper in Japanese.^[38,39] By employing kirigami via incision of graphene oxide (GO) – polyvinyl alcohol (PVA) nanocomposite, the sheet is able to increase stretchability to 370% from originally 4% (Figure 2.8a). In contrast to manipulating micro/nanostructures in stretchable electronics, this origami/kirigami method demonstrated a top-down patterning with extendable length scale. However, such origami/kirigami structures have critical size due to the limitation of fabrication precision. More importantly, the stretchability cannot be extended to the whole device surface, which means it cannot be conformally contacted to human tissue surface, so true stretchability is still needed in active material region.

Another strategy is to change the originally solid form active materials into liquid form, and encapsulate it with stretchable elastomer. Because the liquid form materials are intrinsically stretchable, the whole device can obtain stretchability while maintaining electrical performance.^[40,41] The employment of Ga-In alloy liquid metal was investigated for elastomer conductors. The mask deposition removes the trouble of liquid metal injection and following encapsulation, obtaining a feature size as small as 200 μm and spacing of 25 μm , while achieving stretchability the same as the elastomer substrate. However, this method employs liquid materials which is usually incompatible with conventional fabrication process. Also, it needs encapsulation for wearable/implantable application, which means the active material cannot be conformal to tissue surface, limiting its application field.

Figure 2.8 (a). Nanocomposite composed of GO-PVA with designed incision via top-down patterning technique, increasing the strain capability of conductive materials. Reproduced with permission.^[38] Copyright 2015, Springer Nature. (b). A liquid-embedded-elastomer with good feature size and spacing size, showing endurance of twisting and stretching. Reproduced with permission.^[41] Copyright 2013, John Wiley & Sons, Inc.

The comparison and representative performance of the abovementioned stretching strategies are summarized in Table 2.1. For ultrathin strategy, since it mostly relies on flexible substrate, the devices can only be flexible rather than intrinsically stretchable, although some of them shows small bending radius. For microcrack based strategy, it can be both stretchable and conformal, in which the latter depends on the total film thickness. For buckling strategy, since the electronics has initial status of buckling structures such as wavy or herringbone, the conformal contact between such electronics and human tissue surface was largely inhibited. For percolation strategy, the expensive active materials must be mixed with the elastomer substrate in a 3D form, making it cost inefficient compared to other strategies which only require a surface thin film. Other strategies such as origami also cannot form conformal contact with human tissue surface, since it is not intrinsically

stretchable. For liquid metal strategy, the conductivity and stretchability can achieve high values, but the liquid metal cannot make direct contact with human tissue, making direct, conformal contact impossible. Therefore, in this thesis, the microcrack strategy to enable stretchability was chosen in both stretchable strain sensors and stretchable electrodes.

Table 2.1 Comparison and representative performance of stretching strategies.

Stretching Strategy	Stretchability or Bending Radius	Conductivity (Ohm sq. ⁻¹)	Stretchable or Not	Conformal or Not	Cost Efficient	Ref
Ultrathin	2 mm	3				[42]
	2.5 mm	50	✗	✓	✓	[43]
	30 μm	8				[44]
Microcrack	65%	5				[45]
	170%	7.28				[46]
	50%	22.1	✓	✓	✓	[47]
	20%	35				[48]
	80%	10				[49]
	60%	44.7				[29]
Buckling	140%	0.2				[50]
	100%	450	✓	✗	✓	[51]
	100%	211				[52]
Percolation	450%	0.06				[53]
	90%	0.01	✓	✓	✗	[54]
	100%	0.63				[55]
Other (Origami)	383%	9.1	✓	✗	✓	[56]

Other						
(Liquid metal)	1000%	0.01	✓	✗	✓	[57]

2.3 Stretchable Electronics - Materials, Performance and Challenges

Given the aforementioned strategies of achieving stretchability, there has been enormous progress in the materials, designs, fabrication process for such stretchable electronics system. A typical stretchable electronics system integrated with human body exhibits how stretchable electronics change the methodologies for human-machine interaction (Figure 2.9). Firstly, different kinds of signals from human body are collected via stretchable electronics, which is laminated on skin or implanted inside body, or integrated with surgical tools. These signals include physical signals such as strain and pressure, electrophysiological signals such as electromyography (EMG), electrocardiography (ECG), electroencephalography (EEG), chemical signals such as glucose, biomarkers and so on. Such signals come from different parts of the human body, which possess various mechanical properties, thus generate different requirements for stretchable electronics. Next, most of these signals was sent into data storage devices such as memory for information storage and extraction, while some of the signals may manifest itself in visualization way. The data was then sent wirelessly through techniques such as Bluetooth or near field communication, to data analyzation center for advanced algorithm to analyze. Finally, personalized and useful information was extracted, containing large amount of healthcare information, providing chance for remote healthcare. Besides, feedback such as actuator, drug delivery, electrical stimulation can be activated in response of the healthcare information, forming a closed loop of health diagnostics and therapy.

Figure 2.9 The bio-integrated stretchable electronics systems, using wearable/implantable/minimally invasive stretchable devices to collect healthcare information from human body. The information is stored, wirelessly sent, and analyzed via advanced algorithm, which provides personalized and remote healthcare service. Finally, feedback based on such healthcare information in form of mechanical actuation, electrical stimulation or drug delivery enables the close loop for whole healthcare system. Reproduced with permission.^[58] Copyright 2016, John Wiley & Sons, Inc.

In such stretchable electronics healthcare system, the most fundamental elements are stretchable sensors which collect information from human bodies. This is because other elements such as data transmission can still rely on silicon-based elements to some extent, especially in case of hybrid stretchable system. But the stretchable sensors are demanded to be directly mounted/implanted in human body, which means achieving stretchability is critical and inevitable. In this chapter, two of the most important stretchable sensors – stretchable strain sensors and stretchable electrodes are introduced, including material, fabrication process, application and current problems and challenges.

2.3.1 Stretchable Strain Sensors

Stretchable strain sensors constitute a vital and indispensable part in stretchable electronics.^[59,60] They transduce mechanical strain stimuli into readable electrical signals and thus have attracted tremendous attention in recent years. Since their softness and stretchability solve the mechanical mismatch between electronics and biological organs, stretchable strain sensors exhibit enormous potential in wearable healthcare bioelectronics.

The reason why stretchable strain sensors are so important is that most of tissues in our human body endure mechanical strain in everyday life (Figure 2.10a), and this ubiquitous strain reveals our physical status with tremendous amount of information. For example, the vocal cords endure strain of 15% when people talk or sing. This mechanical strain can be used to analyze respiratory disorder, or restore damaged vocal cord via analyzing vocal cord strain and translate them into apprehensible language. Human heart, beating every second inside our body, endure expansion and compression in each heartbeat cycle. In case of cardiovascular disease, the blood supply of heart is limited due to blockage in coronary artery, hence limiting the contraction of heart. This means using the strain in heart tissue one can continuously monitor the heart condition and prevent for disease deterioration. Besides, urinary bladder may hold as much as 600 ml of urine, meaning the bladder wall can be extended to several times of its original size. Disease like urinary incontinence may be detected through monitoring of bladder strain. Also, joint motion detection is critical for athlete training or rehabilitation exercise, showing precisely how elbow or knees move/bend, making it possible for remote instruction from coach or rehabilitation therapist. For example, motion-related neurological disorders can be diagnosed via stretchable strain sensors, which can control a drug delivery system as a feedback therapy.^[61]

Figure 2.10 (a). Ubiquitous strain in human body which are related to health condition or disease signals, including mechanical strain from vocal cord, heart, bladder and joint motion. (b). Applications of stretchable strain sensors for human-machine interface. All reproduced with permission. Wearable sensors: Wearable gloves using strain sensors.^[62] Copyright 2011, Springer Nature. Piezoelectric motion sensor.^[63] Copyright 2015, John Wiley & Sons, Inc. Acoustic wave form and auditory spectrogram.^[15] Copyright 2014, Springer Nature. Implantable sensors: Sensor trip wrapped around pig carotid artery.^[64] Copyright 2012, Springer Science+Business Media, LLC2012. 3D multifunctional membrane wrapped around rabbit heart with ECG recording.^[65] Copyright 2014, Springer Nature. Smart textile sensors: Self-powered fiber-shaped strain sensor.^[66] Copyright 2015, John Wiley & Sons, Inc. Interwoven carbonized silk fabric.^[67] Copyright 2016, John Wiley & Sons, Inc. Soft robotics: Tattoo-like strain sensor for remote robotic arm control.^[68] Copyright 2015, American Chemical Society. Embedded 3D printed soft actuators for different bending.^[69] Copyright 2018, John Wiley & Sons, Inc.

Because mechanical strain in human body is closely connected to health condition, stretchable strain sensors can be applied for numerous fields (Figure 2.10b). These applications can be categorized into wearable sensors, implantable sensors, smart textiles and soft robotics, depending their applied position. For wearable sensors which laminates on human skin, stretchable strain sensors can precisely capture the motion of hand gesture

in form of soft glove, or monitor the body movement via joint motion. As to implantable sensors inside human body, stretchable strain sensors can be used for ablation therapy, or electromechanical network for detection and therapy of cardiovascular disease. For smart textile, which is compatible with mature, existing manufacturing process, stretchable strain sensors can be integrated with wearable textiles in one-dimensional form, endowing multiple functions of textiles. For soft robotics, stretchable strain sensors with sensitivity comparable to biological counterparts can endow soft robotics with ability to sense mechanical strain, pressure, twisting or bending, making the robot more intelligent for interaction with human.

To quantitatively characterize the performance of stretchable strain sensors, performance metrics are defined and investigated including sensitivity or gauge factor, stretchability, cyclic durability, linearity, adhesion, defects sensitivity and so on.

First of all, sensitivity or gauge factor (GF) is the most important and frequently used performance parameter, which is expressed as the ratio of relative output change versus applied strain:

$$GF = \begin{cases} \frac{\Delta R}{\varepsilon R_0} & \text{for resistive strain sensors} \\ \frac{\Delta C}{\varepsilon C_0} & \text{for capacitive strain sensors} \end{cases} \quad (2-2)$$

Here R and C represent the electrical resistance or capacitance respectively, and ε represents the applied strain, which is the end-to-end engineering strain as the ratio of relative deformation to original length. Regarding the relationship between resistance and resistivity, the equation of resistive type strain sensors can be transformed into formula of resistivity:

$$\frac{\Delta R}{R} = (1 + 2\nu)\varepsilon + \frac{\Delta\rho}{\rho} \quad (2-3)$$

The gauge factor plays an extremely important role in stretchable strain sensors, since it quantifies the precision level of the transformation from mechanical strain to electrical readout. There would be two drawbacks for low sensitivity: one is the lost information in transformation process, because the low sensitivity obstructs strain information collection

and leads to low signal-to-noise ratio (SNR). The other drawback of low sensitivity is regarding to following processing circuit, where sensors with low sensitivity requires amplifier or advanced algorithm, increasing the complexity and cost of the whole system.

Another important parameter for stretchable strain sensors is stretchability, which measures the maximum elongation of sensor without losing its electrical properties under cyclic loading. For conventional silicon, the stretchability would be less than 1%, which definitely cannot meet the requirement for matching human body. As mentioned before, different human tissues correspond to different strain, thus stretchability of strain sensor is required to change from 5% (spinal cord) to 70% (skin).

Other parameters include cyclic durability, linearity, adhesion, defects sensitivity and so on. Cyclic durability describes the ability for strain sensor to endure repeated cycles of stretching and releasing, which has profound significance for practical application. For example, our elbows or knees moves several hundreds to thousands of times every day, requiring strain sensors mounted on these regions also endure so many times of stretching without changing its readout property. Besides, linearity is regarded as critical parameters for both conventional and stretchable strain sensors, because good linearity can largely reduce the complexity of calibration and subsequent data processing. Apart from these, adhesion within the different components of stretchable strain sensors is also important. These components are made of materials with different mechanical properties or surface energy, so the adhesion is significant to tightly couple these components together, endowing the strain sensors with scratch-resistance or washing machine endurance. Other parameters include defects sensitivity, where initial incision or damage in small area should not be enlarged during stretching, endowing more reliability for strain sensors.

For the most important parameters of sensitivity or gauge factor, stretchability and linearity, the recent progress in literature are summarized in Table 2.1.

Table 2.2 The performance parameters of stretchable strain sensors in recent literature.

Sensor type	Materials	Stretchability (%)	Gauge factor	Linearity
Resistive ^[70]	AgNWs-PDMS	70	2-14	Linear up to 40%
Resistive ^[71]	CNTs-Ecoflex	500	1-2.5	Linear
Resistive ^[72]	CBs-PDMS	30	29.1	Linear
Resistive ^[62]	Aligned CNTs-PDMS	280	0.82	Two linear regions
Resistive ^[73]	ZnONWs-PDMS	50	114	Linear
Capacitive ^[74]	CNTs-Dragon-skin elastomer	300	0.97	Linear
Resistive ^[75]	Graphene foam-PDMS	70	15-29	Linear
Resistive ^[76]	CBs-TPE	80	20	Nonlinear
Resistive ^[77]	CBs-PDMS	10	1.8-5.5	Two linear regions
Capacitive ^[78]	CNTs-Ecoflex	150	1	Linear
Resistive ^[79]	CBs-Ecoflex	400	3.8	Nonlinear
Capacitive ^[80]	CNTs-silicone elastomer	100	0.99	Linear
Resistive ^[81]	Graphene-rubber	800	10-35	Nonlinear
Capacitive ^[82]	AgNWs-Ecoflex	50	0.7	Linear
Resistive ^[15]	Platinum-PDMS	2	2000	Nonlinear
Resistive ^[68]	AuNWs-PANI-rubber	149.6	20.4-61.4	Linear
Resistive ^[83]	AgNWs-PEDOT:PSS/PU	100	1.07-12.4	Nonlinear

Resistive ^[84]	AuNWs-latex rubber	350	6.9-9.9	Linear
Resistive ^[85]	CNTs- PEDOT:PS/PU	100	8.7-62.3	Nonlinear

As shown in the above table, the sensitivity of current stretchable strain sensors are usually lower than requirements, which is gauge factor of 50.^[59] The low gauge factor not only lead to loss of information which contains valuable healthcare information, but also increase the burden to following processing circuit and calibration process. Therefore, numerous efforts are devoted to enhancing sensitivity of stretchable strain sensors. Generally, these efforts follow the same methodology, that is to change and optimize the constituent materials including elastomer and active materials, trying to achieve a combination of high sensitivity.

This method of optimizing materials to achieve high sensitivity employs various kinds of stretchable elastomer substrates and active materials. For stretchable substrates, silicone-based elastomers and stretchable rubbers are most commonly used. But generally, the influence of elastomer substrate type on sensitivity is relatively smaller than that of active material. The most frequently used and efficient method is to optimize conductive materials, including carbonaceous materials, metal, conductive polymers, liquid metal and so on (Figure 2.11). For carbonaceous materials, graphene, CNTs, carbon black (CB) and carbonized biomaterials were investigated. For example, carbonized silk fabrics (CSF) with good electrical conductivity and large-scale production capability can be used for fabrication of stretchable strain sensors. The CSF has a plain-weave structure composed of interwoven yarns, in which the weft yarns are composed of parallel fibers and warp yarns with twisted fibers. Such CSF strain sensor exhibits wide sensing range as large as 500%, with gauge factor of 9.6 at 200% strain, and gauge factor of 37.5 at 300%-500% strain, in virtue of its interwoven structure. Besides, it demonstrated fast response time (< 70 ms) and good cyclic durability (10000 cycles).

Another active conductive material commonly used is the conductive metal, in various form of nanoparticles, nanowires, deposited film and so on. For example, platinum coated interlocking nanofibers were employed for stretchable strain sensors, with capability of sensing pressure, shear and torsion (Figure 2.11b). The two layers of high-aspect ratio platinum coated polyurethane nanofiber interlocks with each other, thus mechanical deformation changes their geometries and electron pathway, giving electrical resistance output. It exhibits high gauge factor of 11.45 for pressure, 0.75 for shear and 8.53 for torsion, with applied strain range of 2%.

Apart for carbonaceous materials and metals, conductive polymer and liquid metal can also be employed as active materials in stretchable strain sensors. A textile-based stretchable strain sensor with fully polymeric conducting fibers was fabricated, with high initial electrical resistance of $\sim 600 \Omega \text{ cm}^{-1}$ (Figure 2.11c). The PEDOT was served as conductive active material, and polymerized in situ on surface of polyester fiber, retaining the original mechanical properties of fibers such as softness and stretchability. It possesses gauge factor of ~ 1 and stretchability of 100% (same as polyester fiber itself), which can further be integrated with fabric for a wireless wearable glove, capable of sensing the finger and wrist motions. Liquid metal such as gallium indium also provides a promising way for stretchable strain sensors, because of its low toxicity, low vapor pressure in room temperature and low viscosity (Figure 2.11d). The typical way to incorporate liquid metal with stretchable elastomer is to embed the liquid metal inside the hollow core of elastomer fiber. A double-helix structure can be fabricated by intertwining two such fibers together. In case of torsion, strain or touch, the distance in between electrodes and the electrode area has been changed, reflecting in capacitance change. Such sensor can detect torsion as large as 10800 rad m^{-1} , and has gauge factor of 0.66-0.82 under strain within all torsional levels except 0 rad m^{-1} . Besides, touch sensing ability is also achieved where different touch in length can be differentiated, promising to be further used in soft touch screen.

Figure 2.11 Changing conductive materials to achieve high sensitivity. (a). Carbonaceous silk fabric composed of interwoven fiber. Reproduced with permission.^[67] Copyright 2016, John Wiley and Sons. (b). Deposited platinum on interlocking polymer nanofibers. Reproduced with permission.^[86] Copyright 2012, Springer Nature. (c). Intrinsically conductive PEDOT in-situ deposited on polyester fiber. Reproduced with permission.^[87] Copyright 2017, American Chemical Society. (d). Liquid metal embedded in hollow PDMS fibers, forming double helix structure. Reproduced with permission.^[88] Copyright 2017, John Wiley and Sons

Though numerous efforts have been devoted in optimizing active materials to enhance sensitivity of stretchable strain sensors, the challenge of low sensitivity and stretchability still remains. For capacitive-type strain sensors, the theoretical gauge factor is 1, limiting its achievable sensitivity (Figure 2.12a). The resistive-type strain sensors usually possess larger sensitivity and comparable stretchability, making it promising for achieving practical requirement of gauge factor of 50. Besides, there is a general trade-off in between

sensitivity and stretchability. In cases of high gauge factors larger than 50, the stretchability is usually too low to meet the mechanical property of human tissue. For example, the platinum coated interlocking polymer nanofibers achieves high sensitivity of ~ 2000 only for strain range of 2%.^[86] Therefore, achieving both high sensitivity and stretchability has become the main challenge for stretchable strain sensors, which needs to be solved for practical application (Figure 2.12b).

Figure 2.12 (a). Current challenge in stretchable strain sensors is to simultaneously achieve high gauge factor ($GF > 50$) and stretchability ($\epsilon > 50\%$). Reproduced with permission.^[59] Copyright 2016, John Wiley and Sons. (b). Resistive-type strain sensors are promising to achieve high sensitivity, towards enhancing the slope of relative resistance change versus applied strain. Reproduced with permission.^[89] Copyright 2018, American Chemical Society.

2.3.2 Stretchable Electrodes

Stretchable electrodes are another highly critical category of stretchable electronics, because it serves as the basic element of stretchable system, such as sensing components for electrophysiological signals, conductive interconnects, current collector in stretchable batteries/supercapacitors, conductive layer in transistors for logic circuits.^[90] For example, stretchable electrodes implanted in human brain can detect electrocorticography (ECoG) signals from cerebral cortex, or stimulate the deep brain for therapeutic use. Such electrophysiological signal collection can be dated back to 18th century using rigid

electrodes, and chronic electrode implants were developed which inserted deep into the brain. Nowadays, the most commonly used electrodes for brain/muscle stimulation still rely on silicon-based rigid electrodes (Figure 2.13), where microelectrode array (MEA) has been developed for spatiotemporal resolution.

However, these rigid stimulation/recording electrodes are mechanically heterogeneous to human body, triggers acute and long-term response after implantation. Therefore, stretchable electrodes have been developed for electrophysiological signal collection and other applications in stretchable system. In this chapter, the recent advance of stretchable electrodes is described, including materials, performance parameter, requirements, application and challenges.

Figure 2.13 Conventional rigid, silicon-based electrodes. (a). Utah electrode array, consisting of tens to hundreds conductive silicon needles. Reproduced with permission.^[91] Copyright 2005, Springer US. (b). Cuff electrode placed around peripheral nerve. Reproduced with permission.^[92] Copyright 2006, IEEE. (c). Microelectrode arrays (MEA) with planar distributed 64 TiN electrodes on glass substrate. Reproduced with permission.^[93] Copyright 2011, licensee MDPI.

The materials of stretchable electrodes generally consist of conductive materials and elastomer substrate, often with chemical modification to lower impedance. The conductive

materials include conductive carbonaceous materials such as CNTs, graphene, graphite and their composites, while elastomer substrate includes silicone-based elastomer and stretchable rubbers. Although the materials share similarity with stretchable strain sensors, the ultimate application goal and hence requirement of materials are significantly different. For stretchable strain sensor, the electrical performance change needs to be enlarged under applied strain, while for stretchable electrodes, the electrical performance needs to maintain the same as original unstretched state.

To characterize stretchable electrodes, several parameters have been investigated, including stretchability, conformal contact, softness, adhesion, surface modification, encapsulation, biocompatibility and so on. The most important parameter, stretchability, describes the maximum strain the electrode can endure without losing its conductivity. Using the strategies described in aforementioned chapters such as microcrack-based structure,^[94] buckling strategy, percolation method, stretchable electrodes can achieve stretchability, and for planar substrate the electrical stretchability can achieve 30%-50%,^[9] where for surface structured substrate it can achieve 60%-120%.^[95,96]

The other important parameter for stretchable electrodes is the ability to conformally contact with soft, curvilinear human skin/tissue, which brings additional requirements such as biocompatibility, long-term durability, or even gas permeability. To solve this challenge, several strategies have been proposed including ultrathin substrate design, microhair design and substrate-free design. For ultrathin substrate, it has been proved that decreased thickness can increase the conformal contact at the biotic/abiotic interface (Figure 2.14a). Decreasing the film thickness from 500 μm to 5 μm , it shows clearly that the film made much more conformal contact with the curvilinear underlying surface. Below a critical thickness depending on interfacial contact and elastic energy, adhesion energy of contact, the van de Waals forces can be sufficient to drive conformal contact with curvilinear surface, which is about 25 μm in this case.

Apart from decreasing the overall thickness, microhair design can also enhance conformal contact, inspired by the hairy structure of gecko feet (Figure 2.14b). In this configuration,

the microhairs can efficiently fill in the voids in between electrodes and underlying irregular substrate, as well as enhancing adhesion energy. Similarly, the mushroom-shaped micropillar array can also generate strong adhesion than conventional single-level microhair, for contact with curvilinear surface.^[97] This strategy can be widely used for next generation conformal electrodes.

(a) Ultrathin design

(b) Microhair design

(c) Substrate-free design

Figure 2.14 Strategies to achieve conformal contact for stretchable electrodes. (a). Ultrathin design to decrease the overall thickness. Reproduced with permission.^[98] Copyright 2013, John Wiley and Sons. (b). Microhair structure to fill the voids between electrodes and curvilinear surface. Reproduced with permission.^[99] Copyright 2015, John Wiley and Sons. (c). Substrate-free for highly conformal and adhesive contact, as well as high gas-permeability. Reproduced with permission.^[100] Copyright 2017, Springer Nature.

Another strategy for conformal contact is the substrate-free design, in which conductive active materials are directly laminated with human skin without elastomer substrate (Figure 2.14c). The gold was evaporated on electrospun polyvinyl alcohol (PVA) fiber, following

by dissolving the PVA mesh by spraying water. In this way, the gold in form of nanomesh show high conformality and adhesion when laminated on fingertip. Since the substrate-free structure, the whole electrode is highly gas-permeable, minimizing the risk of inflammation. The resistivity increased for 3 times under 40% strain even after 10000 stretching and releasing cycles, as well as good adhesion after cycling.

The abovementioned parameters of stretchable electrodes (stretchability, conformality and so on) originate from the practical application requirements, which includes electrophysiological signals from human body, as well as basic element for more complex electronic device.^[101-107] Electrophysiological signals are the most vital applications for stretchable electrodes, such as electromyography (EMG), electroencephalography (EEG), electrocorticography (ECoG), electrocardiography (ECG) (Figure 2.15). EMG is an important electrical potential biosignal generated from muscles and is vital for constructing both wearable /invasive human-machine interface. To solve the problem of electrode-bio interface failure and mechanical noise, stretchable electrodes are employed for simultaneous recording of EMG signal and strain detection (Figure 2.15a).^[101] Here high adhesion between gold active material and soft PDMS substrate was achieved from nanopile interlocking design, avoiding active material peel off during usage. Due to this high adhesion, the stretchability of electrode can achieve 40%, and after cyclic friction test the signal-to-noise ratio (SNR) during EMG recording can remain 20, in stark contrast to ~3 of control electrodes.

Other electrophysiological signals such as EEG from scalp, ECoG from cerebral cortex and ECG from heart, can be recorded via stretchable electrodes, where these electrodes also provide stimulation tools.^[102-104] For example, a soft and self-adhesive micropillar electrode which efficiently decrease the contact impedance and increase signal fidelity, was applied for long-term EEC and ECG recording even underwater (Figure 2.15b). The EEG recording was challenging since its low amplitude (μV range) and impediment of hairs. This stretchable soft electrode exhibits advantages in EEG recoding, showing characteristic alpha wave peak around 10 Hz.

(a) EMG from muscle **(b) EEG from scalp** **(c) ECoG from cerebral cortex** **(d) ECG from heart**

Figure 2.15 Application of stretchable electrodes for electrophysiological signal recording. (a). EMG signals from muscles, recorded via high adhesion, friction-resistant on-skin stretchable electrodes. Reproduced with permission.^[101] Copyright 2017, John Wiley and Sons. (b). EEG signals from scalp, recorded via micropillar, high adhesive stretchable electrodes. Reproduced with permission.^[102] Copyright 2018, John Wiley and Sons. (c). ECoG signals from cerebral cortex of healthy and epilepsy rat, recorded via polymeric electrode array. Reproduced with permission.^[103] Copyright 2017, John Wiley and Sons. (d). ECG from heart muscles, recorded from on-skin, fully printed electrodes with polymer and ionic gel. Reproduced with permission.^[104] Copyright 2017, John Wiley and Sons.

In contrast to EMG, ECG, and EEG which are on-skin biosignals, ECoG from cerebral cortex is invasive electrophysiological signal which needs implantable stretchable electrodes. Polymeric microelectrode arrays were designed to provide a useful tool, in which polypyrrole (PPy) electrodes exhibit high stretchability ($\sim 100\%$), excellent electrode-substrate adhesion (1.9 MPa) and cycling ability of 10000 stretching-releasing

cycles (Figure 2.15c). ECoG signals from both normal and epileptic rat was recorded and analyzed, where epileptic rat clearly showed intensified signals, showing capability of stretchable electrodes to achieve high fidelity ECoG signals. Also, ECG signals from heart muscles can also be recorded via fully printed stretchable electrodes, with conductive polymer PEDOT:PSS as active materials and pantyhose substrate, showing stretchability of 200% (Figure 2.15d). The characteristic waves of ECG were clearly detected even after 40 days' long-term experiment, with SNR slightly decreased from 13.75 dB to 10.37 dB.

For now, challenges for stretchable electrodes still exist despite of the advancements mentioned above. The most essential challenge lies in the stretchability of electrodes. Though the stretchability can reach high value in current research, the electrical performance has changed a lot in this strain region, inducing noise in the signal detection process. This challenge, which is completely opposite to requirement of stretchable strain sensors, is still being explored to obtain reliable performance in stretchable electronics. Another challenge lies in the conformal contact between electrodes and curvilinear skin/tissue surface, which highly influences the signal fidelity. Though several approaches have been proposed as mentioned, the simultaneous achievement of both stretchability and conformal contact still remains a challenge. Other challenges include adhesion between different components with various mechanical properties, encapsulation, integration for multifunctional system and so on.

2.4 Auxetic Mechanical Metamaterials

Stretchable electronics, sharing similar mechanical properties with human tissues, strongly relies on the mechanical parameters of the constituent materials and structure design, as discussed above. To solve the challenges of stretchable strain sensors and electrodes, advanced mechanical design as well as material improvement is needed. Therefore, we turn to mechanical metamaterials with unique or extraordinary mechanical properties different from natural materials.

The term “metamaterials” was firstly used for man-made materials with unusual optical or electromagnetic properties which are not available in nature. These unusual properties originate from their microstructural (and mostly periodic) geometry, rather than from chemical composition. With development, the range of metamaterials have been expanded to wider fields to represent every kinds of materials which exhibit unusual properties opposite to their natural counterparts, including mechanical, acoustic, thermodynamics and so on. As defined, the mechanical metamaterials can exhibit mechanical properties such as negative Poisson’s ratio,^[108,109] ultralight and ultrastiff,^[110] negative compressibility,^[111] tuning compressibility,^[112] negative incremental stiffness,^[113] stretch densification^[114] and so on.

2.4.1 Mechanical Properties of Auxetic Metamaterials

Among these mechanical metamaterials, auxetics are one of the largest branches. The term “auxetics” was derived from Greek work “auxetikos”, which means “a tendency to increase”, and was firstly introduced by Evans in 1991.^[115] Auxetics was defined as materials with zero/negative Poisson’s ratio, where Poisson’s ratio ν_{xy} describes the resultant strain ε_y in transverse direction for an isotropic material under longitudinal strain ε_x :

$$\nu_{xy} = -\frac{\varepsilon_y}{\varepsilon_x} \quad (2-4)$$

This Poisson’s ratio describes the deformation in directions perpendicular to the direction of stretching/compressing.^[116] Generally, most natural materials have positive Poisson’s ratio ranging at +0.3~+0.5. Specifically, elastomer used in stretchable electronics is normally assumed to have low compressibility, therefore the theoretical Poisson’s ratio of elastomer is +0.5.

From this definition, normal/natural materials with positive Poisson’s ratio would endure transverse compression, when stretching in longitudinal direction (Figure 2.16). For materials with zero Poisson’s ratio, the material does not encounter any deformation in

transverse direction, while materials with negative Poisson's ratio expands in two perpendicular directions upon stretching.

Figure 2.16 Transverse deformation for materials with positive, zero and negative Poisson's ratio under longitudinal stretching. Here the auxetics are defined as materials with zero/negative Poisson's ratio. Reproduced with permission.^[117] Copyright 2017, Springer Nature.

In material mechanics, the Poisson's ratio is related to other mechanical properties. The four basic elastic constants are the Young's modulus E , shear modulus G , bulk modulus K and Poisson's ratio ν , where the major material properties of stiffness, rigidity and compressibility can be derived from. Young's modulus describes the mechanical stiffness of solid materials, in terms of relationship in stress-strain curve in linear elasticity region. Shear modulus G describes the deformation of materials when it experiences a force parallel to its surface, and generally refers to changing of shape without changing volume, thus in ideal gas or liquid $G = 0$. For bulk modulus K , it describes the resistance of a material in response to compression, meaning changing the volume without changing the shape. Given their definition and correlation, two basic charts can be derived to describe their relationship, that is the modulus-density ($E-\rho$) chart called Ashby chart, and the bulk-shear modulus ($K-G$) map where the first quadrant is called Miton map (Figure 2.17).^[118]

Among these two charts, the Ashby chart can be corresponded to mechanical metamaterials with strong and lightweight properties, representing by E/ρ , which is the Young's modulus E divided by density ρ . The other one, K - G map provides clear classification of other mechanical metamaterials in terms of relationship between bulk modulus and shear modulus, including auxetic metamaterials ($G \gg K$), pentamode metamaterials ($G \ll K$) and negative compressibility ($-4G/3 < K < 0$).

(a) K (shear modulus) - G (bulk modulus) map

(b) Auxetic metamaterials ($G \gg K$)

(c) Pentamode metamaterials ($G \ll K$)

(d) Negative compressibility ($-4G/3 < K < 0$)

Figure 2.17 K (shear modulus)- G (bulk modulus) map showing relationship between mechanical parameters with mechanical properties,^[118] which can be used to classify mechanical metamaterials as auxetic metamaterials ($G \gg K$),^[119] pentamode metamaterials ($G \ll K$)^[120] and negative compressibility ($-4G/3 < K < 0$)^[111]. All reproduced with permission. K - G map: Copyright 2017, Elsevier Ltd. Auxetic metamaterials: Copyright 2015, Acta Materialia Inc.. Pentamode metamaterials: Copyright 2012, AIP Publishing. Negative compressible metamaterials: Copyright 2012, Springer Nature.

The Poisson's ratio of auxetics metamaterials can range from 0 to -20, measured experimentally for various materials depending on their structural design (Figure 2.18). Few natural materials exhibit low-level auxetic properties with no less than -0.7, such as some cubic metals when stretched in [110] direction.^[108,121] The re-entrant foams and honeycombs with polymeric or metallic structures are most commonly fabricated and used, with medium level auxeticity of -0.5~-1. Rather than in honeycombs with regular hexagonal cells, these re-entrant honeycombs possess honeycomb structures with inverted cells, leading to negative Poisson's ratio in honeycomb plane.^[122] Some microporous polymers also exhibit similar level of auxetic properties, such as microporous polyethylene with ultrahigh molecular weight and nodules interconnected by fibrils.^[115,123] The incorporation of metallic fiber networks may achieve higher level of auxeticity with Poisson's ratio less than -1.^[124,125] For example, auxetic composite was fabricated by embedding auxetic fiber network with conventional matrix, proving the effective auxetic network interconnected by entanglement for auxetic material design.^[125]

Figure 2.18 Auxetic metamaterials with different range of Poisson's ratio. Reproduced with permission.^[119] Copyright 2015, Acta Materialia Inc..

2.4.2 Auxetics Design with 2D and 3D Structures

Aiming to achieve these mechanical properties, different types of auxetic metamaterials have been developed in the recent decades, with various fabrication techniques. Generally, they can be divided into two-dimensional (2D) and three-dimensional (3D) auxetic structures, where the former contains deformation within the plane of nano/microstructures, and the latter comprises deformation of all three orthogonal axes.

For 2D auxetic designs, various structures have been investigated both theoretically and experimentally, such as re-entrant design, de-wrinkling design, rotating-square design, chiral-integrated design and so on (Figure 2.19). Among these, re-entrant design is the most commonly used pattern to achieve auxetic property.^[126] It consists of honeycomb structures with inverse cells, in contrast to traditional hexagonal cells. Via structural optimization through geometric parameters, such design can exhibit nearly constant Poisson's ratio even over large deformation (20% nominal strain) (Figure 2.19a). Generally, the negative Poisson's ratio in auxetic metamaterials is only stable at small strain range and increases with the nominal strain, thus linear models usually induce small deformation as assumptions. However, some geometrically non-linear model describes constant Poisson's ratio with large deformation range, without deterioration of Poisson's ratio. This optimization minimized the gap between experimental value and modeled value in Poisson's ratio, ensuring the constant Poisson's ratio. Besides, such structure can be printed via multi-nozzle arrays, experimentally proving such constant Poisson effect.

As another kind of 2D auxetic structure, de-wrinkling design resembles the mechanism of crumpled paper in terms of macroscopic view (Figure 2.19b).^[127] For graphene with orderly arranged carbon atom, their mechanical and electrical properties strongly depend on the integrity or defects. However, these defects are proven to be sometimes beneficial to achieve unique auxetic properties via molecular dynamic stimulation. This simulation with no more than 10% uniaxial nominal strain animated auxetic graphene sheet in presence of defect sites, and the extent of auxeticity can be rationally designed through

defect concentration. The mechanism can be resembled as that of macroscopic crumpled paper, where de-wrinkling of the material sheet leads to negative Poisson's ratio.

Figure 2.19 Structures of 2D auxetic metamaterials, including re-entrant design,^[128] de-wrinkling design,^[127] rotating square design^[129] and chiral integrated hybrid design^[130]. All reproduced with permission. Re-entrant design: Copyright 2015, John Wiley and Sons. De-wrinkling design: Copyright 2015, John Wiley and Sons. Rotating square design: Copyright 2017, Springer Nature. Chiral hybrid design: Copyright 2018, Springer Nature.

Other 2D auxetic structures include rotating square design and chiral integrated design. The pattern of rotating square was first proposed as an auxetic design in 2000, where such rotating units accommodates deformation through rotation, leaving actual strain negligible

in the whole sheet.^[131,132] This macroscopic model can also be applied to molecular structures (Figure 2.19c). Using screening methods for such structures, undiscovered auxetic materials can be found such as α -cristobalite SiO_2 , HT- AlPO_4 and α -cristobalite GeO_2 , with their directional Poisson's ratio map showing auxeticity. On the other side, the chiral integrated design combined chiral core cell and re-entrant core cell together to achieve cell-opening mechanism and tunable Poisson's ratio at large nominal strain of 52.6% (Figure 2.19d).^[130] The tunable independent geometric parameters of cell size ratio and re-entrant angle can govern the effective Poisson's ratio and other mechanical properties, forming a new hybrid auxetic metamaterial type.

Expanding the 2D auxetic designs into 3D structures makes the auxeticity in all 3 orthogonal dimensions possible.^[133-135] Because the auxetics relies on nano/microstructures in materials, 3D auxetic designs are highly dependent on advanced fabrication techniques, which can be divided into structured design and unstructured foam design. For structure design, the geometric parameters of nano/microstructures are rationally designed with precise value, thus relies much on nano/micro fabrication techniques (Figure 2.20a). For example, auxetic structures with sub-micro feature size and millimeters overall height have been developed through 3D direct laser writing, with three-dimensional re-entrant structures. Such structure made of Al_2O_3 endures expansion in planar dimensions upon longitudinal compression in z directions, exhibiting tailored Poisson's ratios which is large enough to be macroscopically detected, paving a novel way to achieve complex structures in mechanical metamaterials. For unstructured 3D auxetic foam, the nano/microstructures are randomly distributed and achieved via top-down method, so it is difficult to precisely control the exact geometries inside (Figure 2.20b). For example, auxetic polyurethane (PU) foams with re-entrant microstructures was fabricated through a room-temperature, CO_2 assisted technique. Experimentally, pristine PU foam with glassy styrene acrylonitrile copolymer (SAN) particles was tri-axially compressed into a chamber, following by filling the chamber with compressed CO_2 . According to the phase diagram of CO_2 , as long as the processing temperature was higher than the glass transition temperature of SAN, the compressed status of foam can be

maintained. Therefore, such pre-compressed foam will endure lateral expansion under longitudinal stretching, achieving negative Poisson's ratio and thus auxeticity.

Figure 2.20 Structured and unstructured designs of 3D auxetic metamaterials. (a). Structured 3D lattice composed of anisotropic arrangements of basic re-entrant structure. Reproduced with permission.^[136] Copyright 2012, John Wiley and Sons. (b). Unstructured porous foam without accurate control of inner microstructure, fabricated by CO₂ assisted phase transition method. Reproduced with permission.^[137] Copyright 2016, John Wiley and Sons.

As mentioned above, auxetic mechanical metamaterials with negative Poisson's ratio can deform in a different way from traditional natural materials, as well as exhibiting other unique mechanical properties. Such control of deformation is very promising to be employed into stretchable electronics and solve their current challenges, since stretchable electronics endure various mechanical deformation including bending, twisting, shearing and stretching during use.

2.5 Ph.D. in Context of Literature

This work is to develop a new strategy to fabricate stretchable strain sensors and stretchable electrodes with high performance, which is auxetic mechanical metamaterials employment. The proposed strategy is based on the unique mechanical properties of auxetic

metamaterials, especially their negative Poisson's ratio, to solve the challenges of sensitivity, stretchability and conformality in stretchable strain sensors and electrodes. For stretchable strain sensors, the auxetic metamaterials changed uniaxial stretching with transverse Poisson compression into bi-axial stretching. Such bi-axial stretching can efficiently enhance sensitivity of stretchable strain sensors, proven by both experimental data and finite element analysis. Besides, this strategy can be employed for various materials because the mechanical metamaterials relies on mechanical structures rather than chemical composition. For stretchable electrodes, three dimensional auxetic foam was employed, where the auxetic structure changed the volume decrease in thickness-direction into volume expansion, which is beneficial for both high stretchability and conformal contact.

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Chapter 3

Experimental Methodology

In this chapter, the characterization techniques with underlying principles, and theoretical simulation methods are discussed. The stretchable strain sensors and electrodes characterizations includes material and electromechanical characterization, mechanical simulation and data analysis. The material characterization mainly focuses on the microscopic morphology and chemical composition of the materials. The electromechanical characterization describes the measurement of electrical performance upon strain. The mechanical simulation is focused on simulation assumption, principles and methodologies, and data analysis is also presented here. The principles behind these characterization techniques were investigated and discussed, explaining why particular methods are employed in this work.

3.1 Materials and Mechanical Characterization

All chemicals are purchased as use. For PDMS thin film, the silicon wafer substrate was cleaned and treated using 1H, 1H, 2H, 2H perfluoro-octyl-trichlorosilane (48931-10G, Sigma Aldrich) to obtain hydrophobic surface, by evaporating the silane with vacuum pump and heat for 2 hours. PDMS was purchased from Sylgard 184, Dowsil company, and mixed in ratio of 10:1 of monomer to crosslinker. Defoaming of PDMS was conducted by centrifuge, with 5000 rpm for 1 minute. After the defoaming, bubbles in uncured PDMS was removed and the appearance of PDMS should be clear and transparent. Then the PDMS was casted on the pretreated silicon wafer surface, and spin coated using 600 rpm for 1 minute for thickness of $\sim 100\ \mu\text{m}$. For PDMS with auxetic structures, the auxetic pattern for 3D printed mold was designed by commonly used commercial software of Solidworks. Then Veroclear (RGD810, Stratasys Co.) was used as the printing material, and SUP705 (Stratasys Co.) as the soluble supporting materials. The SWCNTs with carboxylic functional group was purchased from Carbon Solutions Inc. (P3-SECNT), and dispersed in de-ionized water with 0.5 mg/ml. The dispersion was then ultrasonicated for 2 days, using 200 W power (Fisher Scientific FB15051). The SWCNTs dispersion was then placed for 6 hours to stabilize, and only supernatant solution was used to avoid SWCNT aggregation.

For synchronous electrical and mechanical signal testing, two kinds of characterization equipment were employed: electrical testing equipment and tensile testing equipment. The electrical testing was conducted by semiconductor characterization system (Model 4200 SCS) or through digital multimeter (UNIT 72). The tensile testing was conducted by customized hand-stretching machine or automatic tensile machine (C43, C42, MTS Criterion). The automatic tensile tester uses 250 N or 100 N load cell and 100 N screw action grip, with extension rate of 0.1 mm/s for crossheads. The characterization of surface topography was conducted by scanning electron microscopy (JEOL JSM-6340F or 7600) using 5 kV electron beam. The simulation of voltage drop model was conducted via commercial software Matlab, and finite element analysis was conducted via commercial

software Abaqus. The image analysis of microcrack length or quantity was conducted by commercial software Image J.

3.2 Principles behind Characterization Techniques

The principles behind characterization techniques mentioned above are described in view of fundamental understanding, which is the basis of particular method selection in this work.

3.2.1 Scanning Electron Microscopy (SEM)

SEM provides the surface morphology of a sample by scanning the surface with an electron probe, providing resolution beyond the limit of normal optical microscope (Figure 3.1a). The electron beam was emitted from thermionic or field-emission cathode, accelerated by a voltage of 1-50 kV. This beam was then condensed by one or two condenser lens and focused via object lens as a very fine electron probe carrying current of $10^{-10} \sim 10^{-12}$ A on the surface of sample.

The electrons interact with the sample in form of elastic or inelastic scattering and provide useful information of topological surface and chemical composition. Primarily, two types of electrons are detected, which are backscattered electrons (BSE) and secondary electrons (SE) (Figure 3.1b). The BSE are generated by elastic scattering of incident electrons in primary beam, resulting a change in the trajectory of electrons. Compared to lighter atoms, the larger atoms provide stronger scattering events of electrons. Therefore, the number of backscattered electrons received by detector is proportional to their Z number, which means larger atoms produces higher signal. The relationship between atom number and signal intensity provide a way for distinguishing different phases of sample composition. Besides, BSE images also provides sample information about magnetic field, topography or crystallography. The broad spectrum of BSE was in range between nearly incident beam to 50 eV, which is relatively high compared to the secondary electrons. In contrast, the SE are generated by inelastic interaction between the primary electron beam and sample. The energy transfers to sample atom and excites the electrons to overcome its work function,

leading to secondary electrons with low energy less than 50 eV. The SE carry information from the near-surface region of sample, and thus are useful to detect surface topography. In this work, the topology information of stretchable strain sensors or stretchable electrodes was obtained by collecting SE from the detector.

(a) Principles of SEM

(b) Sample-electron interaction

Figure 3.1 (a). Principles and common configuration of SEM. (b). Sample-electron interactions in SEM, including backscattered electrons (BSE), secondary electrons (SE), Auger electrons and so on. Reproduced with permission.^[1] Copyright 1985, Springer-Verlag Berlin Heidelberg.

The reason SEM is extensively employed in material characterization including this work is because it has high resolution compared to optical microscopy. The definition of resolution is the minimum distance where two structures can still be distinguished. Such resolution limit depends on the wavelength of incident illumination source, as proved by Ernst Abbe. This is because the light projects a disk like circle instead of perfect dot, due to light diffraction and interference. This disk has the most intensive light density in the

center (84% of energy), with secondary and tertiary wave decays dramatically, referred to as the Airy disk (Figure 3.2a).

(a) Airy disk

(b) Wave front and resolution

Figure 3.2 (a). Airy disk formed by light spot through a perfect lens. (b). Wave front of light and the resolution definition. Reproduced with permission.^[2] Copyright 2006, Science+Business Media, LLC.

The distance between the center peak and second order peak is defined as the radius of Airy disk. As long as the distance between two objects is less than the radius of Airy disk, they can be distinguished from each other (Figure 3.3b), where Abbe's equation can describe such resolution d :

$$d = 0.612 \frac{\lambda}{n \sin \alpha} \quad (3-1)$$

where λ represents the wavelength of illumination source, n represents the index of refraction in medium where light passes through, and α represents the half angle of the light cone accepted by the objective. The n and α is generally constant for given SEM configuration, referred to as numerical aperture. From Abbe's equation, the resolution of optical microscopy was limited by the wavelength of incident visible light (390~700 nm). In contrast, SEM employed electron beam with wavelength dependent on accelerating energy:

$$\lambda = h / \sqrt{2meV} \quad (3-2)$$

where h , e and m represent Planck's constant, electron charge and electron mass, respectively. Normally, the acceleration voltage of 5 kV generates electron beam with wavelength of $\sim 0.17 \text{ \AA}$, which is much smaller than that of optical microscope, providing high fidelity information of surface topography of the stretchable strain sensors and electrodes.

3.2.2 3D Printing

Three-dimensional printing (3D printing), also referred to as additive manufacturing and rapid prototyping technology, describes the process for fusing or solidifying functional materials to create a 3D object under computerized control.^[3-7] The first 3D printing was invented by Chuck Hull in 1983, known as stereolithography at that time. Because it has the advantages of materials/cost saving, customized design, fast prototyping, precise resolution and so on, 3D printing gains tremendous attention in these years with technology advancement. Various commercial companies for 3D printer/materials were also founded to accelerate this technological innovation process, such as HP, Proto Labs, 3D Systems, Stratasys, Materialize and so on. According to market research, the global 3D printing market will reach US\$44 billion in 2025, a compound annual growth rate (CAGR) of 21.8% from 2019 to 2025. This rapid growth in both commercial industry and academic research was fueled by the broad application of 3D printing, especially those with requirements of personalized design, such as biomedical devices, healthcare products, automotive parts, art and jewelry, low-cost prototyping and innovation and so on.

The basic mechanism for 3D printing includes the process from computer aided design (CAD) model to fabrication of a physical 3D object (Figure 3.3). Firstly, computerized model was designed based on CAD/3D modeling software such as Sketchup, Autodesk 3Ds Max, Solidworks and so on, which exports printable STL files. Next, the slicing software converts the STL files into printing instructions for 3D printer, exporting 3D printer readable files such as G-code file. In this process, the slicing software cuts the model into horizontal layers, generate the pathway of extruder/laser and calculate the materials/time required. Generally, the STL-based slicing method was employed here

because it is compatible for various sets of materials and machines. After generation of layer slices and tool path, the additive manufacture process was carried out via 3D printer with different mechanism, and finally accomplishing the physical 3D objects with same geometry with the original CAD model.

Figure 3.3 Typical procedure for 3D printing, from 3D CAD model to physical 3D object. Reproduced with permission.^[8] Copyright 2016, ACM Inc..

As mentioned above, 3D printing with advantages of rapid prototyping, material/cost efficiency, customized design and precise resolution has been widely applied for different applications. These applications generate different requirements for materials and final product, thus different 3D printing technologies has been developed for practical applications. Typically, 3D printing technologies includes polyjet printing, selective laser melting/sintering, fused deposition modeling (FDM), stereolithography and so on (Figure 3.4). Polyjet printing employs an array consisting of hundreds to thousands of heads to spray photosensitive resins on XY plane, followed by roller flattening and UV lamp curing (Figure 3.4a). Then the build-in elevator plate moves down to unit thickness, and the next layer started on top of the previous one. This polyjet technology can print different materials simultaneously with high precision because of its spray head array, achieving multi-material objects with different color, modulus, stiffness and transparency. Also, it can provide high resolution with layer thickness of 16-30 microns, and in-plane thickness of 40-100 microns. However, the materials including supporting materials and printing material consumption are high, which is not very cost efficient. Another commonly used 3D printing technology is selective laser melting/sintering, which uses laser as power

source to sinter the powdered materials such as metal, nylon or polyamide, to build a solid 3D model (Figure 3.4b). This method was employed for 99% of metal 3D objects, and the mechanical properties are comparable to their conventional counterparts. Besides, the post-processing can further improve the accuracy and surface smoothness of final object.

(a) Polyjet printing

(b) Selective laser melting/sintering

(c) Fused deposition modeling (FDM)

(d) Stereolithography

Figure 3.4 Typical types of 3D printing technologies, including polyjet printing, selective laser melting/sintering, fused deposition modeling (FDM), stereolithography. Reproduced with permission.^[7] Copyright 2019, John Wiley and Sons.

Fused deposition modeling is another popular 3D printing technology, also referred to as fused filament fabrication (Figure 3.4c). Typically, the filament of thermoplastic materials is heated and melted, followed by extruded via a nozzle for single-layer deposition and following superposition to form 3D entities. Compared to other 3D printing technology, it

has the advantages of low cost, easy fabrication and low pollution. Besides, stereolithography is another form of 3D printing technology, using ultraviolet laser to polymerize liquid resin inside the chamber (Figure 3.4d). After completing one layer, the plate was lowered the thickness of a layer, and the uncured liquid resin fills in for solidification of next layer. It has the advantages of high speed and capability to fabricate complicated geometries, but the requirements of supporting materials also lead to large material consumption and processing time increase.

3.2.3 Electromechanical Characterization

In stretchable electronics, it is important to maintain electrical performance upon strain, which requires synchronous testing of mechanical and electrical signals (Figure 3.5). In this work, two kinds of mechanical testing methods were employed for electromechanical characterization, with customized manual stretching equipment and automatic tensile machine, respectively.

Figure 3.5 Mechanism of synchronous electromechanical characterization for stretchable electronics.

For customized manual stretching equipment, the sample was fixed using the two screws, and stretched by the screws on the two ends (Figure 3.6a). The electrical resistance was measured through eutectic GaIn (495425, Sigma-Aldrich) and thin copper wires. For automatic tensile method, tensile machine (C43, C42, MTS Criterion) was employed with

250 N or 100 N load cell, and corresponding grips. The electrical characterization was conducted by Keithley 4200-CSC or digital multimeter (UNIT 72) (Figure 3.6b).

Figure 3.6 (a). Customized tensile machine for stretching/releasing testing. The electrical resistance was measured via eutectic GaIn and thin copper wires on the two ends from the sample. (b). Automatic tensile machine with programmable process.

3.2.3 Plasma Surface Treatment

In stretchable electronics, silicone rubbers are commonly used substrate/matrix due to their intrinsic softness and stretchability. Among these materials, poly(dimethyl siloxane) (PDMS) elastomer has been the most widely used and versatile materials, because of its stability, commercial availability, chemically inertness, optical transparency and biocompatibility. However, in spite of these many advantages, the surface of PDMS is intrinsically hydrophobic, which is incompatible for water-solution based fabrication process or further applications such as in microfluidic field. Hence, many efforts have been made to modify PDMS substrate to enhance the hydrophilicity, extending its use especially in stretchable electronics field.

Among these surface modification methods including both physical and chemical treatment, the plasma surface treatment is the most widely used method.^[9] The plasma treatment with O₂ or other gases generate silanol groups, which can enhance adhesion between PDMS and other substrates to form microfluidic device, or change the PDMS surface from hydrophobic to hydrophilic. Also, such surface changing or etching can be used to detect the self-healing ability (Figure 3.7a).^[10] For example, the

superhydrophobicity from PDMS and camphor soot composite can be reduced due to oxygen plasma etching, but because of the molecular chain movement and rotation, the introduced polar groups are gradually concealed inside the coating layer, restoring the original superhydrophobicity. This changing of hydrophobicity can be characterized via contact angle and droplet curvature investigation (Figure 3.7b).^[11] For example, acrylate resin droplet was pipetted on solidified PDMS surface with argon and oxygen plasma, showing reduced contact angle with plasma treatment time increase.

Figure 3.7 (a). Schematic illustration of oxygen plasma treated PDMS/camphor soot composite. Reproduced with permission.^[10] Copyright 2017, the Royal Society of Chemistry. (b). Contact angle changed by oxygen plasma. Reproduced with permission.^[11] Copyright 2018, Optical Society of America.

Besides the hydrophilicity changing, surface plasma treatment may induce thin, brittle, silica-like layer on top of the originally elastic PDMS, causing the cracks of brittle layer upon 10% strain, with tensile strength of 10-100 kPa.^[12,13] Another effect of oxygen plasma on PDMS surface is the hydrophobicity recovery with time.^[14] The main reason of such recovery is because the low molecular weight PDMS chains or uncured oligomers can

diffuse to the PDMS surface, counteracting the surface functional group from oxygen plasma. Hence many methods were developed to reduce this hydrophobicity recovery, including chemical treatment, or eliminating the uncured oligomers. In this work, because the oxygen plasma treatment was closely followed by next fabrication step, thus one-step oxygen plasma is enough for hydrophilicity requirement.

3.3 Theoretical Simulation

To investigate the underlying mechanism behind the stretchable strain sensors and stretchable electrodes, mechanical simulation and image analysis are employed to build a reasonable model for experimental results. Two kinds of simulation and analysis methods are described here, including finite element analysis for strain distribution and microscopic microcracks, and voltage drop simulation based on SEM images for electrical properties. In addition, data processing and analysis are conducted with commercial software of Matlab, Origin, while figure analysis is conducted with open-source software Image J.

3.3.1 Finite Element Analysis

In this work, new strategies are proposed to solve the challenges in stretchable strain sensors and stretchable electrodes. In characterization and demonstration, these stretchable electronics are required to endure mechanical deformation, especially uniaxial stretching and releasing, which is required for conformal contact with surface of human tissues. Such mechanical deformation needs to be comprehensively understood and quantified, especially the strain distribution and deformation. Although the stretchable electronics is stretched end-to-end where macroscopic measurement can provide nominal strain, the local strain distribution is still unknown, which is critical especially for heterogeneous device design (Figure 3.8). Actually, the strategy of auxetic mechanical metamaterials employment will largely change the strain distribution in stretchable electronics, which needs to be quantified and used to investigate the strategy efficiency. On other hand, structural deformation is also important, where structural Poisson's ratio in local regions

may be different with the whole sample. Therefore, a useful tool to analyze the mechanical deformation in stretchable electronics is highly demanded.

Figure 3.8 Changing strain distribution in stretchable strain sensors to enhance stretchability, proven via finite element analysis. Reproduced with permission.^[15] Copyright 2018, John Wiley and Sons.

Here we chose finite element analysis to simulate the mechanical deformation status and provide valuable data for analysis. Finite element analysis is commonly used as numerical method for solving problems in engineering and mathematical physics. In short, its underlying mechanism is to solve complex problem by breaking the system into smaller and simpler parts (Figure 3.9). Normally these problems can generate a group of partial differential equations with boundary value problems, where accurate analysis needs analytical solutions. However, it is usually very difficult to analytically solve these equations, driving the demand of finite element method, an alternative approximation method. To solve the equations, it subdivided a large system into finite elements, which are smaller and simpler parts that can be described via simple equations. Then these simple equations are bonded together to rebuild the large system via the boundary condition. Therefore, it changed the problems which are originally impossible to solve into approximation problems, leading to its success in solving lots of problems.

Figure 3.9 Representation of finite element idealization of a milling machine, by breaking the machine into smaller elements. Reproduced with permission.^[16] Copyright 2011, Butterworth-Heinemann.

Given the basic foundation of finite element analysis, it is important to apply this principle in practical mechanical problems. The basic steps in finite element analysis via ABAQUS software for mechanical problems contains preprocessing, analysis and postprocessing.

Firstly, the preprocessing step contains creation of solid model via computer-aided-design (CAD) program, boundary constraints of the loading or forces, material properties and so on. For CAD solid models, the units can be arbitrary as long as they satisfy the proportional relationship, because the finite element software ABAQUS does not rely on exact unit. For boundary constraints, the loading or forces are given to the CAD model to simulate the real situation of the stretchable electronics. For material properties, the mechanical, thermal and other properties are described, usually from experimental results. For example, the experimental stress-strain curve of elastomers provides the parameters in PDMS materials, which was assumed as hyperelastic material and described by two term Mooney-Rivlin model. In this preprocessing step, the continuous geometry of the model is discretized into individual elements, which are connected by nodal points referred to as a mesh (Figure

3.10). The type and division method of mesh is critical for accurate analysis. Normally coarse mesh with more nodes describes better approximation to real case than fine mesh with fewer nodes, therefore is beneficial for accurate results. However fine mesh will also consume more computational resource, so the mesh refinement will be done if further refinement does not influence the final result much. As a rule of thumb, the minimal requirements of nodes are no less than 4 elements in thickness direction, and no less than 8 elements in radial directions. Secondly, the analysis step is executed by FEA program solver, where different types of solver has unique advantages of disadvantages for specific applications. In this work, the default iterative linear equation solver was used. Finally, the postprocessing step involves exporting and analyzing the results in form of data or graphs.

Figure 3.10 Meshing the CAD model into discretized nodes and elements, while meshing type is important for accurate results. Reproduced with permission.^[17] Copyright 2019, SAGE Publication.

3.3.2 Voltage Drop Simulation

Electrical properties of stretchable strain sensors are measured via electromechanical characterization discussed in above sections. However, this characterization only reflects the electron status in the whole device, which is very useful for practical application, but not enough for mechanism study. For example, for heterogeneous stretchable strain sensors, the conductive active materials are distributed unevenly, thus the investigation of electrical properties in specific region is beneficial to explain the experimental

phenomenon and guide the further optimization as a feedback. Therefore, we developed voltage drop simulation to analyze the electrical properties based on experimental SEM images, providing a microscopic picture of electrical performance.

The mechanism behind this voltage drop simulation relies on the microcracks on stretchable active material layers (Figure 3.11). In this work, CNT or metal gold layer are employed as conductive active material on top of elastomer substrate. Originally, metals are brittle and can only endure strain of $<5\%$, while bundled CNT layer also cannot be stretched for large strain. However, the microcrack mechanism enabled stretchability of the whole device composed of brittle active layer and elastomer substrate. This is because microcracks will form in the active material layer during applied strain. The microcracks exposed the underlying elastic substrate, which accommodated the applied strain. Meanwhile, the electron pathway can still be maintained via the path in between microcracks, which helps to maintain the electrical performance under strain, enhancing the stretchability.

Figure 3.11 Illustration and SEM images of stretchable electrodes composed of gold film on top of PDMS substrate. (a). Initial microcracks under 0% strain, which are formed due to the thermal volume change in fabrication process. (b). Microcracks under 100% strain, the elongated and opened microcracks accommodates applied strain and provide electron pathway. Reproduced with permission.^[18] Copyright 2019, John Wiley and Sons.

This microcrack mechanism provided foundation of voltage drop simulation, which uses experimental SEM images for electrical resistance analysis. Upon strain, because the microcracks are elongated and open, the underlying elastomer is exposed. Due to the mechanism of SEM mentioned in above sections, the difference between conductive active materials and insulating exposed elastomers can be easily distinguished via SEM images. Firstly, the SEM images of grey scale was changed to black-and-white color, where black color represents the conductive area and white color represents the insulating area. Then discretized Ohm's law was employed in this SEM matrix, where each pixel refers to an individual element with electricity flow. By solving the matrix problem with boundary condition of applied voltage, the total resistance and voltage drop distribution of this SEM image can be obtained qualitatively with a phenomenological $R(\epsilon)$ model. Therefore, this voltage drop simulation method is suitable to analyze the resistance change based on SEM images in stretchable strain sensors and stretchable electrodes.

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Chapter 4*

Auxetic Mechanical Metamaterials to Enhance Sensitivity of Stretchable Strain Sensors

This chapter mainly presents the experimental results of a novel strategy: employing auxetic mechanical metamaterials to enhance sensitivity of stretchable strain sensors. Stretchable strain sensors possess a pivotal role in wearable devices, yet these viable applications are often limited by low sensitivity. This inadequate sensitivity stems from the Poisson's effect in conventional strain sensors, where stretched elastomer substrates expand in longitudinal direction, but compress transversely. In stretchable strain sensors, expansion separates the active materials and contributes to sensitivity, while Poisson compression squeezes active materials together, and thus intrinsically limits the sensitivity. Alternatively, auxetic mechanical metamaterials behave 2D expansion in both directions, due to their negative structural Poisson's ratio. Herein, we demonstrate that such auxetic metamaterials can be incorporated into stretchable strain sensors to significantly enhance the sensitivity. Compared to conventional sensors, sensitivity is greatly elevated with a 24-fold improvement, with elongated microcracks. As a proof of concept, human radial pulse wave was detected with high signal-to-noise ratio and abundant medical details.

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4.1 Introduction

Stretchable strain sensors, which transduce mechanical excitation into readable electrical or optical signals, play an important role in the emerging area of wearable devices,^[1-5] healthcare monitoring,^[6-8] soft robotics^[9-12] and electronic skins^[13-15]. For instance, stretchable strain sensors on neck muscles benefits diagnostic of damaged vocal cords, respiratory disorder and throat cancer,^[16] while those on human wrist assist tremor detection in epilepsy and Parkinson's disease.^[17] In order to be viably employed in these applications, stretchable strain sensors must exhibit excellent performance in three crucial parameters: sensitivity, stretchability and cyclic durability. In particular, sensitivity is of extreme importance, as it allows for precise detection of minute movements such as in the case of phonation vibration, thus providing exhaustive information for accurate diagnosis or analysis even under stretching. The sensitivity of resistive stretchable strain sensors is defined by the gauge factor

$$GF = (\Delta R/R_0)/\varepsilon \quad (4-1)$$

where $\Delta R/R_0$ refers to relative resistance change and ε refers to tensile strain. However, it still remains a big challenge to achieve high sensitivity (gauge factor ≥ 50)^[18] under large strain (e.g. 5.5% for hand motion detection),^[19] which is required for practical implementation.^[20-24]

Typically, resistive stretchable strain sensors are composed of conductive active materials, and thin film elastomer substrate or matrix.^[25-30] To solve the challenge of sensitivity, most of the research focuses on changing and optimizing active materials, yet the achievable sensitivity still remains limited.^[31-35] The reason of inadequate sensitivity is that thin film elastomer in conventional strain sensors endures transverse Poisson compression under stretching. As incompressible material, conventional thin film elastomer exhibits theoretical Poisson's ratio of 0.5.^[36] Under stretching, it expands in longitudinal direction, but compresses in transverse direction. Microscopically, sensitivity of strain sensors depends on the separation degree of conductive active materials.^[37-39] Expansion moves the active materials away from each other and contributes to sensitivity, while compression squeezes active materials and produces an inverse response. Thus, sensitivity induced by

longitudinal stretching is counteracted by transverse Poisson compression, which intrinsically limits the sensitivity (Figure 4.1a). Therefore, how to regulate and reduce the conventional transverse Poisson compression under stretching remains a critical issue for sensitivity enhancement.

Thus, we sought to significantly enhance sensitivity of stretchable strain sensors through the incorporation of auxetic mechanical metamaterials, which endure expansion in both longitudinal and transverse directions under stretching (Figure 4.1b). Mechanical metamaterials, by virtue of their artificial structures rather than composition, can be endowed with extraordinary mechanical behaviors including negative structural Poisson's ratio,^[40-43] compressibility tuning ability,^[44,45] mechanical instability,^[46] as well as strong yet lightweight properties^[47,48]. Among these, auxetics with negative structural Poisson's ratio is one of the most important subfield in mechanical metamaterials.^[49] The structural Poisson's ratio of conventional thin film and auxetics is demonstrated by normalized transverse displacement $D_{\perp}$ calculated from finite element analysis (FEA), under 0 to 60% nominal strain (Figure 4.1c). Here the negative and positive value of $D_{\perp}$ represents transverse compression and expansion respectively, and structural Poisson's ratio ν is defined as

$$\nu = -D_{\perp}/D_{\parallel} \quad (4-2)$$

Where $D_{\parallel}$ is longitudinal displacement. It can be observed that conventional thin film structure and auxetics exhibit a positive and negative structural Poisson's ratio, respectively. In contrary to conventional Poisson compression, bi-directional expansion in auxetics promotes the separation degree of active materials, thus is promising to enhance sensitivity of stretchable strain sensors.

Figure 4.1 Stretchable strain sensors based on auxetic mechanical metamaterials. (a). Conventional thin film structure and (b). auxetic metamaterial structure with 4-unit array, with corresponding deformation under 15% tensile strain from FEA simulation. (c). Normalized displacement in transverse direction ($D_{\perp}$) under longitudinal tensile strain. Negative and positive $D_{\perp}$ represents transverse Poisson compression and transverse auxetic expansion respectively. (d). Illustration diagram of stretchable strain sensors based on auxetic metamaterials, which is composed of: auxetic frame, thin film and conductive SWCNT network.

To this end, we rationally designed a highly sensitive stretchable strain sensor, as illustrated in Figure 4.1d, which comprises a 1-unit auxetic metamaterial structure. The sensor is composed of conductive single-wall carbon nanotube (SWCNT) network on polydimethylsiloxane (PDMS) thin film, with a PDMS auxetic frame. This auxetic frame regulates the structural Poisson's ratio and transverse displacement in conductive SWCNT area. The strain sensing process occurs via the following: under stretching, microcracks originate and propagate within conductive SWCNT network, which block the otherwise fluent electron pathway and change the electrical resistance.^[50-53] We were able to greatly

increase the gauge factor to ~ 835 under 15% nominal tensile strain, which is ~ 24 fold improvement over conventional sensors (~ 35). This sensitivity improvement stems from synergistic effect of reduced structural Poisson's ratio and strain concentration, both induced by auxetic mechanical metamaterials. As shown in SEM images (Figure 4.11, 4.12), microcracks are elongated by auxetic metamaterials. As proof of concept, we demonstrated the detection of human radial pulse wave with high signal-to-noise ratio (~ 105 dB). This strategy for sensitivity enhancement is independent of constituent materials, and can be further employed to other stretchable strain sensors. Furthermore, it provides a new perspective to utilize the unusual, extraordinary properties of mechanical metamaterials into stretchable electronics.

This chapter mainly provide experimental results of auxetic metamaterial based stretchable strain sensor, in order to prove the feasibility and effectiveness of this strategy. In next chapter, theoretical models are established to investigate the underlying mechanism and guide the further employment and optimization of mechanical metamaterials.

4.2 Experimental Methods

4.2.1 Fabrication of 3D printed auxetic mold

Inverse patterns of auxetic metamaterials or non-auxetic structures are printed out by 3D printer (Eden260VS, Stratasys Co.) via digital UV light curing, with CAD built models. Veroclear (RGD810, Stratasys Co.) was used as mold material, and SUP705 (Stratasys Co.) as soluble supporting material, which was washed away immediately after 3D printing process.

4.2.2 Fabrication of stretchable strain sensor based on auxetic metamaterials

Having established the rational design of auxetic structures in stretchable strain sensors, we employ fabrication process of 3D printing-assisted molding in conjunction with SWCNT self-spinning method^[54] (Figure 4.2). Monomer and cross linker of poly(dimethyl

siloxane) (PDMS, Sylgard 184) were mixed together at ratio of 10:1, stirred by stick and defoamed by centrifuge. Then PDMS precursor was poured into 3D printed mold, and cured in 40 °C oven for 1 day. After peeling off, the PDMS auxetic frame and thin film were successfully fabricated together. To cast a conductive thin layer on the PDMS thin film, single wall carbon nanotube solution (P3-SWCNT, Carbon Solutions Inc.) was prepared by dispersing SWCNT in de-ionized water with 0.5 mg/ml. The solution was ultrasonicated (Fisher Scientific FB15051) for 2 days, and placed for around two hours for stabilization, and only the supernatant solution was used.

Figure 4.2 Illustration of the fabrication method for stretchable strain sensors based on auxetic metamaterials.

Hollow masks with certain patterns to define hydrophilic area on PDMS thin film were fabricated by lithography method. A PET lithography shadow mask was printed by a normal inject printer (HP LaserJet M4345 mfp PCL6). Four sheets of PET with the same patterns were stacked together to prevent UV light permeation. Then photoresist (AZ1518) was spin coated upon Cu foil on glass substrate, at 3000 rpm for 60 seconds. Then standard photoetching procedure was executed. After development, the Cu foil was etched by 1 mol/L FeCl_3 solution, making a hollow Cu mask with designed pattern. The hollow Cu masks were put on top of PDMS thin film, and oxygen plasma was applied with pressure

of 5 mbar, 50% of power, and 0.5 minutes. 10 μL of SWCNT solution were dropped on hydrophilic area, and dried in room temperature.

Figure 4.3 a, b) Actual photo images for auxetic metamaterial-based stretchable strain sensors with structural Poisson's ratio of 0.19, before and after 15% nominal strain. c) By using open-code image analyzing software ImageJ, the structural Poisson's ratio in SWCNT area of auxetic strain sensor was calculated to be 0.200 at 15% strain, which is consistent with the FEA calculation. d). Illustration of the basic unit (bow-tie shape) in auxetic metamaterial structure. Auxetic structures with different side length represent different structural Poisson's ratio, of 0.19, 0.25 and 0.41 respectively.

By tuning side length of auxetic frame, which could be easily achieved in 3D printing, the structural Poisson's ratio of auxetic sensors is regulated from 0.41 to 0.19 (Figure 4.3), which was proven by both experimental photos and displacement distribution from FEA simulation. The stretching direction was shown in Figure 4.3d, the same as in characterization and practical application situation, when the top and bottom edges were fixed. Also, in following FEA simulation, the tensile strain was also in this direction. This reduced structural Poisson's ratio in auxetic sensors stems from the combination of auxetic frame and thin film substrate (Figure 4.4). As non-auxetic control, a conventional flat

strain sensor without auxetic frame was employed (referred to as flat sensor henceforth), whose structural Poisson's ratio is 0.5 as discussed before.

Figure 4.4 Tuning structural Poisson's ratio by changing side length.

4.2.3 Material and Electromechanical Characterization

Synchronous electro-mechanical characterization: Wire bonding from the stretchable strain sensors was achieved by using liquid metal (Gallium-indium eutectic, Aldrich) on both sides of the conductive SWCNT network, with initial resistance of $\sim 1.0 \text{ k}\Omega$. Common copper wires were used to connect liquid metal to Keithley 4200-SCS for resistance measurement. Tensile machine (Instron 5848) with a customized oven was employed to apply tensile tests, at speed of 0.1 mm/s .

For surface morphology investigation, stretchable strain sensors were stretched to 15% nominal strain and glued to a glass slide by AB glue. The scanning electron microscope was conducted by Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-7600F), without additional conductive coating.

4.3 Principle Outcomes

The sensitivity of auxetic sensors with different structural Poisson's ratio was demonstrated using tensile test of 15% nominal strain (Figure 4.5a, b). With structural Poisson's ratio of 0.5, relative resistance change and average gauge factor of conventional flat sensors only reached ~6 and ~35 respectively. This value of sensitivity is consistent with our previous study.^[54] In sharp contrast, strain sensors based on auxetic metamaterials displayed much larger relative resistance change. With structural Poisson's ratio of 0.41, 0.25 and 0.19, average gauge factor in auxetic sensors was enhanced to ~393, ~433 and ~835, respectively. Compared with conventional flat strain sensors, our auxetic metamaterial strain sensors demonstrate high sensitivity as high as a 24-fold enhancement, and such sensitivity enhancement is robustly responsive to structural Poisson's ratio.

Besides sensitivity, it's also important to achieve cyclic durability in stretchable strain sensors, which represents the ability to maintain electrical function and mechanical integrity under long-term cycling. The stretchable strain sensors based on auxetic metamaterials exhibit good cyclic durability, under more than 2,000 consecutive loading and unloading cycles (Figure 4.5c). The relative resistance change of different cycles under 15% tensile strain shows high degree of similarity (Figure 4.5d). The maximum relative resistance change is 137.5 for 1st cycle, and remained 128.6 for 2,000th cycle.

Figure 4.5 Performance of stretchable strain sensors based on auxetic metamaterials, and regulatory role of structural Poisson's ratio. (a). Relative resistance change and (b). average gauge factor under 25 tensile cycles, demonstrating sensitivity enhancement by auxetic structures. (c). Cyclic durability test of 2,300 cycles under 15% tensile strain (structural Poisson's ratio of 0.19). Inset demonstrates enlarged vision, with the "up" and "down" arrows showing loading and unloading process respectively. (d). Relative resistance change of different cycles, with high similarity.

The linearity is also vital for stretchable strain sensors, considering the post processing. In mass fabrication, the sensors will inevitably have variety in electrical performance upon strain, even within the same batch of sensors. Also, the initial status is also different for each sensor, which largely influences initial electrical performance, especially with strain sensors of high sensitivity. Generally, sensors as final products need to be calibrated via setting initial electrical performance, and this initial status will be treated as the point of origin when calculating the applied strain during usage.

In such sensor calibration process, linearity of the sensors is very important. This is because good linearity can avoid the trouble of calibration, helping to know the electromechanical curve without the need to know initial stretching status. Hence, the linearity of auxetic metamaterial based stretchable strain sensors are characterized, by measuring average gauge factor under different tensile strain range (0-2%, 2-5%, 5-15%) (Figure 4.6). The value of gauge factor in different strain range are close, though it is slightly higher for 2-5% strain range, suggesting a relatively good linearity. Besides, for over 2,000 stretching cycles, the gauge factor in different strain regions have little change, showing good cyclic durability for partial strain.

Figure 4.6 Gauge factor in different cycles and strain ranges, showing high sensitivity even under large strain.

Furthermore, the strain sensing performance of stretchable strain sensors also relies heavily on stretchability, since it needs to accommodate the whole strain range in practical application. Maximum stretchability of our auxetic strain sensor achieves 98%, with relative resistance change of ~4600 at breaking point (Figure 4.7a). Since human skin accommodates body movement with stretchability up to 30-70%,^[55] this maximum stretchability fulfills the requirements for skin-mounted wearable devices.

The stretchability is probably limited by small defects from fabrication process (Figure 4.7b), thus can be further improved.

Figure 4.7 (a). Stretchability of stretchable strain sensors based on auxetic metamaterials, with maximum strain of 98%. Noise in large strain range comes from wire bonding and sample clamping. (b). Stress-strain curve of flat PDMS film, with stretchability of >160%.

In addition, since the size requirement of stretchable strain sensors depends on specific application, it's necessary to maintain the sensor performance after scaling the sensor size. Programmability of 3D printing method allows this size scaling, thus auxetic sensors were fabricated with 0.512 and 0.125 of the original volume. Also, auxetic sensors composed of a 5-unit auxetic array were fabricated, each unit representing a 0.125 downsized auxetic structure (Figure 4.8). All of the scaled and arrayed strain sensors achieved high gauge factor of >500, which validates the sensor flexibility to fulfill practical requirements of multifarious sizes.

Figure 4.8 Illustration diagrams (a), relative resistance change within 25 tensile cycles (b), and average gauge factor (c) of different stretchable strain sensors. Scaling 1.0, 0.8, 0.5 represent sensors with dimensions scaled down to corresponding values, while array represents 5-unit auxetic array with 0.5 scaling, and flat as the non-auxetic control.

Next, we investigate the sensitivity in various strain range of auxetic strain sensors, to suggest their competence in detecting small deformation even under stretching status. Three control strain sensors were employed, including pillar and square sensors with replaced auxetic frame, and the conventional plank sensors (Figure 4.9). The area of whole sensor and conductive SWCNT network are kept the same as in auxetic sensors.

Figure 4.9 Illustration diagrams of auxetic metamaterial structure, and non-auxetic control with square, pillar and flat structures.

Relative resistance change of auxetic sensors within 25 tensile cycles is much larger than all non-auxetic control (Figure 4.10a). Here local gauge factor (LGF) is defined as the slope of relative resistance change curve:

$$\text{LGF}(\varepsilon) = \frac{f(\varepsilon) - f(\varepsilon_0)}{\Delta\varepsilon} \quad (4-3)$$

where $f(\varepsilon) = \Delta R(\varepsilon)/R_0$ represents the relative resistance change curve, and ε represents tensile strain. The difference between GF and LGF lies in the strain range, with $0 \sim \varepsilon$ in the former, and $(\varepsilon - \Delta\varepsilon) \sim (\varepsilon + \Delta\varepsilon)$ in the latter. LGF plays a vital role in practical applications since strain sensors often work under pre-stretching status. Stretchable strain sensor based on auxetic metamaterials exhibits LGF of 21.3, 7.2 and 4.4 at 3%, 9%, 15% tensile strain (Figure 4.10b), which indicates high sensing ability for subtle movement $\Delta\varepsilon$ at large strain. In sharp contrast, LGF in all non-auxetic strain sensors are 1-2 orders of magnitude lower than auxetic ones. These observations demonstrate that in varied strain range, strain sensors based on auxetic metamaterials possess unparalleled sensitivity over non-auxetic ones.

Figure 4.10 Local sensitivity within various strain range. (a). Relative resistance change curves of auxetic and three nonauxetic strain sensors (pillar, square, and flat). (b). Local gauge factor (LGF) as the slope of relative resistance change curves, showing sensitivity advantages of auxetic strain sensors in various strain range.

To investigate the underpinning working mechanism of auxetic metamaterial strain sensors, SEM images of SWCNT area were taken under 15% vertical strain (Figure

4.11). For SEM images with low magnification as $\times 500$, microcracks can be observed in both flat substrate sensor and auxetic metamaterial sensor. This is because the SWCNT layer is much more brittle than underlying PDMS substrate, thus microcracks will randomly form when stretching the whole sensor. The microcracks exposed the underlying insulating PDMS substrate, thus it shows white color under SEM images. A closer investigation with larger magnification suggests that microcrack length are different in flat substrate sensor and auxetic metamaterial sensor. For flat substrate sensors, the microcracks are short as highlighted in red circle, while for auxetic metamaterial sensor the microcrack is long enough to nearly cut through the whole SEM image. In addition, SEM images of $\times 35k$ magnification display the SWCNT layer is composed of SWCNT bundles and network, with microcrack opening length of 500-600 μm .

Figure 4.11 SEM images of microcracks on SWCNT layer of auxetic metamaterial sensor and flat substrate sensor, showing longer microcracks in presence of auxetic structure.

The quantitative calculation of microcrack length under SEM images was conducted via open source software Image J. First the number of pixels of scale bar in SEM images was calculated, together with the number of pixels of microcracks. Then using simple proportional calculation, the length of microcracks can be calculated for statistic measurement. Microcracks in auxetic metamaterial sensor nearly cut through the whole SEM image (27.7 μm in average), while microcracks of flat sensor runs just half of the width, with average of 14.8 μm (Figure 4.12).

Figure 4.12 Average microcrack length in auxetic and conventional flat strain sensors under 15% tensile strain, calculated from SEM images.

To demonstrate the practical application of our highly sensitive stretchable strain sensors based on auxetic metamaterial, human radial artery pulse was detected from a healthy female volunteer. A strain sensor of 5-unit auxetic metamaterial array was attached to human wrist (Figure 4.13a). Due to the high sensitivity, auxetic metamaterial sensor exhibits high signal-to-noise ratio (SNR) of 104.8 dB, while SNR of conventional flat sensors was only 39.4 dB (Figure 4.13b). Pulse peak can be distinguished from signals of both auxetic and conventional flat sensors (Figure 4.13 c, d). However, only signals from auxetic sensors exhibit discernible medical details within one pulse, providing information of forward wave, peak systolic pressure, discrotic notch and tricuspid valve opening. In comparison, due to low sensitivity,

conventional flat sensor only obtains one single beat in pulse profile, losing detailed medical information. These data suggest that our auxetic metamaterial sensors demonstrate great potentials to continuously monitor daily health with high precision and abundant medical details.

Figure 4.13 Detection of human radial pulse wave, using stretchable strain sensors based on auxetic and conventional flat structures. (a). Photograph of stretchable strain sensor with 5-unit auxetic array (Scale bar: 5 mm), and sensor attaching to human wrist for radial pulse detection (Scale bar: 1 cm). (b). Signal-to-noise ratio (SNR) comparison of auxetic and conventional flat sensors. (c, d). Human radial pulse profiles, in which enlarged signal from auxetic strain sensor shows discernible stages and abundant medical details, due to its high sensitivity.

In order to investigate the internal interactions in deformed materials, we employ microscopic point of view. Here our auxetic metamaterial based stretchable strain

sensor contains two kinds of materials: conductive active material and stretchable elastomer.

For conductive active material (in this case, single-walled carbon nanotubes), microcrack strategy was employed to endow stretchability. Upon 30% vertical stretching, the surface of conductive material was torn and microcracks were formed and aligned in horizontal direction (Figure 4.14). In this way, the microcrack opening accommodates the applied strain and release the energy, protecting the active material layer from being totally torn. If we enlarge such microcrack pattern into macroscopic view, it would be just like a piece of paper with cutting: when we stretch the paper, the opening of the crack become larger, accommodating the applied strain without tearing the paper itself.

Figure 4.14 Microcracks in auxetic strain sensors under 30% nominal strain. a, b) SEM images with different magnification. Scale bar: a) 40 μm , b) 10 μm , Inset: 500 nm.

Therefore, the electrical performance is determined by the length and distribution of microcracks in active materials, which influence the electron pathway. In this work, the most important electrical performance is high sensitivity, which has been proven to be achieved by auxetics-induced elongated microcracks. Such elongated microcracks have been analyzed through SEM images (Figure 4.11, 4.12), showing auxetic metamaterial structure can improve the microcrack length. In next chapter,

theoretical model and voltage distribution model was built to prove that such elongated microcracks can indeed influence electrical performance, thus obtain high sensitivity.

For stretchable elastomer, (in this case, polydimethylsiloxane) it is viscoelastic polymer with very weak intermolecular forces, which allows the polymer to stretch in response to macroscopic stresses. A typical stress-strain curve of polydimethylsiloxane (PDMS) shows its mechanical behavior upon applied strain (Figure 4.15). The long polymer chain with knots of cross-links can reconfigure themselves under applied stress, giving them the elasticity, while the covalent cross-links ensure the elastomer to return to its original configuration after stress release. In our case, the large strain nonlinear behavior of PDMS will be modeled as hyperelastic material by two-term Mooney-Rivlin Model, because this model has advantages in rubber-like material:

$$W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + D(J - 1)^2 \quad (4-1)$$

Where W is the strain energy density function, C_{10} and C_{01} are material constants related to the distortional response, D is material constants related to volumetric response, and $J = \det(F)$ where F is the deformation gradient. This model is often used for rubber-like materials including natural rubber and silicone. In our case, the value of constants C_{10} , C_{01} and D were determined by curve-fitting of stress-strain curves from experiment (Figure 4.15), with $C_{10}=0.3378$, $C_{01}=0.0834$, $D=0.0096$. This model based on experimental stress-strain curve reflects the internal interaction in between polymer chains, and will be employed for finite element analysis in the next chapter.

Figure 4.15 Stress-strain curve of PDMS, showing mechanical properties upon stretching.

As to the desired electrical performance, since the stretchable elastomer only serve as substrate to support active materials and microcracks, it just contributes the stretchability in desired performance. As discussed previously, the practical requirement varies according to different applications, and for on-skin electronics it would be no more than 70%. Therefore, from the stress-strain curve, the stretchable elastomer material with physical stretchability of more than 160% can satisfy such requirement.

4.4 Conclusion

In conclusion, experimental results of the new strategy were presented, which employed auxetic metamaterials to significantly enhance sensitivity of stretchable strain sensors. Instead of the transverse Poisson compression in conventional thin film, auxetic metamaterial frame exhibits bi-directional expansion due to the reduced Poisson's ratio. Compared to conventional sensors, sensitivity is greatly elevated with a 24-fold improvement, from ~24 to ~800. The microcrack on active layer of auxetic strain sensors exhibits elongated microcracks due to auxetic structures. As a proof of concept, human radial pulse wave was detected using auxetic stretchable strain sensors, exhibiting high signal-to-noise ratio due to their high sensitivity, beneficial for high fidelity signal collection. Importantly, this study demonstrates a radically new strategy to enhance sensitivity of stretchable strain sensors, which further enables their practical applications. Moreover, our strategy is independent with active materials employed, thus can be utilized to other stretchable strain sensors. Ultimately, this pioneering work brings the whole mechanical metamaterial field into the view of stretchable electronics. The functionalities of stretchable electronics are heavily dependent on mechanical properties under deformation, thus metamaterials with superior mechanical behaviors could inject vitality and build momentum to this field.

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Chapter 5*

Theoretical Model for Auxetic Strain Sensors

Auxetic mechanical metamaterials have been proved to effectively enhance sensitivity of stretchable strain sensors, verified via experimental results. However, the underlying mechanism of such sensitivity enhancement needs to be investigated. Therefore, this chapter presents the theoretical models for auxetic strain sensors. Firstly, finite element analysis was employed to investigate the strain distribution and microcrack length in stretchable strain sensors, explaining why auxetic structures leads to elongated microcracks. Next, voltage drop model explains why elongated microcracks enhance the sensitivity. Finally, an overall model based on elongated microcracks and heterogeneous strain distribution was established. Such theoretical investigation is of great significance: On one side, it can explain the intrinsic relationship in between phenomenal experimental results in view of scientific foundation; on the other side, mechanism is highly crucial for practical processing of further device optimization and customized design.

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5.1 Introduction

Stretchable strain sensors transduce mechanical strain stimuli into readable electrical signals and thus have attracted tremendous attention in recent years. Since their softness and stretchability solve the mechanical mismatch between electronics and biological organs, stretchable strain sensors exhibit enormous potential in wearable healthcare bioelectronics. For example, motion-related neurological disorders can be diagnosed via stretchable strain sensors, which can control a drug delivery system as a feedback therapy. Here the sensitivity or gauge factor (GF) in resistive-type sensors is defined as

$$GF = (\Delta R/R_0)/\varepsilon \quad (5-1)$$

where $\Delta R/R_0$ is the relative resistance change under an applied strain ε . Capacitive-type sensors are not discussed in this chapter, since they exhibit very low sensitivity due to theoretical limitations. The sensitivity limitation restrains sensor accuracy in wearable bioelectronics because subtle yet valuable strain details would be lost during signal transduction. Besides, low sensitivity largely increases the demand for postprocessing circuits, raising the cost exponentially. Therefore, there is a strong need to develop a strategy to enhance the sensitivity of stretchable strain sensors to fulfill practical requirements.

In last chapter, a novel strategy of employing auxetic mechanical metamaterials was proposed to enhance sensitivity of stretchable strain sensors, presented with experimental results. It has been proved that auxetic strain sensors can achieve high gauge factor and stretchability at the same time, as well as good cyclic durability. The performance comparison with other representative stretchable strain sensors further shows the advantages of auxetic strain sensors (Figure 5.1).

Figure 5.1 Performance comparison with other stretchable strain sensors reported in the literature.^[1-19]

However, the underlying mechanism of this sensitivity enhancement is not investigated. It is highly demanded to clarify the logical relations in between experimental results, which is crucial for both scientific understanding and experimental optimization. Therefore, in this chapter, theoretical models for auxetic strain sensors are established, to investigate the underlying mechanism in between the intricate experimental phenomenon. In this work, the general methodology is to bridge the gap between different experimental results, and build the whole model based on our heterogeneous strain distribution theory (Figure 5.2). In this illustration of methodology, the experimental results shown as the blue color represent phenomenon via observation. Some relationship in between experimental parameters can be observed via experiment, for example, the gauge factor reveals relationship between applied strain and electrical resistance change. Nonetheless, linkage between other experimental results needs to be explained through semi-quantitative models, such as that between applied strain and microcrack length. Finally, a whole model explaining the underlying mechanism will be established using theory of heterogeneous strain distribution. Such theoretical modeling casts the observed phenomenon into a mathematical description, thus it is very crucial in stretchable electronics, especially those with microcrack-induced stretchability. It can not only establish reasonable and

scientific foundation of auxetic stretchable strain sensors, but also provide guiding function for strain sensor designs.

Figure 5.2 Methodology for establishing theoretical models for auxetic metamaterial stretchable strain sensors, linking and explaining experimental results with model and simulation.

5.2 Simulation Methods and Outcomes

In this chapter, two kinds of simulation are conducted to explain the linkage between experimental results, together with an overall model for the whole auxetic stretchable strain sensors.

Firstly, finite element analysis (FEA) is employed to analyze both the strain distribution and microcrack length in auxetic stretchable strain sensors, linking the auxetic structural design with mechanical properties. Next, voltage drop model is established to mathematically describe the relationship between microcrack length and resistance change. Finally, an overall model is built based on heterogeneous strain

distribution and elongated microcracks, which explains and guides the whole working mechanism of auxetic strain sensors.

5.2.1 Finite Element Analysis

Firstly, finite element analysis (FEA) is employed to analyze the strain distribution of stretchable strain sensors based on auxetic metamaterials under stretching. Four different designs of stretchable strain sensor were simulated: auxetics, pillar, square and flat.

Due to the structural symmetry of the stretchable strain sensors, a 1/4 representative part was simulated, and full contour results for whole device were conducted in post-process. The PDMS structures were modeled with the same size as experimental specimen. SWCNT conductive network was modeled as a thin sheet contacted on the middle of PDMS thin film, also with the same size as in experiments (4*6 mm²).

In this FEA simulation, the large strain nonlinear behavior of PDMS was modeled as hyperelastic material by two term Mooney-Rivlin Model. A hyperelastic materials is ideally elastic materials where elasticity shows non-linear behavior, and the stress strain relationship are normally expressed in terms of strain energy density. Hyperelastic materials are often used to model rubber-like materials including natural rubber and silicone, so it is suitable for modeling our auxetic strain sensors, which was fabricated by PDMS. There are many hyperelastic materials model to choose in commercial FEA software. The Mooney-Rivlin model is advantageous when the behavior of hyperelastic material is unknown, so it is one of the most commonly used model. The Mooney-Rivlin model is a special case of generalized Rivlin model:

$$W = \sum_{i+j=1}^N C_{ij} (\bar{I}_1 - 3)^i (\bar{I}_2 - 3)^j + \sum_{k=1}^N \frac{1}{d_k} (J - 1)^{2k} \quad (5-2)$$

Where W is the strain energy density function, C_{ij} are material constants related to the distortional response ($C_{00} = 0$), $1/d_k$ is material constants related to volumetric

response, and $J = \det(F)$ where F is the deformation gradient. The Mooney-Rivlin model can be expressed as a sum of invariants:

$$W = \sum_i \sum_j C_{ij} (I_1 - 3)^i (I_2 - 3)^j + D(J - 1)^2 \quad (5-3)$$

Where constants C_{ij} and D will be determined by curve-fitting experimental stress-strain curve. From the first few terms of the above formula, we can write the two-term Mooney-Rivlin model:

$$W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + D(J - 1)^2 \quad (5-4)$$

In our case, the value of constants C_{10} , C_{01} and D_1 were determined by curve-fitting of stress-strain curves from experiment (Figure 5.3), with $C_{10}=0.3378$, $C_{01}=0.0834$, $D_1=0.0096$. The density of PDMS was set as 9.7×10^{-10} tonne/mm³. SWCNT was modeled as isotropic elastic material, with Young's modulus of 300 MPa.

The boundary conditions are set as free in X and Z directions and nominal strain was applied in Y direction. This boundary conditions are in consistence with experimental setup and practical application, where the top and bottom edges of devices are fixed. Also, this boundary condition is in the same direction with where we calculated structural Poisson's ratio. From the FEA simulation result, the strain distribution in auxetic sample shows an obvious strain concentration in the conductive SWCNT region, with >30% peak strain (maximum principle strain).

Figure 5.3 Material properties of PDMS in FEA are determined by curve-fitting of stress-strain curve of PDMS film.

Strain distribution from FEA simulation allows insights into the auxetic/non-auxetic frames, revealing the regulatory effects of strain re-distribution and concentration (Figure 5.4a). Bottom view with the underlying frames is adopted here, with 15% nominal strain applied in vertical direction. In our simulation, the highlighted area lies in middle conductive SWCNT network, since it serves as the resistance testing region. It is evident that both auxetics and pillar strain sensors exhibits strain re-distribution and concentration in the highlighted SWCNT area, while square and plank strain sensors show a nearly uniform strain distribution. Strain concentration ε_c in SWCNT area is further calculated from FEA (Figure 5.4b). Obvious differences are observed in ε_c , with 32%, 32%, 20% and 18% in auxetic, pillar, square and plank strain sensors respectively. However, auxetic strain sensors exhibit average gauge factor as high as ~ 835 , although its ε_c is similar to non-auxetic pillar sensors. Within three non-auxetic control sensors, average gauge factor only reaches ~ 108 , ~ 35 and ~ 35 of pillar, square and plank sensors respectively. It can be concluded that the sensitivity improvement by auxetic metamaterials can be attributed to two factors: reduced structural Poisson's ratio as a main reason, and strain concentration as a secondary reason.

Figure 5.4 (a). Strain distribution from FEA simulation, under 15% nominal strain. (b). Average gauge factor and strain concentration ε_c in conductive SWCNT area (resistance testing area).

Secondly, finite element analysis was employed to quantitatively explain the microcrack elongation resulted from auxetic metamaterials, through stress and strain field effect. Based on fracture mechanics, the stress concentration would occur at crack tips when service loading increased generally (Figure 5.5). This is due to the stress concentration at the crack tip area, which can achieve several times larger than other area, which is also proved via crack strain distribution from finite element analysis.

Figure 5.5 (a, b). Illustration of stress concentration along a specimen with a crack. σ_m , σ_0 , a and ρ_t represent the maximum stress at crack tip area, nominal applied tensile stress, half length of crack, and radius of curvature at crack tip, respectively. (c). Stress concentration at crack tip area, from FEA simulation.

Therefore, cracks would propagate when the driving force on structures exceeds fracture threshold. FEA simulation was conducted to qualitatively explain the variations of microcracks in auxetic metamaterial stretchable strain sensors. A representative area with single microcrack was modeled. A small initial crack was employed in the center, and the remaining midline was connected by contact interaction property, with damage condition of maximum normal stress (41 MPa), shear stress (41 MPa) and fracture energy (100 mJ). Material properties were set the same as in previous FEA simulation for strain and stress analysis. In both models of auxetic metamaterial and conventional flat sensor, the displacement was applied on the ends, which are equivalent to 0%, 7.5%, 15% nominal strain. The difference between auxetic and flat sensor was shown in boundary conditions: free boundaries represents free Poisson compression, while fixed boundaries represents limited

transverse effect by auxetic structure. The crack of auxetic strain sensors in this FEA cut through the whole simulated area at 14.1% nominal strain. For fair comparison, final crack length of conventional flat sensor in FEA was also taken at 14.1% nominal strain.

The FEA simulation results showed propagation of a representative microcrack, under stretching loading on auxetic and conventional flat structures respectively (Figure 5.6a). Upon 14.1% normal tensile strain, microcrack within auxetic structure cuts through the width of simulation area completely. In comparison, microcrack with conventional flat structure is obviously shorter under same stretching loading. The qualitative investigation in microcrack length was conducted, which shows auxetic structure is much easier to cause crack propagation under same applied strain (Figure 5.6b). The simulation results manifest good consistency with experimental SEM observation. It provides a simple explanation that auxetic metamaterials regulate the propagation of microcracks within SWCNT network.

Figure 5.6 (a). Illustration of microcrack length and strain distribution in auxetic and conventional flat stretchable strain sensors, under 0%, 7.5% and 14.4% tensile strain, from FEA simulation. (b). Crack length (a.u.) within auxetic and conventional flat sensors under different tensile strain, from FEA simulation. A small initial crack was employed in both FEA models to enable crack propagation, resulting in similar crack length in small strain range (<5%).

5.2.2 Voltage Drop Model

This phenomenological model was based on a previous work of Wagner's group.^[20] It qualitatively explains why longer microcracks lead to higher resistance, which results in high sensitivity of stretchable strain sensors.

The flow chart of computational process was illustrated (Figure 5.7). Firstly, experimental SEM images of auxetic and conventional flat sensors are binarized from gray scale to black-and-white color (Figure 5.7a, b). Black and white pixels represent exposed PDMS in microcracks (non-conductive area) and SWCNT network (conductive area), respectively. The criterion of binarization is:

$$\sigma_{i,j} = f(x) = \begin{cases} 1, & x < threshold \\ 0, & x \geq threshold \end{cases} \quad (5-2)$$

where x means the gray scale of original SEM image pixel, (i,j) means the serial number of pixel, and $\sigma_{i,j}$ means the converted binary value. Threshold value was chosen on criterion that the converted binary SEM has the same microcrack pattern as original SEM. Thirdly, we apply an electrical potential difference on two sides of the binary SEM images, which can be regarded as a Dirichlet-type boundary (Figure 5.7d). In this case, current flow of each pixel obeys the continuity condition:

$$J_{x,in} + J_{x,out} + J_{y,in} + J_{y,out} = 0 \quad (5-3)$$

where J is the surface current density. Discretized Ohm's law was also employed to solve electrical current of each pixel. Finally, potential of each pixel can be solved from this matrix formula:

$$Ax=b \quad (5-4)$$

where A contains conductive information $\sigma_{i,j}$ of each pixel, x contains the potential distribution information, and b contains boundary condition information (applied potential drop). By solving matrix problem by Matlab software, potential distribution x of SEM images can be obtained. In our case, potential drop is faster in auxetic strain sensors than conventional flat ones, which phenomenologically verified the improved sensitivity enhancement by auxetic metamaterials.

Figure 5.7 Flow chart of voltage drop simulation based on experimental SEM images. (a). SEM image of microcracks in strain sensors based on auxetic metamaterials, under 15% tensile strain. (b). Converted binary SEM, with white and black pixels representing conductive SWCNT and insulating cracks, respectively. (c). Current flow of pixel $V_{i,j}$ with the neighboring pixels. (d). Applied potential difference (1 V) on both top and down sides, as the matrix boundary condition (Scale bar: 10 μm).

This voltage drop model elucidates why long microcrack length leads to high gauge factor of stretchable strain sensors, based on experimental SEM images (Figure 5.8). It is clearly shown that the voltage distribution of auxetic strain sensors drop much faster than flat sensors, representing a larger resistance under stretching. This larger resistance is consistent with intuitive point of view: longer microcracks in SWCNT networks hinders the electron pathway and thus increases resistance under stretching. It can be concluded from this model that larger microcrack length in auxetic metamaterial sensors leads to sensitivity enhancement, which is in good agreement with experimental results.

Figure 5.8 Microcracks within stretchable strain sensors based on auxetic and conventional flat structures. (a, b). SEM images exhibit different microcrack length under 15% nominal strain (Scale bar: 10 μm). Inset: Microcrack opening (Scale bar: 100 nm). (c, d). Voltage distribution simulation, based on experimental SEM images. Auxetic strain sensors exhibit fast voltage drop and thus large resistance, consistent with their high sensitivity.

5.2.3 Overall Model

Combining the aforementioned experimental and simulation results together, the sensitivity improvement of auxetic metamaterial sensors is explained by model of elongated microcracks via heterogeneous distributed strain (Figure 5.9). The active material, conductive SWCNT network, can be regarded as SWCNT islands due to the microcracks within it.^[21] In relaxed state, these SWCNT islands contact with each other, thus provides an unblocked electron pathway, corresponding to initial resistance R_0 . Under longitudinal tensile strain ϵ , transverse Poisson compression on SWCNT islands squeezes them together, and thus makes short microcracks (Figure 5.9a). Alternatively, reduced structural Poisson's ratio of auxetic metamaterial structure decreases transverse Poisson compression, which promotes the separation of SWCNT islands and thus resulting in longer microcracks (Figure 5.9b). As proven in voltage drop simulation, the electron pathway depends on the length of microcracks. Therefore, auxetic strain sensors would provide smaller current than conventional flat ones, indicating large relative resistance change and sensitivity.

Figure 5.9 Whole model of Microcrack model of auxetic stretchable strain sensors, explaining gauge factor enhancement induced by auxetic metamaterial structure, due to heterogeneous strain distribution.

5.3 Conclusion

A novel strategy to enhance sensitivity of stretchable strain sensor was proposed, via employment of auxetic mechanical metamaterials. The experimental results prove the enhanced sensitivity of 24-fold increase, together with high stretchability and cyclic durability. This chapter aims to investigate the underlying mechanism of this sensitivity enhancement, via simulation and models to theoretically explain linkage in between experimental phenomenon. Firstly, finite element analysis was employed to quantitatively investigate the strain distribution and theoretical microcrack length in auxetic strain sensors. The analysis results reveal that the reduced structural Poisson's ratio and strain concentration serves as two main factors for sensitivity improvement. Next, voltage drop simulation model was established to understand why elongated microcracks in experimental results leads to enhanced sensitivity. Finally, combining the abovementioned models, a whole model was built based on heterogeneous strain distribution and elongated microcracks. Such theoretical investigation is the abstract model for real experimental process, revealing the underlying linkages in between

superficial phenomenon, which is beneficial for scientific understanding, practical sensor optimization, as well as customized design.

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Chapter 6

Auxetic 3D Foam Based Stretchable Electrodes

Stretchable electrodes serve as a basic element in stretchable electronics since they can be used as electrophysiological signal sensors, interconnects, conductive layer in transistors for logic gates and so on. Foam-based stretchable electrodes are developed due to their advantages of softness and gas permeability, which are required for on-skin applications to avoid blocking of sweat or sebum secretion. However, such foam-based electrodes cannot fulfill the requirements of electrical and mechanical stretchability and conformality, which is crucial to maintain electrical conductivity and physical integrity within large strain. Here, a novel strategy of employing auxetic three-dimensional foam was proposed to fabricate auxetic foam based stretchable electrodes. The auxetic polyurethane foam exhibit negative structural Poisson's ratio of -0.3 at 40% strain, leading to transverse expansion upon longitudinal stretching. Such auxeticity originates from the re-entrant porous structures inside, and can be easily regulated. In virtue of auxetic structures, the mechanical stretchability was enhanced from 150% to 190%, while electrical stretchability increased from 20% to 150%. The underlying microscopic mechanism lies in the heterogeneous strain distribution in gold thin film, leading to heterogeneous microcrack length, which maintains the electron pathway and electrical conductivity.

6.1 Introduction

Recent years witness the paradigm shift in research field from rigid, silicon-based electronics to stretchable electronics with similar mechanical properties as human tissues. Such transformation originated from the practical requirements for human-machine interface such as wearable sensors, implantable bioelectronics, soft robotics and so on, where rigid electronics cannot integrate conformally with soft, stretchable human tissues. Therefore, tremendous efforts have been devoted in stretchable electronics field, such as flexible interfaces,^[1,2] stretchable sensors for Internet of Things (IoT),^[3,4] implantable diagnostic/therapeutic bioelectronics,^[5,6] flexible batteries/supercapacitors,^[7,8] soft robotics^[9,10] and so on.

Among all types of stretchable electronics, stretchable electrodes, also referred to as stretchable conductors are one of the most important core element and fundamental units, which requires maintenance of electrical conductivity under required strain. This is because the stretchable electrodes are required in many components in the whole stretchable system, such as interconnects, physiological signal sensing, or the conductive layer of stretchable transistors for further logic circuit. However, there is hardly intrinsically stretchable, fully conductive materials in nature, where conductive materials such as metal or carbon are usually brittle, and stretchable elastomers or polymers are usually insulating. To achieve stretchability and conductivity simultaneously, several strategies have been developed such as ultrathin substrate design, microcrack strategy, buckling effect, percolation strategy and so on. Among these strategies, microcrack strategy using randomly distributed microcracks in brittle conductive layers to accommodate applied strain are most commonly employed strategy, with high stretchability, compatibility with conventional fabrication process, tolerance to local damage and so on. A lot of efforts have been devoted in microcrack-based stretchable electrodes in virtue of their advantages, for various applications such as physiological signal detection, synaptic transistor conducting and so on.^[11-15] However, the stretchability, conformality still remains the challenge in stretchable electrodes. For stretchability, the practical requirement varies according to different applications, such as 70% for on-skin

wearable electronics. The conformality between electrodes and human skin also needs to be address, because low conformality largely decrease the fidelity and accuracy of the collected signal from human body. Besides, gas permeability is also important for on-skin applications, since the non-breathable electronics on skin will block the normal sweating, cooling and other biological process, leading to skin discomfort or irritation.^[16,17] To address these challenges, foam-based stretchable electrodes have been developed, because the polymer-based foam are intrinsically soft and stretchable with gas permeability.^[18-20] For example, stretchable electronics based on PU foam and metal thin film was developed, while folds and cracks forms upon stretching, leading to localized cracking regions and electron conductive region, increasing the stretchability from 20% to 100%.^[21] However, such foam-based electrodes have not address the challenges of both high stretchability and conformality. This is because the foam structure endures compression in thickness direction upon stretching, which influence the electron pathway as well as driving the electrodes to delaminate from the underlying curvilinear surface.

Here, a new strategy employing 3D auxetic foam was proposed for stretchable, conformal and gas permeable electrodes. Conventional foam experience compression in both transverse and thickness direction upon strain, thus the electrodes with fixed ends tend to delaminate from the skin. 3D auxetic foam as mechanical metamaterials has negative Poisson's ratio in all 3 axes, thus they can expand laterally when stretching longitudinally. Therefore, for on-skin applications, 3D auxetic foam expands in thickness direction and make intact contact to underlying curvilinear skin, promising its conformality. Such auxetic foam are prepared from normal polyurethane foam with reaction of a polyisocyanate with a polyol in the presence of a blowing agent. The normal polyurethane foam was then compressed tri-axially with thermal processing, and the compressed status are kept due to its thermoplastic properties. Then gold conductive thin film was integrated on top of the auxetic foam via thermal evaporating. Such auxetic foam based stretchable electrodes shows negative Poisson's ratio of ~ -0.35 , high mechanical stretchability of 180%, high electrical stretchability of 140%, good conformality and so on. Therefore, the obtained high-performance stretchable electrodes proved the strategy of inducing

mechanical metamaterials into stretchable electronics, a solid step towards the practical applications of stretchable electronics.

6.2 Experimental Methods

6.2.1 Preparation of Polyurethane Foam

Polyurethane foam was formed via mixing components from commercial product Flex Foam It-III (Smooth-on company) together in ratio of 1:1 volume, and poured into customized mold with fixed size. Due to the exothermic reaction between the hydroxyl groups of a polyol with the NCO groups of an isocyanate, the carbon dioxide bubbles were formed as blowing agent, leading to volume expansion of ~15 times (Figure 6.1a). To precisely control the final size and surface morphology of polyurethane foam, a lid was put on top of the customized mold with an overpressure to constrain its vertical expansion. This ensured a fine control of density, size and surface roughness of the polyurethane form. After solidification for ~3 hours, the polyurethane foam was peeled-off from the mold, with the help of pre-sprayed lubricant (Ease Release Smooth-on company) in the inside walls of the mold (Figure 6.1b).

6.2.2 Preparation of Auxetic Foam Stretchable Electrodes

The auxetic foam with different Poisson's ratio were prepared from the conventional pristine polyurethane foam, via a 4-stage process of compression, heating, cooling and relaxation (Figure 6.1c). Firstly, the conventional polyurethane foam with specific dimensions were tri-axially compressed into a customized, rectangular mold, where the buckling in foam cell ribs leads to a 3D re-entrant structure. To ensure the future peeling off process, the inner walls of the mold was sprayed with lubricant (Ease Release, Smooth-on company). Two customized lids made of aluminum are also used to ensure the compression during following process. Then the foam was put into oven with pre-heating of 180 °C for 15 mins to "set" a new configuration due to its thermoplastic property. Then the mold was taken out from the oven with cooling for 1 hour, and the foam was taken out

with gentle stretching in each of the three orthogonal direction to avoid adhesion of inner cell ribs.

Figure 6.1 Fabrication illustration of auxetic polyurethane foam. (a). Chemical mechanism of carbon oxide assisted formation of conventional polyurethane foam. (b). Polyurethane foam fabrication with ~15 times volume expansion and self-forming surface skin, with porosity, stretchability and softness. (c). Fabrication process of auxetic polyurethane foam, with four stages of triaxial compression, heating, cooling and relaxation.

Later, the auxetic polyurethane foam was integrated with conductive materials using thermal evaporation (Figure 6.2). In the inner region, the auxetic foam has the porous structures because the carbon dioxide bubbles from fabrication process. But the outer surface of auxetic foam is smooth and continuous, because during fabrication process the bubbles contacted with the inner walls of the mold and broken, forming a skin-like thin film on the surface of the foam. This self-formed skin enabled continuous gold thin film after thermal evaporation, providing electron pathway and thus electrical conductivity.

Figure 6.2 Fabrication of auxetic foam based stretchable electrodes, with thermal evaporating gold thin film on top of the self-formed skin of auxetic foam.

6.2.3 Material and Electromechanical Characterization

For synchronous electrical and mechanical signal testing, two kinds of characterization equipment were employed: electrical testing equipment and tensile testing equipment. The electrical testing was conducted by semiconductor characterization system (Model 4200 SCS) or through digital multimeter (UNIT 72). The tensile testing was conducted by customized hand-stretching machine or automatic tensile machine (C43, C42, MTS Criterion). The tensile tester uses 250 N or 100 N load cell and 100 N screw action grip, with extension rate of 0.1 mm/s for crossheads. The characterization of surface topography was conducted by scanning electron microscopy (JEOL JSM-6340F or 7600) using 5 kV electron beam. For characterization of structural Poisson's ratio, the deformation of all three orthogonal axes are measured by digital camera beside the tensile machine, and analyzed through open source software Image J (Figure 6.3).

Figure 6.3 Characterization of 3D deformation and structural Poisson's ratio, with synchronized testing of mechanical and electrical performance.

6.3 Principle Outcomes

To investigate the inner morphology of auxetic polyurethane foam, the cross section of foam was characterized using scanning electron microscopy (Figure 6.4). Conventional polyurethane foam has the normal porous structure with cell walls and cell ribs. This structure is generated by the carbon oxide bubbles and overpressure during fabrication, which can be modeled as a hexagonal arrangement with cell wall length of $\sim 250 \mu\text{m}$, width of $< 1 \mu\text{m}$ and angle of ~ 60 degree. The cell ribs act as the skeleton of the structures with higher thickness and stiffness, while the thin cell walls in between the ribs are much thinner and flexible. Such conventional porous foam structures are similar to that of the soccer, which also possesses the hexagonal surface morphology. On the contrary, for auxetic foam, the inner structure forms three-dimensional re-entrant honeycomb structure, which can be modeled as an inverse rib-wall structure. Compared to conventional foam, the pore size of auxetic foam is largely reduced because of the tri-axial compression before heating. This compression also bent the cell ribs into the original bubble chamber, and the thin cell walls were concaved inside together with the stiff cell ribs. The inner structures are hardly stick to each other, even for the thin cell walls, which means the relaxation of gentle stretching after demolding the auxetic foam is effective. Such independent skeleton and cell wall are

beneficial for auxetic deformation, otherwise the stretchability will be decreased due to the sticking.

Figure 6.4 (a). SEM image of conventional polyurethane foam, showing honeycomb, porous structure. (b). SEM image of auxetic polyurethane foam, with re-entrant three-dimensional structure and decreased pore size.

Photos of manual stretching provides an intuitive impression of auxetic foam upon stretching (Figure 6.5). For conventional polyurethane foam under longitudinal stretching, the inner honeycomb structures are elongated, and the whole foam endures transverse compression because of the Poisson's effect. Since it is an isotropic foam material, this transverse compression takes place in both two axes as shown in the photos. On the contrary, the auxetic polyurethane foam experience transverse expansion upon stretching, demonstrating a negative structural Poisson's ratio in three-dimensional scale. Such three-dimensional expansion comes from the microscopic structures inside the foam, where applied strain straightens the inverted cell ribs and pulls them out, together with the thin cell walls connected with ribs. Such pulling out phenomenon takes place in all three axes because of the tri-axial compression, leading to three-dimensional expansion. The color difference in between conventional and auxetic foam are purely due to the exposure parameters of the camera.

Three-dimensional auxetic deformation is beneficial for conformal contact between stretchable electrodes and human tissues. For conventional foam electrodes, it attaches to

skin with two ends fixed with glues or adhesive. But upon stretching, the Poisson compression in thickness direction results in the decrease in electrodes' height, leading to delamination of the electrodes and skin. Alternatively, for auxetic foam electrodes, the electrodes expand in thickness directions even when the two ends endure stretching, where such expansion drives the electrodes to contact with skin to avoid delamination. Besides, such auxetic foam exhibits improved indentation resistance compared to conventional foam, because the materials contracts laterally and flows in the impact region and absorbs the energy, beneficial for long-term usability of stretchable electrodes.^[22,23]

Figure 6.5 (a). Photo of original and manually stretched conventional polyurethane foam, with transverse compression upon longitudinal strain. (b). Photo of original and manually stretched auxetic foam, with transverse expansion in two transverse directions. The color difference is purely due to exposure settings of camera.

The quantitative investigation of structural Poisson's ratio of three-dimensional auxetic polyurethane foam was conducted, via analyzing photos through open-source software Image J. The photos were taken upon stretching under automatic tensile machine, which has more precise control than manual stretching. The software analysis changed the original and stretched length and width to pixel length, which was calibrated by ruler scale bar. Then longitudinal strain ε_1 and thickness direction strain ε_t was calculated through following formula:

$$\varepsilon_l = \frac{l - l_0}{l_0} \quad (6-1)$$

$$\varepsilon_t = \frac{t - t_0}{t_0} \quad (6-2)$$

Structural Poisson's ratio was calculated as definition:

$$\nu_t = -\frac{\varepsilon_t}{\varepsilon_l} \quad (6-3)$$

To investigate the structural Poisson's ratio, conventional polyurethane foam and auxetic foams with different auxeticity were characterized. Here the auxeticity of foam can be tuned by the original foam size before thermal processing. The original foam size before thermal processing was $4 \times 2 \times 2 \text{ cm}^3$ for low auxeticity foam, and $6 \times 3 \times 3 \text{ cm}^3$ for high auxeticity foam, and the mold size is fixed in $3 \times 1.5 \times 1.5 \text{ cm}^3$. The calculation of structural Poisson's ratio showed different transverse deformation upon longitudinal strain (Figure 6.6). For high auxetic foam, it endured higher level of triaxial compression during thermal processing, thus the cell ribs are more severely bent inside the honeycomb chamber. Such highly re-entrant structure accommodates more strain under applied longitudinal strain, exhibiting lowest structural Poisson's ratio of -0.3 at 40% strain. The structural Poisson's ratio was first decrease with applied strain, then elevated to positive region. This is because under small strain level (<50%), the cell ribs and cell walls in inner structures experienced an unfolding process, in which the bent cell ribs were stretched to straight and the cell walls were stretched to flat. To some extent, the ribs and walls were stretched to recover its honeycomb structure. As the strain continuous to increase, the already flattened cell ribs and cell walls starts to be stretched, demonstrating a positive Poisson's ratio. For low auxetic foam, the trend of structural Poisson's ratio was nearly the same with high auxetic foam, with slightly different turning point. For low auxetic foam, the lowest structural Poisson's ratio of ~ -0.35 exhibits in $\sim 22\%$ strain, which is lower than that of 40% strain in high auxetic foam. This is because the low auxetic foam endures less compression during thermal processing, leading to lower level of re-entrant bending in cell ribs and cell walls. Therefore, it would recover to flattened status much earlier than high auxetic foam, and demonstrates positive structural Poisson's ratio after that. For conventional polyurethane foam, the structural Poisson's ratio is nearly 0.38-0.45 upon 0% to 100% strain. This

positive value comes from the original honeycomb inner structures, and the mechanical properties of polyurethane itself.

Figure 6.6 Structural Poisson's ratio of high auxetic foam, low auxetic foam and conventional polyurethane foam, calculated by photos of stretched samples.

Since the stretchable sensors are required to endure deformation such as stretching, compressing, bending, twisting, which is all correlated to strain, the inner structures of foams under different strain level were investigated (Figure 6.7). For conventional polyurethane foams with honeycomb structures under 0% strain, the transverse compression is obvious under 50% vertical strain due to Poisson's effect. The compression level of cell ribs and walls under 100% vertical strain is slightly larger than that of 50%, in proportion with the ~ 0.45 structural Poisson's ratio calculated macroscopically. For low auxetic foam, the originally three-dimensional re-entrant structure was stretched to flatten under 50% vertical strain, which means the structures have already been stretched to recover honeycomb configuration. Upon 100% vertical strain, transverse Poisson compression was observed, exhibiting a positive structural Poisson's ratio. For high auxetic foam, the originally folded and bent cell ribs and walls are stretched a bit under 50% vertical strain, but the re-entrant structure still slightly maintained. This is because high auxetic foam endured larger tri-axial compression during thermal processing, which can

accommodate more strain before structural Poisson's ratio turns back to positive value. Under 100% vertical strain, the high auxetic foam also experienced vertical stretching and transverse compression, though not as obvious as that of low auxetic and conventional foam. The SEM investigation of inner structures are consistent with the macroscopic analysis and calculated structural Poisson's ratio. It proves that auxetic foam with negative Poisson's ratio in three dimensions are successfully fabricated, while the auxeticity can be tuned to fulfill different requirements of applications.

The material of this auxetic cells are polyurethane elastomer. Therefore, in low strain level ($\sim 50\%$) it has elastic behavior, without structural damage in microstructures and can recover from tensile strain. However, while in large strain level ($\sim 100\%$) there are damage and ruptures in microstructures as shown in Figure 6.7, therefore the cyclic durability will be diminished. For on-skin applications, the 50% strain level can satisfy most of the cases, and therefore still can be utilized for stretchable electrodes.

Figure 6.7 SEM images to investigate the inner structures under 0%, 50% and 100% vertical strain, for high auxetic foam, low auxetic foam and conventional foam, respectively.

For stretchable electrodes, the mechanical properties are important because it should match that of human skin or other tissues to fulfill a comfortable, conformal contact, which is the driving force to transform the conventional rigid, silicon-based electrodes. Therefore, the mechanical properties of foams with different auxeticity and conventional foam were characterized (Figure 6.8). For conventional polyurethane foam, the mechanical stretchability is under 150% for physically breaking, with stress of ~40 kPa. This is originated from its foam structure, where pores constitute large volume and the intrinsic stretchability of polyurethane. In contrast, the mechanical stretchability is ~180% and 190%, for low auxetic foam and high auxetic foam, respectively. The increased stretchability is originated from their re-entrant inner structures. The bent-in cell ribs and walls are first stretched to flattened states as in honeycomb structure, where this unfolding process accommodates additional strain and leaves the ribs with negligible strain. Since the bending status in foam under 0% strain lies in the compression level, the mechanical stretchability is also influenced by auxeticity, with high auxetic foams demonstrating larger mechanical stretchability.

Figure 6.8 Stress-strain curve of high auxetic foam, low auxetic foam and conventional foam, with different stretchability, which is consistent with their microscopic inner structures.

Besides the mechanical properties, electrical properties especially electrical stretchability is also vital for stretchable electrodes. Here 60 nm gold thin film as active material was coated on top of the foam surface via thermal deposition and forms a continuous electron pathway. This is because of the self-formed skin on top of the foam, which is formed by carbon dioxide bubble breakage during polyurethane foam fabrication. The synchronous electromechanical testing was conducted to investigate the electrical stretchability (Figure 6.9). For conventional foam electrodes, the electrical stretchability was as low as 30%. Though the mechanical stretchability is much larger (150%), such electrodes cannot fulfill their function in strain range larger than 30% although the electrodes are not physically broken. In contrary, the electrical stretchability was much higher in foam electrodes with different auxeticity, which is ~150% for both auxetic electrodes. This largely enhanced electrical stretchability provides larger fields for practical applications. For example, the

stretchability of human skin is ~70%, setting requirements for larger electrical stretchability from on-skin stretchable electrodes.

Figure 6.9 Electrical stretchability of conventional foam electrodes, and auxetic foam electrodes with different auxeticity, showing largely enhanced stretchability from auxetic foam structure.

To investigate the underlying mechanism of electrical stretchability, SEM image of top surface in auxetic foam electrode was taken under 50% vertical strain (Figure 6.10). This continuous surface formed from breakage of carbon dioxide bubbles provides continuous electron pathway and thus electrical conductivity. It is clearly shown that the underlying foams greatly influenced the morphology on the top surface. This is because in region with underlying cell ribs, referred to as ridge region, the thickness is much higher than that without ribs, leading to heterogeneous strain distribution in the gold thin film. Upon stretching, the gold thin film forms randomly distributed microcracks, in which the microcracks exposed underlying polyurethane and become insulating. The magnified SEM images of ridge region under 50% strain shows much shorter microcracks compared to that of the middle region. Since such microcracks hinder the electron pathway, the electrical resistance is much smaller in the ridge than in the middle. The ridge region forms a

continuous electron pathway, therefore ensuring the electrical resistance even under large strain, enhancing the electrical stretchability of auxetic foam electrodes. Besides this heterogeneous strain distribution effect, another reason for increased electrical stretchability may lie in the large wrinkles in the auxetic foams, which was formed by tri-axial compression.

Figure 6.10 SEM images showing surface morphology and gold microcracks in auxetic foam electrodes under 50% strain, exhibiting short microcracks in ridge region, and long microcracks in middle region.

6.4 Conclusion

In summary, a new strategy, auxetic 3D foam was employed to obtain stretchable electrodes with high mechanical and electrical stretchability, conformality and gas permeability. The auxetic foams possess three-dimensional re-entrant structures, with cell ribs and cell walls bending inwards. Upon stretching, the inward cell ribs and cell walls are flattened and then stretched, exhibiting macroscopic negative Poisson's ratio as low as -0.3 at 40% strain. Such negative Poisson's ratio was proven by photo analysis in macroscopic view, and SEM images in microscopic view. Besides, the auxeticity of foams can be easily regulated by the tri-axial compression level during fabrication, beneficial for fulfilling different requirements of applications. The mechanical stretchability of auxetic foam was enhanced to 190%, compared to 150% of conventional foam, accommodating

much strain before physical breakage. Equally important, the electrical stretchability was largely enhanced to 150%, in contrast to only 20% in conventional foam electrodes. The underlying mechanism is the heterogeneous strain distribution on gold thin film regulated by auxetic foam, leading to high strain accommodation in middle-cell region and low strain endurance in ridge region, ensuring the electron pathway and electrical conductivity.

This study opens up a new perspective of employing three dimensional auxetic foam for high performance stretchable electrodes, where mechanical and electrical performance can be regulated via auxeticity. Following this new routine and strategy, many other methods can be proposed in virtue of negative Poisson's ratio in auxetic foam to develop other high-performance stretchable electronics.

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Chapter 7*

Discussion and Future Work

In this chapter, the main conclusions of this thesis are summarized, as well as the ongoing challenges. The preliminary results of substrate modification in order to obtain binder-free stretchable electrodes for interconnects are presented, as well as the surface modification to lower electrical impedance for practical applications. At last, the future work in order to obtain long-term stable stretchable electronics are discussed.

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7.1 General Discussion

This thesis aims at achieving highly sensitive stretchable strain sensors and highly stretchable electrodes based on employment of auxetic mechanical metamaterials: the negative Poisson's ratio of auxetic structure leads to 2D or 3D expansion upon strain, mediating the mechanical properties of stretchable electronics, thus enhancing their electrical performance. For stretchable strain sensors, the auxetic metamaterials elongated the microcrack length by bi-axial stretching trend, enhancing the sensitivity. For stretchable electrodes, three-dimensional auxetic metamaterial foam increase the stretchability and conformality via expansion in thickness direction. Since auxetic metamaterials obtains their mechanical properties via structural design rather than chemical composite, they can be further extended to a variety of materials, providing more possibility for stretchable electronics.

Firstly, the current status of stretchable strain sensors and stretchable electrodes is introduced, with different strategies to achieve stretchable electronics, and the importance of solving challenges of sensitivity, stretchability and conformality is elucidated. The hypothesis of auxetic mechanical metamaterials for stretchable electronics are analyzed and proposed. Besides, the methods of material and mechanical characterization, principles behind chosen characterization, theoretical simulation including finite element analysis and voltage drop simulation are also discussed.

Based on auxetic mechanical metamaterials, new stretchable strain sensors and stretchable electrodes are developed for strain sensitivity enhancement, stretchability, conformality and so on, solving the challenges towards practical applications. The underlying mechanism of auxetic metamaterial employment was proven by both experimental investigation and theoretical analysis: the auxetic structures mediate the originally uniform strain distribution along the stretchable electronics, leading to heterogeneous strain distribution which can regulate electrical properties such as sensitivity, stretchability and conformality.

In detail, the strategy of employing 2D auxetic metamaterial was proposed to enhance sensitivity of stretchable strain sensors. The conventional flat film-based strain sensors with positive Poisson's ratio endure transverse compression upon longitudinal strain. Such transverse compression counteracts the stretching effect on electrical resistance, hindering the sensitivity, because stretching corresponds to separation of active material and sensitivity enhancement, while compression squeezes the active materials and lower the sensitivity. Hence the auxetic metamaterials with bi-axial expansion intension was employed, to obtain a two-directional stretching in both transverse and longitudinal direction. Such auxetic strain sensors greatly elevated the sensitivity to ~ 800 , a 24-fold improvement from conventional flat film sensors. Also, the stretchability of 100% and cyclic durability of over 2,000 cycles suggested great potential for practical application. For demonstration, the human radial pulse wave was detected via auxetic strain sensors, which shows high signal-to-noise ratio due to their high sensitivity, extracting abundant medical details through the pulse waveform.

To investigate the underlying mechanism of auxetic metamaterial based stretchable strain sensors, the finite element analysis and voltage drop simulation was conducted based on the randomly distributed microcrack theory. Finite element analysis proves the auxetic structure regulation on sensor deformation upon stretching, consistent with experimental result. Also, the auxetic structure effect on microcrack length was investigated via finite element analysis, proving that elongated microcracks are originated from auxetic structure. To investigate the relationship between elongated microcracks and electrical resistance, the voltage drop simulation using experimental SEM images are built and solved as a discretized matrix problem. An overall model was established in mechanism of heterogeneous strain generated elongated microcracks, which not only assists in scientific understanding, but also helps practical device customization and optimization.

Apart from 2D auxetic structures, 3D auxetic foam was employed into stretchable electrodes, with auxetic expansion in both XY plane and thickness direction upon stretching. This 3D auxetic foam was fabricated through thermoplastic polyurethane foam, using elevated temperature to fix the re-entrant structure, which is intrinsically stretchable.

By integrated with metal thin film on it, the electrical stretchability can be largely enhanced due to the underlying structures. Besides, the Young's modulus was much reduced from the originally foam, providing conformality and gas permeability. Also, the auxetic expansion in thickness direction also allows conformal contact with the underlying human skin.

In all, the employment of auxetic mechanical metamaterials in stretchable strain sensors and stretchable electrodes effectively enhanced the performance such as sensitivity, stretchability, conformality and so on, proven by both experimental results and theoretical simulations. The end application of stretchable strain sensors and electrodes in this thesis is on-skin situation, instead of temporary surgical tools or permanently implantable devices. With this ultimate goal, the stretchable strain sensors were demonstrated for human radial pulse wave detection. This application suggested that the high sensitivity (~ 800) improved by auxetic mechanical metamaterials leads to high signal-to-noise ratio (104.8 dB), which helps to distinguish meaningful diagnostic details in the pulse wave including forward wave, peak systolic pressure, discrotic notch and tricuspid valve opening. Besides, the strain induced by pulse wave pressure is within the range of auxetic metamaterial strain sensors. The cyclic durability of $>2,000$ cycles can also fulfill the requirement of this application. In brief, the unique mechanical properties of auxetic structures provides a new design platform for stretchable electronics, and the chemical composition can be further developed and optimized based on this strategy.

7.2 Future Work

The urgent requirement of human-machine interface including wearable sensors, implantable bioelectronics, transient surgical tools, soft robotics accelerates the electronics transformation from conventional, silicon-based, rigid form into soft, stretchable, biocompatible electronics. Despite the current progress in academia and industry, there is still gaps between research in stretchable electronics and practical applications. This thesis proposed the strategy of auxetic mechanical metamaterials with negative Poisson's ratio, regulating the mechanical properties and hence electrical performance. Such strategy is

based on structural design rather than chemical composition, providing huge space for material development and modification.

Although the thesis raised the auxetic metamaterials to solve the sensitivity and stretchability challenges in stretchable electronics, the end application still needs further modification and advancements. For example, a complete multifunctional stretchable system should include different components, each with a simple function such as strain sensing, electrophysiological signal detecting, powering, memory and so on. Modular electronics in traditional electronics enabled free combination in between different simple electronic unit in a customized way, but for stretchable electronics such technique is still very limited. That means it is only possible to fabricate a complete stretchable system in the beginning without customized freedom, which largely increase the complexity and cost of fabrication process. Therefore, we discussed the binder-free interconnects as a future work in Chapter 7.2.1, which helps the modular stretchable electronics composed of simple building blocks.

Another requirement from end application of on-skin electrophysiological signal detection is the signal-to-noise ratio under DC situation. This raised the request for low impedance rather than low resistance because the electrophysiological signal are DC signals. In previous chapter, the impedance was not taken into consideration, but by using active material surface modification we can lower the impedance of our device, in order to get high quality electrophysiological signal. Fortunately, the strategy of auxetic metamaterials in this thesis focuses more on mechanical engineering, leaving huge space to surface modification. Therefore, we discussed the active material surface modification in Chapter 7.2.2, aiming at increasing signal fidelity and signal-to-noise ratio for electrophysiological signal detection.

7.2.1 Substrate Modification for Binder-free Interconnects

Based on discrete stretchable components, it is highly demanded for integration of stretchable system. The most reasonable and practical solution is the hybrid stretchable

electronics system, which combines stretchable sensors or electrodes with silicon-based IC chips for multifunctional, wireless healthcare monitoring. This is because the core components such as stretchable sensors and electrodes which directly in touch with human tissue needs to be soft and stretchable, while other circuit components such as data storage, wireless data transmission can maintain its rigid properties. In such hybrid system, the interconnects in between different components become a challenge, because the components are generally fabricated separately and requires a combination method. Traditionally used soldering method for silicon-based circuits is not suitable for interconnecting stretchable components, because the bad wettability and adhesion between solder and stretchable elastomer, as well as the enhanced strain concentration due to mechanical mismatch. Therefore, it is in great request to develop strategy for convenient and swift interconnects in stretchable electronics system, while maintaining their electrical properties.

To solve this challenge, substrate modification of stretchable electronics has been investigated. Stretchable electronics requires elastomer or hydrogel substrate for accommodating applied strain and maintain integration of active materials, thus huge efforts have been devoted to substrate modification, towards high mechanical performance such as self-healing, high stretchability, shape memory and so on. Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) is one of widely used thermoplastic elastomers with good thermal stability, good elasticity and processability. Based on SEBS block polymers, stretchable electrodes for systematic interconnects are developed and investigated.

Firstly, stretchable electrodes based on SEBS was fabricated as the components for further interconnects formation. SEBS in form of granulate was dissolved into toluene to be compatible with solution-based process. The SEBS solution was then poured uniformly on clean glass petri dish and evaporated in fume hood for over 2 days to form a thin film. Next, 60 nm of gold thin film was deposited on top of the SEBS thin film using thermal evaporation, with different evaporation speed. Such SEBS based electrodes exhibit high electrical stretchability since it maintains the electrical conductivity until ~150% strain

(Figure 7.1a). Besides, the adhesion between gold active layer with underlying SEBS substrate was high enough to pass the tape peeling test, suggesting robustness of the whole electrode. This good electrical stretchability may results in the interaction between gold nanoparticles and SEBS molecule chain during thermal evaporation process, thus the evaporation speed may influence the electrical performance. To investigate the evaporation speed on stretchability of SEBS based electrodes, evaporation via various speed was conducted and analyzed (Figure 7.1b). With speed increasing, the electrical stretchability decreased substantially, from $\sim 150\%$ at $0.1 \text{ \AA/s}$ to only 60% at $2 \text{ \AA/s}$. The current explanation for this speed-resulted influence is that the molecular chain may endure movement when interacting with gold particles during evaporation. At low evaporation speed, the gold particles provide more time for molecular chain movement and gold particle insertion, therefore enhancing the adhesion between gold particles and substrate, which is beneficial to electrical stretchability. On the contrary, at high evaporation speed substantial gold particles were evaporated on SEBS surface at the same time, which may limit the molecular chain movement and the insertion depth of gold particle, hindering the electrical stretchability.

Figure 7.1 (a). Electrical stretchability of single SEBS-based stretchable electrodes, with molecular structures of SEBS block polymer. (b). The influence of evaporation speed on electrical stretchability, suggesting low evaporation speed is beneficial for interactions between gold particles and underlying substrates.

Based on the stretchable electrodes, the stretchable interconnects can be easily achieved by simply layering two stretchable electrodes together with little pressure applied. The interesting point is that even though the two surface of gold thin film on PDMS was attached together, such interconnects still maintain its electrical conductivity, making it possible for stretchable interconnects in circuits. Therefore, the electrical and mechanical performance of such stretchable interconnects are characterized. Synchronous electrical and mechanical testing shows high electrical stretchability of over 160% (Figure 7.2), which is much better than PDMS based stretchable electrodes (<60%). Interestingly, this electrical stretchability is higher than single SEBS based electrodes, which means the adhesion area may favorably influence the electrical conductivity, which needs further investigation. For mechanical performance, the stretchability to broken point is as large as 700%, which means the interconnect was not physically broken even after it is not electrically conductive. This pure mechanical stretchability is beneficial for practical use, especially for applications with temporary large strain, because after the high impact or large strain, the electrodes are not physically broken thus the electrical performance can be restored.

Figure 7.2 (a). Stretchable electrical interconnects via two SEBS based electrodes, exhibiting electrical stretchability of 160%. (b). Mechanical behavior of stretchable interconnects, showing physical broken point at 700%.

Since the bonding inside the stretchable interconnects relies on interactions in between two supramolecular electrodes, the bonding temperature may largely influence the robustness and electrical performance of the interconnects because of molecular chain movement. Therefore, the influence of temperature during bonding are also investigated (Figure 7.3). For load upon physical breaking point as shown in left y axis, the load endurance was basically unchanged until temperature reached 150 °C, which shows the bonding at high temperature increase the adhesion between two supramolecular electrodes. For pure mechanical stretchability as shown in right y axis, the stretchability first decreased upon temperature increasing in which the reason still needs investigation, and increased at 150 °C which may result in the enhanced bonding at high temperature.

Figure 7.3 Influence of bonding temperature on maximum load and mechanical stretchability in stretchable interconnects.

7.2.2 Surface Modification of Stretchable Electrodes

Stretchable electrodes require maintenance of electrical conductivity upon stretching, which is originated from practical application needs. However, besides electrical conductivity, the electrical impedance is also important especially for electrophysiological signal measurement, which needs detection of biological alternating current. Low impedance of electrodes helps increasing the signal fidelity and signal-to-noise ratio, allowing more medical details from human body. For conventional, silicon-based rigid electrodes, there are various methods to obtain modification and lower the impedance. The most commonly used method is to deposit metal or metal oxide layers such as iridium oxide and platinum onto the electrode surface.^[1-4] Among these modification materials, iridium

oxide shows high potential stability over a wide range of temperature, large charge inject limit ($1\text{-}10\text{ mC/cm}^2$) and biocompatibility, making it promising to modify the stretchable electrodes. Therefore, here iridium oxide was employed to modify the SEBS/Au electrode surface, in order to lower the impedance in stretchable electrodes, using cyclic voltammetry between -0.8 V to $+0.7\text{ V}$ (Figure 7.4). The phase diagram and impedance curve suggested substantial decrease in impedance after iridium oxide deposition, especially in the low frequency range. Since the interest frequency range is $0.5\text{-}500\text{ Hz}$ for EMG, $0.5\text{-}100\text{ Hz}$ for ECG and $0.5\text{-}20\text{ Hz}$ for EEG, the low frequency range of impedance has the most important biomedical significance, benefited from the iridium deposition. Also, the electrodeposition has the saturation point upon cycles, while in ~ 50 cycles the iridium oxide reach saturation and the impedance almost maintain even further increasing the deposition cycles.

Figure 7.4 (a). Phase diagram of stretchable electrodes after iridium oxide electrodeposition. (b). Impedance diagram showing impedance decrease especially in low frequency region. (c). Iridium oxide saturation for different cycles of electrodeposition.

The surface topography was investigated before and after the iridium oxide modification on supramolecular SEBS electrodes, with 100 cycles of electrodeposition (Figure 7.5). Before deposition, microcracks and nanocracks can be observed because the thermal expansion during gold evaporation. After deposition, iridium oxide particles are clearly seen on surface of the gold particles. Some aggregation of iridium oxide particles may originate from redundant iridium oxide, because the impedance performance suggested iridium oxide saturation in 50 cycles. Such surface modification largely lowers the impedance of supramolecular stretchable electrodes, which is promising to improve quality of electrophysiological signal.

Figure 7.5 SEM images showing surface topography of supramolecular stretchable electrodes, before and after surface modification.

7.3 Outlook

The first decade development of stretchable electronics changed the conventional rigid form of electronics, as required from human-machine interfaces, giving rise to stretchable strain sensors, electrodes and other stretchable components.

In the near future, the stretchable strain sensors with on-skin application should go towards industrialization and mass production as integrated multifunctional system, solving real-world problems such as athlete monitoring, patient rehabilitation, motion caption and so on. This ultimate goal is not yet realized because many engineering problems emerges during the process of industrialization, such as the encapsulation, calibration, wireless transmission, washability and so on. This thesis solved the challenges of sensitivity and stretchability of stretchable strain sensors themselves, but these engineering problems still needs a lot of manpower and research source. Some famous pharmacy or internet companies such as MC10, StretchSense starts to bridge this gap and investigates the related products.

For stretchable electrodes, the future lies in long-term usage both for on-skin applications or implantation with electrophysiological signal monitoring. Though this thesis provides new strategies to solve some problems such as stretchability, gas permeability and conformality, on-skin stretchable electrodes needs other specific properties such as adhesive on skin without irritation, abrasion-resistance and so on, which still needs investigation. The implantable stretchable electrodes face more problems such as biocompatibility, encapsulation, wire bonding and so on. For now, the stretchable electrodes have been successfully employed in animal model for acute implantation test, but long-term implantation (>12 months) is yet achieved, leaving huge space in exploration in stretchable electrodes.

In all, the employment of auxetic mechanical metamaterials modulates the mechanical and electrical properties in stretchable strain sensors and stretchable electrodes, leading to heterogeneous strain distribution and performance enhancement. This new strategy

provides methodology based on mechanical and electrical design of stretchable electronics. Besides the auxetic structure, the broad library of mechanical metamaterials with other unique mechanical properties can also follow this strategy to regulate the electrical performance, providing broad prospects of next-generation stretchable electronics.

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