The Hong Kong University of Science and Technology

President's Cup 2019 Report

Project Title: **Fully-conformable Skin Sensors for Sports Fatigue Detection**

Authors:

Andreas Kenny Oktavius ( )
Program: Year 4/ CBME/SENG
Contact:

Nathaniel Wihardjo ( )
Program: Year 4/ CENG/SENG
Contact:

Olivia Winata ( )
Program: Year 4/ CBME/SENG
Contact:

Stefanus William Sunanto ( )
Program: Year 4/ CEEV/SENG
Contact:

Supervisor: Prof. Ping Gao
Date of Submission: 15 March 2019

Abstract

Over these years, wearable biosensors development has been rising as a promising technology which revolutionizes the conventional health monitoring methods. It is capable of giving precaution warnings when there is health problem detected and thus, informing the users to halt their exercises. In professional sports world, it is crucial for an athlete to know their physical limit and adjust their workout methods accordingly. However, the current existing method is still too bulky which makes it not breathable and difficult to conform with the skin. We had successfully fabricated sweat sensors based on the Ultra-High-Molecular-Weight Polyethylene (UHMWPE) membrane with a thickness range around 100 nanometers. As a result, it can conform perfectly to the skin without any adhesives. Furthermore, it has been tested for its capability to collect sweat as the biomarker and subsequently, be further analyzed on its composition through Raman spectroscopy. From analyzing its composition, we have found the presence of stress hormone called cortisol which is an accurate indicator of fatigue level. This report reviews the manufacturing procedures of sweat sensing device and its installation to the skin. Next, it provides a thorough explanation of the analysis method used as well as the results. According to our prior consultations with Hong Kong Sports Institute (HKSI), our last part of the report discusses several possible applications of our sweat sensor to their current methods for monitoring athletes' physical performance.

1. Introduction

Athletes' physical development has been immensely fast, various records were broken in every summer Olympic; it is undeniable how sports are evolving by time. Cynthia Bir, the lead scientist for ESPN's "Sport Science" show, explained how science has improved athlete's abilities and enabled them to reach points that were unthinkable decades ago [1]. Biometric feedback is one of the methods used by the experts in optimizing the athlete's performance. Understanding the metrics can assist coaches tailor trainings in order to help an athlete get passed a plateau. Sweat is not just merely one forms of human perspiration, but it can also act as performance safety metrics for athletes. In professional athlete trainings, coaches often push the athletes into the "red zone" in order to return stronger after certain adaptation period. The excitement of heightened performance brings the subsequent problem. Driven by high-ambition, both athlete and coach are keep pushing without any certain boundaries which results in a very vulnerable physical condition, or in extreme cases, can lead to metabolic imbalances and chronic diseases of blood vessels, heart and others. Hence, it is very crucial for athletes to know their physical limit and adjust their workout methods accordingly.

This particular research area has been rapidly intensified all around the world. Stanford

University is currently developing state-of-the-art “Lab-on-skin” membrane which also collects sweat for further analysis on its composition. However, their membrane still too bulky and thus, not able to perfectly conform without using adhesives [2]. Herein, this project aims to create a flexible, adhesive and stretchable nanolayer device for monitoring the athletes’ fatigue level during rigorous exercise. The most novel point of our project is, the developed UHMWPE membrane is the first ever membrane having the thickness below 100 nanometers [3]. Such low thickness results in well conformability with skin in the absence of additional adhesive which ease the membrane application on any part of the skin including the actively bending part of the skin. Not only that, our porous membrane has also been proven breathable and hydrophobic. This property allows water contained in sweat to evaporate so that the membrane is not easy to be detached while exercising. The breathability property also does not hinder the movement of athletes and providing the best convenience since the membrane is very light and flexible.

Lee Wai-Sze, Hong-Kong’s best cyclist who has had tremendous achievements this year; contributed 2 gold medals in both Asian Games 2018 and UCI Track Cycling World Championship 2019. Hong Kong Sports Institute (HKSI) has been a prominent pillar behind all those medals achieved, providing a comprehensive training system which comprises of professional coaches, sports science and medicine. Their current method for detecting fatigue level is also by measuring cortisol but through blood plasma instead of sweating. The problem lies when the tests are performed in regular basis. According to Frankie Su from HKSI Sports Nutrition Monitoring Center, the invasive usage of finger prick has been proven not giving any convenience to majority of athletes. Since our membrane just needs to be patched onto the skin, it can provide the cortisol checking through a non-invasive method and definitely, a much more convenient option for all athletes.

In addition to it, other difficulties mentioned were the limitation of time efficiency and accessibility. After collecting the blood samples, it took around 1 hour to analyze its composition and get the results. A more crucial case is when the athletes are having practices or competition abroad, the test could not be performed at all since the blood-analysis machine cannot be carried easily. However, a faster analysis of our membrane is feasible through using portable Raman devices and is not limited to any locations.

Herein, this project aims to create a conformable, non-invasive and stretchable nanolayer device for monitoring athlete’s fatigue level. The application itself is designed for professional athletes but does not close any further developments for commercial use. To achieve so, the membrane will still need to be integrated with electronic devices for a personalized data collection and providing an accurate fatigue detection.

2. Literature Review

2.1. Skin and Sweat

2.1.1. Skin Structure

As the proposed project mainly interacts with skin and the human perspiration, it is essential to discuss the mechanism and properties of both in advance. Skin consists of different layers, that each has its own unique function and characteristic. Epidermis is located on the most outer part, contains a lot of dead skin cells which is highly insoluble [4]. Epidermis is responsible for distributing melanin pigment to give color to the skin, skin's adaptive immune responses, and receptors for touch response.

On the inner side of epidermis, there are dermis layer that essentially is supporting matrix which are linked to its remarkable capacity for retaining water. There are two types of protein fibers in dermis that supports skin's tensile strength as well as its elasticity and resilience [4]. Dermis is where the sweat glands located (Figure 1). In addition, the hypodermis is located in the most inner part of the skin consisting mainly of fat tissues [4].

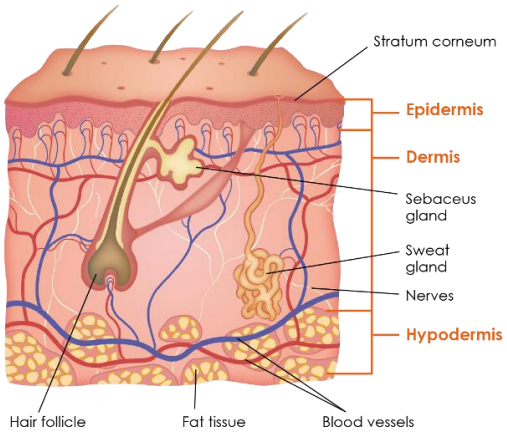


Figure 1. Skin Structure Consisting of Different Layers

The key role of skin is to provide a mechanical barrier against the external environment as well as thermoregulation. Vasodilation or vasoconstriction of the blood vessels under the skin helps regulate heat loss with eccrine sweat glands that can produce ~1 liter of sweat per hour during moderate exercises. This is the sweat that the proposed membrane will be experimented with. On the other hand, secretion from apocrine sweat glands contribute to body odor.

The eccrine gland is responsible for thermoregulatory sweating in humans and hence, distributed over nearly the entire body surface. Its structure consists of a bulbous

secretory coil which is located in the lower dermis, and the duct extends through the dermis and opens directly onto the skin surface.

2.1.2. Perspiration

According to [4], there are two types of human perspiration: insensible perspiration and active sweating. Insensible perspiration involves water loss from respiratory passages, skin and gaseous exchanges in the lungs. The evaporation from skin is supplied from water coming from blood in which depends on several environmental factors like ambient temperature and humidity. On the other hand, active sweating is induced by heat, muscular exercise, mental stimuli and carbon dioxide. Thermal sweating holds an important role to maintain the body's temperature which involves the whole-body surface whereas emotional sweating often appears only on the palms and soles.

The chemistry of perspiration lies on the mechanism of sweat excretion. On the sweat gland, intracellular Ca^{2+} concentrations increase which leads to the increase of the K^{+} and Cl^{-} permeability. As a result, isotonic precursor fluid from secretory cells are triggered and released [4]. As the fluid travels up the duct toward the surface of the skin, sodium and chloride are reabsorbed and causes the resulted sweat in the surface hypotonic relative to plasma. During a rigorous exercise, the rate of sweat production increases, ion reabsorption mechanisms can be overwhelmed since the quantity of sweat secreted into the duct is very large, resulting in a higher ion loss.

This results in the diverse composition of sweat, for which it consists of Chlorides (salt), Lactate, Urea, Creatinine, Uric Acid and Cortisol. Urea was found to be more concentrated in sweat than in the blood. The presence of cortisol as one of the responses of hormonal changes makes sweat as the one of the biomarkers that human produces.

2.1.3. Biomarkers and Cortisol

According to [5], biomarkers, commonly referred as the objective indications of medical / physical state observed from outside the subject, are a broad subcategory of medical signs which can be measured accurately and reproducibly. These biological markers can stand in contrast to medical symptoms; biomarkers are objective and quantifiable characteristics of biological processes which not necessarily correlate with a subject's experience and sense of well-being. Cortisol which is a product of a hormonal change represents the stress level of an individual, be it for mental or physical stress. Due to the characteristic of this compound, cortisol provides an objective variable to monitor the fatigue level [2].

In human anatomy, glands are divided into two main groups, exocrine (secretion

through ducts) and endocrine (ductless). Adrenal glands are a part of endocrine glands which secrete cortisol, a steroid hormone. As a response to stress or fear, the hypothalamic-pituitary-adrenal (HPA) axis activation cascade, often known as adrenal gland, produces cortisol as its product. HPA axis correlates our central nervous system and endocrine system which responsible for neuroendocrine adaptation due to stress. The response is signified by hypothalamic release of corticotropin-releasing factor (CRF). On the anterior pituitary gland, adrenocorticotropic hormone (ACTH) is released when the CRF receptor is bound by CRF. Then, ACTH binds the receptors on the adrenal cortex that stimulates the release of cortisol. At a certain concentration of cortisol, it exerts negative feedback to hypothalamic release CRF and pituitary release of ACTH which then return the systemic homeostasis to a standard level [6]. Therefore, the presence of cortisol is essential for homeostatic maintenance, in terms of modulating, regulating and influencing vital systems like neural, cardiovascular, immune and metabolic systems.

The cortisol levels in various bodily fluids can range from 4 pM to 70 µM depending on the fluid [7]. In sweat, the optimum level of cortisol ranges from 8.16 - 141.7 ng/mL [8,9,10]. The cortisol concentration is a complex variable to be measured as it follows a circadian rhythm through a 24 hours cycle with cortisol highest during daybreak (30 min after awakening) and progressively lower by night sleep. Increased levels of cortisol have detrimental effect on the regulation of various physiological processes such as blood pressure and glucose levels [7]. Abnormal increase in cortisol levels inhibits inflammation, depresses immune system, and increases fatty acid levels in blood [11].

Sweat produced in the eccrine gland contains over 99% of water with less than 1% electrolytes, metabolites, proteins, peptides and hormone [12]. As lactate is often perceived as the variable having linear relationship with fatigue level, it is shown that the lactate concentration in sweat decreases at the higher exercise intensities which is most likely the result of increased sweat production causing a dilution effect on the lactate concentration of sweat, thus limiting its ability to accurately indicate the metabolic activity of the sweat gland [13]. Hence, cortisol provides a more accurate and objective variable to precisely indicate the metabolic activity as well as monitor the fatigue level during exercise.

2.2. Membrane Properties

2.2.1. Membrane Thickness

The membrane thickness is one of the important properties to be observed, as it is crucial for its conformability onto the skin surface. The thin membrane can be fully conformed on top of the skin using the Van Der Waals force, and thinner membrane is proven to better adhere and hence have better resistant to skin movement. The

thickness property can be accurately calculated using the density, weight, and area of the membrane. The UHMWPE membrane consists of 30% of amorphous and 70% of crystalline structure, which makes the density of 0.95 g/cm^3. However, the membrane has 30% porosity, and thus reducing the density to 0.665 g/cm^3. The weight and surface area of the membrane can be easily determined using a microbalance and ruler respectively. With the identification of the mentioned membrane properties, the value of membrane thickness can be obtained by dividing the membrane mass by the multiplication of its density and surface area.

$$Thickness = \frac{mass}{density * surface\ area} = \frac{mass}{\rho_0 * (1 - \%pososity) * surface\ area}$$

Equation 1. Thickness Formula Calculation

The result showed that the membrane thickness is approximately 160 nm. We subsequently used the membrane in different conditions for more than 24 hours.

2.2.2. Young's & Bending Modulus

The tensile test of UHMWPE membrane was conducted in order to measure its Young's Modulus value. Young's Modulus is a value to determine the strength of a specific material. This value can be obtained by implementing tensile test, which the material is stretch and given a specific amount of load to identify its strength. Subsequently, the result of membrane's thickness and Young's Modulus determine its Bending Modulus value, which is essential for identifying the conformability of the membrane to the skin surface.

In order to measure the membrane's Young's Modulus value, a paper frame was attached to the membrane using tapes as a support. The membrane was then cut into a small piece (10 mm x 50 mm) and put in between the two handles of Advance Rheology Experiment System (TA ARIS 2000), the machine that was used to conduct the tensile test. In this tensile test, the position of the membrane was adjusted to be parallel to the second stretching direction of the membrane. Subsequently, the strain was set to 0.1% and the relationship between stress and strain of the membrane was obtained by plotting the data generated from the Advance Rheology Experiment System. As it is shown in Figure 2, the membrane was stretched until it breaks in order to get the maximum stress and strain values. Due to the property of the membrane, its Young's Modulus value was acquired using the maximum slope of the strain and stress curve, which was extracted from the first 2% of the collected data. The test was repeated for three times using three different membranes of the same batch production. The mechanical properties of the membrane including the average Young's Modulus value are shown in Table 1, and the complete stress vs strain graph is shown in Figure 2 for all three membranes. In this case, the yield strength, which is the strength after the

material has gone through a small portion of permanent deformation, and tensile strength, which shows the maximum stress that the membrane is capable to hold, are the same. This because the membrane breaks at the maximum applied stress without going through a lot of permanent deformation.

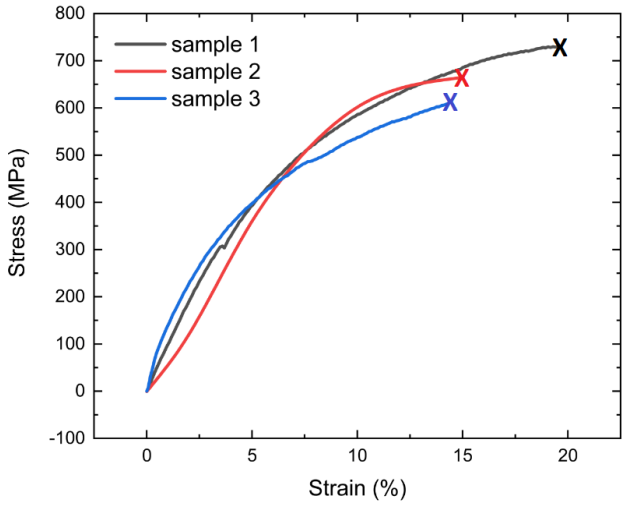


Figure 2. The complete stress vs strain curve of three different membranes ('x' marks the break point)

From the results, it was observed that the membrane's Young Modulus value ranged from 6,177.5 MPa to 10,884 MPa. On the other hand, by implementing the same technique and strain value, it was calculated that the skin's Young Modulus value ranges between 0.1 MPa and 2 MPa [14]. Comparing both Young's Modulus results, the membrane's Young Modulus value is roughly 5000 times higher than the skin's Young's Modulus value. This is undesirable since the membrane must mimic the skin properties in order to fully conform onto the skin surface. However, the range of thickness of the membrane is smaller than the range of thickness of skin epidermis layer, which were 96-110 nm and 0.1-1.5 mm [15] respectively. Since the membrane is approximately 1,000 to 10,000 times thinner than epidermis layer, despite the high Young's Modulus value, the membrane is capable to fully adhere on the skin without any adhesives and other external supports.

The Bending Modulus value provides the information about the object resistance to bending and demonstrates the membrane's deformation, which affect the conformability of the membrane to the skin surface. Since the membrane's Young's Modulus value does not provide information regarding the membrane's flexibility, Bending Modulus of the membrane must be identified using the following Bending Modulus equation [16], where D refers to Bending Modulus, E to Young's Modulus, t to thickness, and v to Poisson's Ratio (ranged from 0.3 – 0.5).

$$D = \frac{E * t^3}{12 * (1 - v^2)}$$

Equation 2. Bending Modulus Equation

The comparison between Young's Modulus calculation and Bending Modulus calculation is illustrated in Table 1. From the calculation, it is known that the result of the membrane's Bending Modulus ranges from 5.2×10^{11} to 1.5×10^{12} Pa.m^3. Even with thickness of nanometer scale, the value of Bending Modulus of the UHMWPE membrane is 2000 times higher than a steel, which has a Bending Modulus value of 638 MPa [17]. The flexibility and elasticity of the membrane results in high ability to deform when load or force is applied, which validates the capability of the membrane to handle high bending force before it is torn or broken. Hence, from the measurement of its mechanical properties, it can be concluded that within a range of thickness between 97 to 110 nm, the membrane can be fully conformed on the skin surface independently or without external supports.

Yield Strength (MPa)	Tensile Strength (MPa)	Ductility (%)	Young's Modulus (GPa)	Bending Modulus (10^{-12} Pa.m^3)
658.0 ± 38.0	658.0 ± 38.0	16.4 ± 2.4	8.9 ± 1.9	1.07 ± 0.09

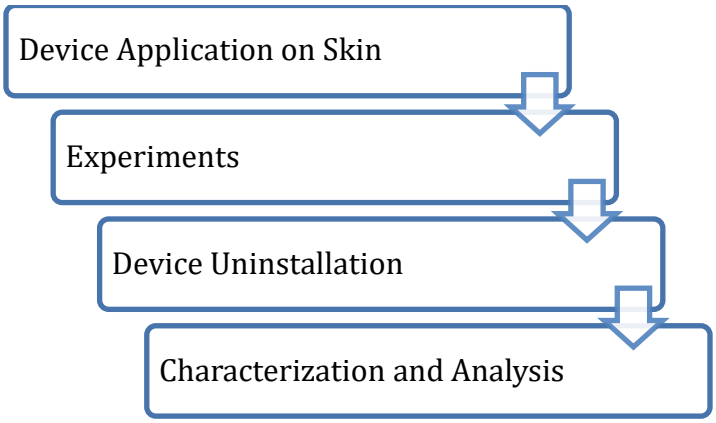
Table 1. Summary of UHMWPE membrane mechanical properties.

2.2.3. Biocompatibility

In recent years, UHMWPE membrane has been implemented in many biomedical applications due to its properties, such as the wear, fatigue resistance and its recognized biocompatibility. It has been widely used to reconstruct damaged body parts, including hip and knee joint replacements. In order to prove its biocompatibility, the cytotoxicity of UHMWPE was checked by incubating fibroblast (L929) with the polyethylene material in a culture medium. The result illustrated an identical growth of the cells as in a cultural plate, which indicates the biocompatibility of UHMWPE. If that particular material is safe enough to be a replacement of human body parts, then its usage in skin surface is definitely harmless [18]. As for zinc oxide (ZnO) nanoparticle, it has also been used especially in biosensing application due to its high catalytic efficiency, strong adsorption ability, fast electron transfer kinetics, and biocompatibility. These properties of ZnO enable immobilization of biomolecules as ZnO particles can have high sensitivity and high affinity binding to organic materials, such as glucose and uric acid [19]. Therefore, it can be concluded that both UHMWPE and ZnO are biocompatible and thus safe to be used directly in contact with the skin.

3. Project Description

3.1. Overview



3.2. Sweat Sensors Type

3.2.1. Sensor-P

In this project, two different types of sweat sensors have been manufactured. **Sensor-P** refers to the sweat sensing device fabricated with pure PE membrane without any additional components. The procedures of manufacturing Sensor-P is discussed on Section 3.3.

3.2.1. Sensor-C

Cortisol is identified using Raman Spectrometry due to the sweat sensor ability to store sweat biomarkers inside its pores. However, there were cases that cortisol could not be detected because of low concentration of cortisol were outperformed by high concentration of other compounds. To tackle this problem, Zinc Oxide (ZnO) nanoparticles were integrated with the sweat sensor to enhance the cortisol peak in the Raman shifts. Thus, the composite sensor integrated with ZnO nanoparticles is referred to **Sensor-C.**

In addition to the procedures discussed on Section 3.3, Sensor-C is fabricated with pre-treatment of the membrane. Initially, the ZnO nanoparticles were suspended and diluted with ethanol. The ZnO solution was then pipetted on top of a new batch PE membrane using spin coat method to equally distribute the ZnO. This method has ~50% efficiency for low viscosity solution, for which 200 µL of ZnO was decided to be used. The first stage of the sprinkler process is to spin the membrane for 400 RPM for 30 seconds. Afterwards, ZnO was introduced on the second stage through pipette while spinning for the same rotation as the first stage for two minutes

3.3. Device Application on Skin

3.3.1. Device Application and Removal Procedures

During extraction, the membranes were held with carbon frame (Figure 3). Then, paper consisting of ten frames with gap size of 10 mm x 15 mm were stuck onto one side of the membrane using double-sided tape (Figure 4a). The purpose of applying paper frames is to provide guidance when cutting the membranes to enable consistent membrane size production. Then, the membranes were cut to ten pieces (Figure 4b), and larger sacrificial film were stuck on top of each piece on the membrane side using ethanol.

Figure 3. Nanometer Thickness Membrane held with Carbon Frames

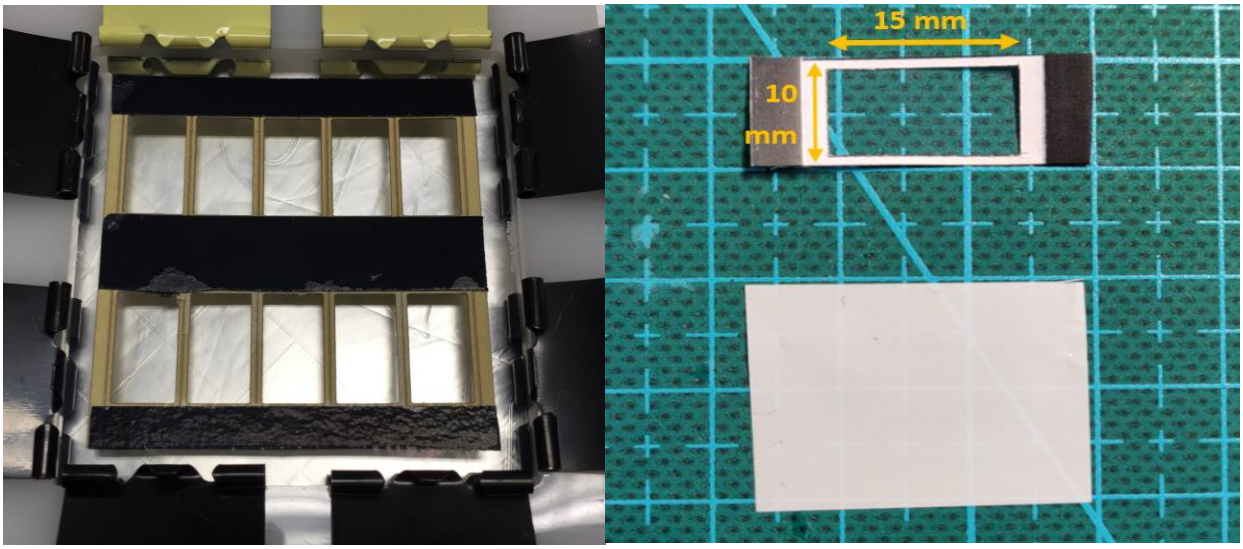


Figure 4. Sweat Sensor Manufacturing Procedures. a) Left: Applying paper frames on sensor. b) Right: A piece of membrane on paper frames and sacrificial film at the bottom

Sacrificial film is referred to UHMWPE with the thickness of 25 µm. It is used to help applying the sweat sensor later on. Subsequently, the sensor, along with paper frame and sacrificial film, were cut based on the paper frame size to yield a 1 cm x 3 cm sensor with larger sacrificial film on the other side. Finally, with the addition of ethanol, the sensor was applied on the skin, with the sensor side facing to the skin (Figure 5a). Sacrificial film can then be removed once the ethanol had vaporized, leaving only the sensor conforms to the skin (Figure 5b). As can be observed on Figure 5b, the sensor able to conform perfectly, even conforms to the wrinkle of the skin.

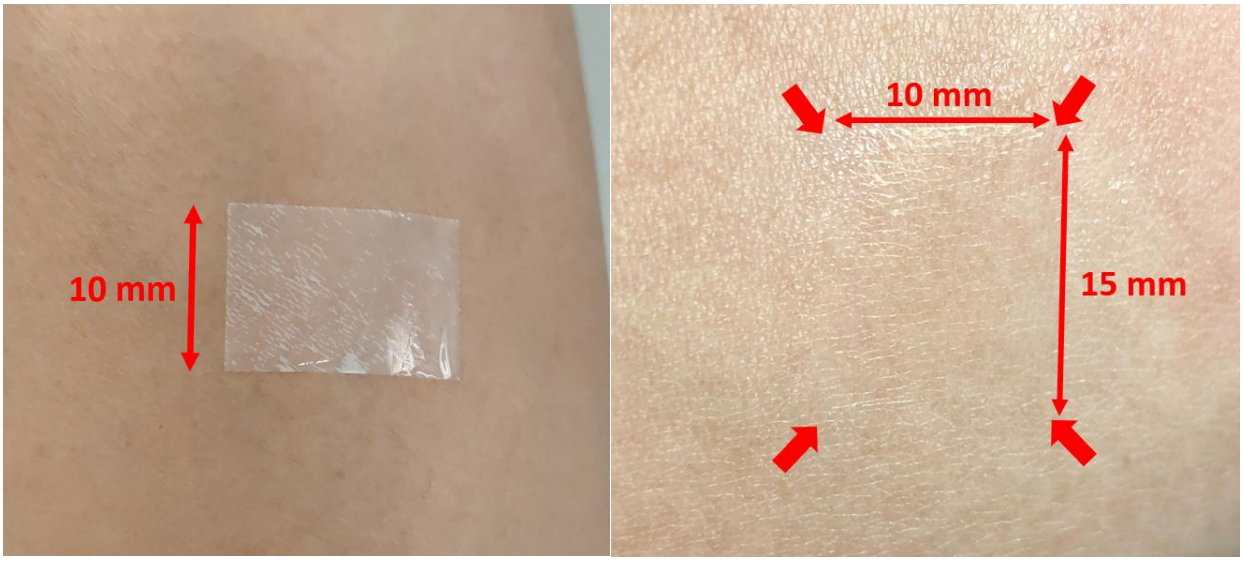


Figure 5. Sweat sensor-P installation. a) Left: Sensor and sacrificial film. b) Right: sensors (the arrows in the figure labels the sensor corners)

Smaller paper frames with double-tape placed on one side were used to remove the sweat sensor. Once the double-tape already affixed to the sweat sensor, the sensor will be removed easily along with paper frame removal.

3.3.2. Location of Sweat Sensor Placement

In most of experimentations performed, sweat sensors were applied on the lower side of either forearm, otherwise specified, as the location has enough strain and stress on the area while still tending to not getting in contact with other objects while having the experiment. In addition, the sweat sensor was applied on the upper side of the wrist for durability test to prove the conformability of the sweat sensor.

3.4. Experiment

For each experiment performed, the device were applied following the procedures discussed on Section 3.2. Samples collected were characterized using the techniques and methods discussed on Section 3.4.

3.4.1. Conformability Test

The conformability of the device was done on three different subjects. The subject used four different thickness of sweat sensors, ranging from 1-layer to 4-layers. Sweat sensing prepared for the conformability test has the thickness of 120 nm for one layer. In this experiment, sweat sensors were applied for 13 - 14 hours including when taking a bath as well as doing sports (weightlifting and badminton).

The conformability test was performed with great attention for the sensors to be not scratched or scraped by contact with other objects. As the result, all sweat sensors were still intact and conform to the skin, although some corners were peeled due to the friction with sweater worn on top of the sweat sensors.

3.4.2. Durability Test

The durability test was performed in order to measure the longest time that the sensors were able to stay intact to the skin and the condition of the device was continuously monitored. Experiment were performed by four subjects. Sensors having 1-layer to 3-layers thickness were used in this experiment on lower forearm area. In addition, 1-layer of sensors were applied on the upper side of the wrist. The prepared membrane has 160nm thickness for 1-layer membrane.

This experiment shows that as the thickness of the sensors decreases, the sensors would be able to conform longer. The average time that the sensors stays intact is 16 hours for 1-layer and 2-layers membrane, and about 13 hours for 3-layers membrane. Most sweat sensors were removed accidentally during sleeping, where there were a lot of contact with the bed.

On the other hand, sweat sensors applied on the upper side of the wrist managed to conform to the skin for 27 hours as it stays conformable after sleeping as well as taking bath. This further proves the conformability of the devoce on area with higher degree of strain and bending.

3.4.3. Performance Test

To test the device ability to collect different components and biomarkers, particularly cortisol, the sweat sensor was applied on the subjects while using static bicycle. The workout done on static bicycle for 25 minutes maintaining at about 140 RPM. If the subjects did not experience fatigue yet and capable of performing further workout, subjects were able to perform further workout such as static cycling and running on the treadmill until they experience fatigue.

3.5. Sweat Characterization

3.5.1. Raman Spectrometry

Raman spectrometry is a technique which used to identify different molecules through vibrational, rotational, and other low-frequency modes from a sample [20]. Monochromatic light from laser is used to interact with the molecular vibrations and other excitations on the sample which causes the laser energy being shifted. As a result, the shifts, commonly referred to Raman shifts, contains information about vibrational modes in the sample; thus, different molecules could be detected [20]. According to Virkler [21], sweat is mainly consist of water, lactate and urea. Under Raman spectroscopy, urea can be found at Raman shift 3300-3500 cm^{-1}, whereas cortisol can be found in the range of 1600-1600 cm^{-1} [22].

All samples collected and blank sensors were placed on top of silicon wafer and analyzed using Renishaw inVia Raman Microscope. Using green laser and extended mode, the Raman peak captured is located within the range between 1000 and 2000 cm^{-1}. The spectrometry was performed with 100% intensity on 10.0 mV laser. Raman analysis were set up to 20x accumulation which enable the observation of different peaks clearly. Then, the data was treated with baseline correction by 12^{th} polynomial degree on the curve fitting and 2 unit of noise reduction as well as peaks smoothing. Finally, the samples were compared with the blank.

The result proves the sweat sensors ability to sense various components present in the sweat, particularly cortisol which can be found on Raman shifts 1600 – 1660 cm^{-1}. On Figure 6, cortisol can be observed on Raman shifts 1653.5 cm^{-1} from the sweated Sensor-P and Sensor-C samples (green and blue line). This cortisol peak is absent on blank sample. Furthermore, Figure 6 proves the ZnO nanoparticles ability to cause further Raman shifts from the O-H bond present in cortisol through higher cortisol intensity compared to the sample without the addition of ZnO.

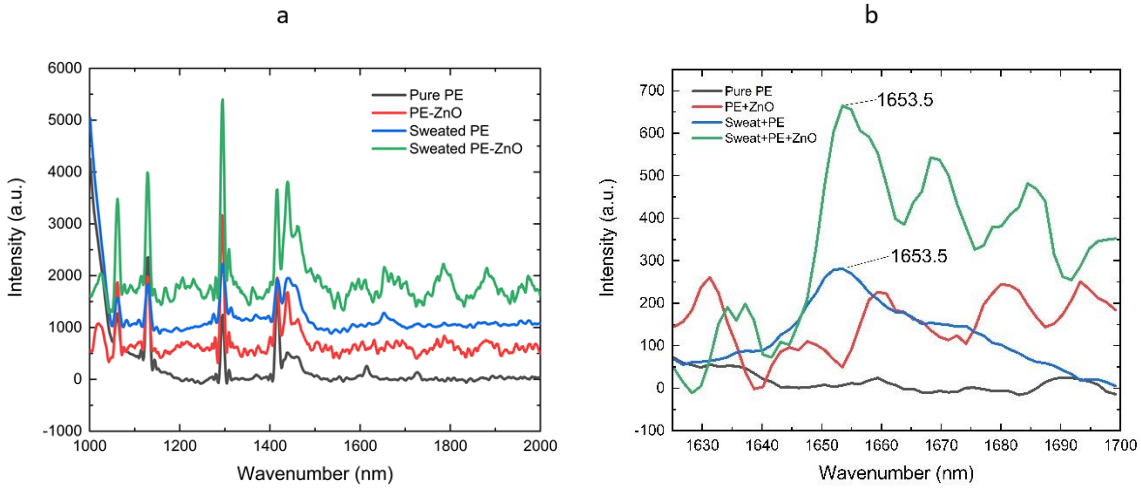


Figure 6. Raman spectrum of four samples: Pure PE (Control Sensor-P), PE + ZnO (Control Sensor-C), Sweated PE (Sample Sensor-P) and Sweated PE + ZnO (Sample Sensor-C). a) Left: 1000-2000 cm^{-1} and b) Right: 1600-1700 cm^{-1} that shows the presence of cortisol in Raman spectrum at 1653 cm^{-1}

3.5.2. Selective Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM and EDS were performed in addition to Raman spectrometry to identify components that is not detected by Raman spectrometry, such as salt ions. The sample sensor-C were scanned with electron beam to observe the structure of the sensor. After observing its surface structure, X-ray was utilized to detect the components collected.

It can be observed that the addition of ZnO and sweat changes the structure of pure PE membrane (Figure 7a) as the pores were filled. The integration of ZnO with the sensor (Figure 7b) changed the PE strain as some of the pores were filled up with nanoparticles. Comparing the samples with each control, it can be observed clearly that less empty pores were available on Figure 7c and 7d due to the sweat and ZnO filling up the pores.

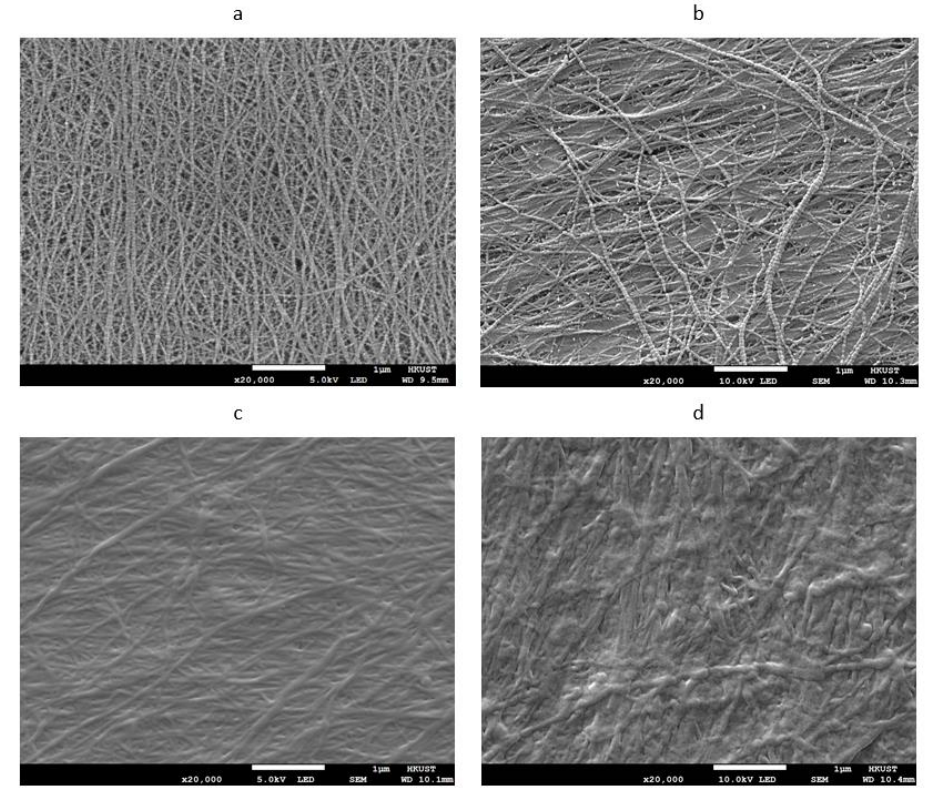


Figure 7. SEM micrographs: a) Sensor-P. b) Sensor-C. c) Sweated Sensor-P. d) Sweated Sensor-C

Based on EDS result, the sweat sensor is clearly capable of collecting sweat shown by the salt content such as Na, Cl, and K. While the control Sensor-C does not contain salt at all.

Sample	Element (Mole%)					
	Zn	O	C	Na	Cl	K
Control Sensor-C	13.7	51.5	34.8	0	0	0
Sweated Sensor-C	10.7	37.9	41.7	4.5	4.5	0.8

Table 2. Weight distribution of components found in the control Sensor-C and the sweated Sensor-C using EDS.

4. Discussion

4.1. Sports Fatigue Determination Analysis

At this stage, the ability of the sweat sensor to capture sweat has been proven through

numerous experiments analyzed using Raman spectroscopy. Although some noise was still present in the spectrum and quantitative analysis of cortisol concentration is to be done in the future, the sweat sensors ability to sense cortisol as a measurement of fatigue level has been a significant progress to this project. In addition, the integration of ZnO with the sweat sensors (Sensor-C) is also proven enhancing the cortisol intensity in the Raman spectrum which also adding the advantage of this device.

4.2. Fitness Level Detection

Cortisol, a stress hormone, can also be triggered by other non-physical reasons such as stress or sicknesses. One of our experiments has shown the presence of cortisol when the subject was having sickness. Then, the analysis results indicated the same intensity of cortisol despite of not having workout as intense as a healthy subject. This advantage shows that the preliminary condition of the user is put as a consideration for determining their maximum physical condition. Subsequently, as mentioned before, to provide a faster analysis method, portable Raman is used and available for in-situ testing. Hence, the results can directly be obtained as soon as user finishes their exercises.

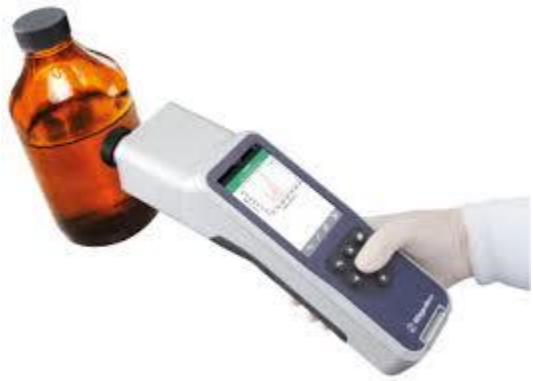


Figure 8. Portable Raman Spectrometer for In-situ Analysis

4.3. Extension for Other Areas and Future Improvement

For further collaboration with the current methods in HKSI, there are 2 points of improvement we can make. Firstly, the coaching staff performed fatigue test before practices in order to check the athletes' preliminary condition pre-exercise. Various reasons such as stress, nervousness and sickness can diminish physical condition of athletes. To minimize the risk of getting injured, the workout portion has to be adjusted according to the results acquired from fatigue tests. Having said that, just because of not having a perfect condition does not leave them out of their daily dose of workouts. There is no such method which is able to tell the athletes when they have actually reached their maximum limit and act as a strong indicator for the coach to halt the workout. Here is where our sweat sensing device comes as its complementary method.

As our sweat sensor is applied during the exercise, our sweat sensor can immediately signal the users as soon as their cortisol level has already gone beyond acceptable ranges.

Secondly, realistically, each athlete has different physical ability which cannot be generalized by one specific ranges. That is why HKSI coaching staff has had a complete database of their athletes' physical ability. They measured the cortisol and testosterone level under a perfect fit condition of the athletes and made it as their baseline level. The deviation from the baseline level is then used as the indicator of fatigue and it will be a far more accurate analysis since it is compared to the athlete's own normal level. To accommodate that level of accuracy for the users, our sweat sensor needs to be further integrated with big data technology. By that, we can store user's physical database and signals its deviation when the cortisol exceeds their normal ranges.

5. Conclusion

In this project, fully conformable sweat sensor from porous polymer nanofilm with nanometer thickness has been proposed. It is discovered that the sensor is capable of detecting cortisol - a hormone secreted by adrenal gland which is used as a key biomarker for sports fatigue detection. The existing technology, particularly used by Hong Kong Sports Institute, measures cortisol level where invasive blood testing is compulsory to be performed both before and after training sessions; this method is found to be very inconvenient for the athletes. In addition, state-of-the-art non-invasive sweat sensors capable of sensing cortisol and monitoring fatigue [1,2,3] are both too bulky and non-breathable which interferes the sports activities. The proposed fully conformable and breathable nanofilm device is the first of its kind worldwide and will revolutionize athlete's future training programs.

Acknowledgement

We would like to acknowledge the help from Mr. Jin Li, Dr. Runlai Li from Professor Ping Gao's group regarding the sensor material preparation and some characterizations. The project would not be able to progress without their help. We also want to thank other parties that have been involved by helping us either directly or indirectly during the process.

References

[1] J. Choi, R. Ghaffari, L. Baker and J. Rogers, "Skin-interfaced systems for sweat collection and analytics", Science Advances, vol. 4, no. 2, p. eaar3921, 2018.

[2] M. Sobieraj and C. Rimnac, "Ultra high molecular weight polyethylene: Mechanics, morphology, and clinical behavior", Journal of the Mechanical Behavior of Biomedical Materials, vol. 2, no. 5, pp. 433-443, 2009.
[3] Y. Liu, M. Pharr and G. Salvatore, "Lab-on-Skin: A Review of Flexible and Stretchable Electronics for Wearable Health Monitoring", ACS Nano, vol. 11, no. 10, pp. 9614-9635, 2017.
[4] Y. Kuno, The Physiology of Human Perspiration, 1st ed. London, UK: J. & A. Churchill Ltd, 1934.
[5] K. Strimbu and J. Tavel, Ncbi.nlm.nih.gov, 2019. [Online]. Available: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3078627/pdf/nihms259967.pdf. [Accessed: 14- Mar- 2019].
[6] Veldhuis JD, et al. Endocrinol Metab Clin North Am. 2013 Jun;42(2):201-25.
[7] O.Parlak, et. al. “Molecularly Selective Nanoporous Membrane-based Wearable Organic Electrochemical Device for Noninvasive Cortisol Sensing”. Science Advances, doi: 10.1126/sciadv.aar2904
[8] Russell, E., Koren, G., Reider, M., Van Uum, S., 2012a. The detection of cortisol in human sweat: implications for measurement of cortisol in hair. Endocr. Rev. 33, 03
[9] J.A. McGrath, J. Uitto, Rook’s Textbook of Dermatology, 8th ed. West Sussex, UK: Wiley-Blackwell, 2010, chapter 3.
[10] H-J, Jang, et.al. “Electronic Cortisol Detection Using an Antibody-Embedded Polymer Coupled to a Field-Effect Transistor. AcS Appl. Mater. Interfaces, doi:10.1021/acsami.7b18855
[11] A. Kaushik, et.al. “Recent Advances in Cortisol Sensing Technologies for Point-of-Care Application”. ScienceDirect, doi:10.1016/j.bios.2013.09.060
[12] M. Jia, et. al. “Quantification of Cortisol in Human Eccrine Sweat by Liquid Chromatography - Tandem Mass Spectrometry”. Analyst, doi: 10.1039/c5an02387d
[13] M.J. Buono, et. al. “The Relationship between Exercise Intensity and the Sweat Lactate Excretion Rate”. The Journal of Physiological Sciences, doi:10.1007/s12576-009-0073-3
[14] K. A, L. A, and A.-J. AM, “Mechanical Behaviour of Skin: A Review,” OMICS International, 24-May-2016. [Online]. Available: https://www.omicsonline.org/open-access/mechanical-behaviour-of-skin-a-review-2169-0022-1000254.php?aid=75008. [Accessed: 18-Nov-2018].
[15] Kolarsick P. A. J., Kolarsick M. A., Goodwin C. (2011). Anatomy and physiology of the skin. Journal of the Dermatology Nurses' Association, 3 (4), 203-213.
[16] Å. Jämting, J. Bell, M. Swain, and N. Schwarzer, “Investigation of the elastic modulus of thin films using simple biaxial bending techniques,” Thin Solid Films, vol. 308-309, pp. 304–309, 1997.
[17] Y. K. Kwak, M. O. Eberhard, W. S. Kim, and J. Kim, “Shear Strength of Steel Fiber-Reinforced Concrete Beams without Stirrups,” Aug. 2002.

[18] Y. F. Huang, J. Z. Xu, J. S. Li, B. X. He, L. Xu, and Z. M. Li, “Mechanical properties and biocompatibility of melt processed, self-reinforced ultrahigh molecular weight polyethylene,” www.elsevier.com/locate/biomaterials, 15-May-2014. [Online]. Available: https://ac.els-cdn.com/S014296121400475X/1-s2.0-S014296121400475X-main.pdf?_tid=e9698316-bec3-4d04-8ff4-3cc71fde86e7&acdnat=1552487479_7ee57f98ba6d15ad4b4208a0b81b88b4.

[19] S. A. Kumar and S. M. Chen, “Nanostructured Zinc Oxide Particles in Chemically Modified Electrodes for Biosensor Applications,” Feb. 2008.

[20] Gardiner, D.J. (1989). Practical Raman spectroscopy. Springer-Verlag. ISBN 978-0-387-50254-0.

[21] Virkler, K. and Lednev, I. (2008). Raman spectroscopy offers great potential for the nondestructive confirmatory identification of body fluids.

[22]Bio-Rad Laboratories, Inc. SpectraBase; SpectraBase Compound ID=EeiU30bYg32 SpectraBase Spectrum ID=FhOIEJ8nutu http://spectrabase.com/spectrum/FhOIEJ8nutu (accessed Nov 26, 2018)