Smart Textile-based Electrochemical Capacitive Ionic Sensors for High-Performance Epidermal Electronics

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***Abstract*— Recently biomedical engineering has placed greater importance on wearable and disposable healthcare monitoring devices. Various degradable biosensors have been developed to measure human parameters such as temperature, pH, pressure, strain, and ion concentration, utilizing bodily fluids like sweat for analysis. In this work, we developed a new textile-based electrochemical capacitive sensor (TECS) employing multi-walled carbon nanotube (MWCNT) coated cellulose cloth. The electrodes for TECS were fabricated using a drop coating method, and their surface morphology was evaluated by scanning electron microscopic images. Cyclic voltammetry analysis of the TECS revealed that the fabricated sensor exhibited a sensitivity of 0.29 μA/log [Na^+] in the concentration range of 0-16 mM NaCl. The device operates on an electrochemical capacitive mechanism, exhibiting a specific capacitance variation of 6.9 μF.cm^{-2} across the NaCl concentration range of 0-16 mM. The electrochemical impedance spectroscopic analysis in the frequency range of 10 mHz to 1MHz indicates the impact of ionic concentration variation, particularly in the low-frequency range. The fabricated TECS offers high sensing performance, biodegradability, and disposability, attributed to its development on cellulose cloth. The developed sensor has potential application in epidermal electronics through integration with smart textiles and offers significant opportunities in wearable biomedical devices.**

Keywords—wearable sensor, Na ion monitoring, electronic textiles, electrochemical capacitor

I. Introduction

Epidermal electronics gained increased attention in wearable biomedical devices due to their excellent performance in monitoring body fluids, and electrophysiological signals and facilitating human-machine interaction[1-4]. This addresses the current issues of the traditional healthcare system in managing chronic diseases, and age-related issues in the population, while also providing long-time nursing support[1]. The rapid progress of wearable sensing technologies has led to a tremendous increase in fabricating various components in epidermal electronics. This automatically leads to large amounts of electronic waste being generated in the environment, posing serious issues due to toxic or plastic materials present in these devices, which affect the ecosystem[1]. Furthermore, ensuring wearer comfort, including addressing issues such as allergies and other skin reactions caused by wearable electronics, is essential. In addition to high performance, biodegradability, disposability, and aesthetic appeal, the design of epidermal electronics by using smart textiles presents significant opportunities in wearable biomedical devices[5-7].

Recent studies on wearable biomedical devices reveal that electronic textiles (e-textiles) offer excellent features, including comfort, environmental friendliness, ultra flexibility, and longevity[7-9]. The implementation of e-textiles as epidermal electronics for monitoring sweat chemicals presents a significant opportunity in healthcare[10]. E-textiles are employed as sensors for monitoring chemical, biological, and physical parameters, as well as energy generators or storage utilizing human sweat[11-13]. For this purpose, conductive or non-conductive textiles are converted into active electrodes by reacting with various polymers, metal oxide, or carbon-based materials[14]. Such electrodes have multiple advantages, including the development of biodegradable and disposable sensors. Various textile-based sensors have been reported for monitoring human sweat chemicals, including sensors for pH, glucose, and dissolved ions[13-16].

Among the various chemical parameters monitored in human body fluid, investigating Na ion is highly important for physiological and mental well-being[17]. The excessive sodium condition known as hypernatremia, can result in the swelling of the tissues due to the retention of excess fluids, increased thirst, and a decrease in urine production[18]. On the other hand, hyponatremia, which denotes low levels of sodium, typically presents symptoms such as headaches, confusion, seizures, muscle spasms, nausea, and vomiting[18]. For a healthy human, the expected Na ion is in the range of 135-145mEq/L) and monitoring the presence of Na ions is highly important[19]. There are various sensors reported for Na ion monitoring. A few of them include (i) potentiometric $Na_{0.44}MnO_2$ sensor (58 mV.dec^{-1}) [20] (ii) carbon fibres based potentiometric sensor (55.9±0.8 mV/log[Na^+]) [21] , resonance sensor (3.7319 dB/%ppm) [22], and (iv) amperometric sensor (4.0 nA/μM) [23]. A summary of wearable Na ion monitoring sensors is given in Table 1[20-26]. It was observed that the stability of the reference electrode, the sensitivity of the active electrode, and the flexibility of the counter electrode are some key challenges in the fabrication of wearable sweat ion monitoring sensors [27]. In addition to this, the powering of wearable sensors and their integration are facing multiple issues [28].

Here we fabricated a textile electrochemical capacitive sensor (TECS) on non-conductive cloth by modifying it with a multiwalled carbon nanotube (MWCNT) for Na ion monitoring. Fabrication of sensors based on the principle of an electrochemical capacitor or as a supercapacitor overcomes the issues related to the requirement of the reference electrode or platinum-based counter electrode.

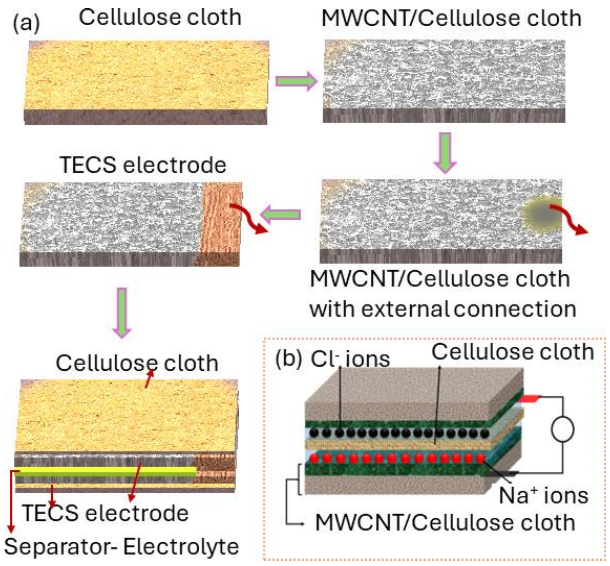

Fig.1: (a) Schematic representation of the fabrication steps of the TECS based cloth electrode. (b) Schematic of TECS for Na ion monitoring

Moreover, the TECS provides an additional feature of high sensing performances, low cost, and biodegradability. Here the sensor is developed entirely on cloth to allow easy absorption of human sweat. The presence of sweat Na ions leads to the formation of an electrochemical double-layer capacitance (EDLC) while reacting with MWCNT. The sensing performances of the TECS were investigated through electrochemical characterization. TECS allows integration on human skin for continued online monitoring of sweat chemicals for wearable biomedicals.

II. Experimental Methods

A. Sensor Fabrication

For the fabrication of the TECS, we followed the same process used for creating an electrochemical capacitor. The fabrication steps are given in Fig. 1a. For the fabrication of the electrodes of TECS, initially, one back side of the cloth insulative layer (JE solutions consultancy Ltd) was coated and heated at 80°C for 30 min to protect the electrodes. The MWCNT (Sigma Aldrich- 698849-1G) was mixed with ethanol (Sigma Aldrich- CAS 64-17-5) under ultrasonication and then drop coated on top of the cellulose/polyester cloth with an area of 2 cm^2. The MWCNT-coated cloths were dried in an oven at 80°C for 30 min. After heating one side of the cloth graphene paste (JE solution) was used to make contact electrode and heat treated in an oven at 80°C for 30 min. After this a protective layer was coated and heat treated at 80°C for 30 min. To construct TECS for biosensing two such electrodes were sandwiched by keeping a cellulose cloth separator and wrapping it with another layer of cellulose cloth.

Table 1: Comparison of performances of Na^+ sensors

Sensors	Sensitivity	Ref
Potentiometric sensor		
$Na_{0.44}MnO_2$	58 $mV.dec^{-1}$	[20]
Carbon	55.9±0.8mV/log[Na^+]	[21]
Au based sensor	56,56.8 mV/log[Na^+]	[24]
Pt based sensor	56 mV/log[Na^+]	[25]
Amperometric sensor		
gold nanodendrite (AuND) array electrode	-4.0 nA/µM	[23]
Ionodes	-0.43nA/µM	[26]
Resonance Sensor (tapered micro fibre based)	3.7319 dB/%ppm	[22]

B. Characterisation

The surface morphology of the TECS electrodes was examined using scanning electron microscopy images (SEM, TESCAN VEGA) at working distances ranging from several micrometers. Furthermore, the sensing performances were evaluated by electrochemical characterization using our workstation (IVIUM, Stat2.h-ivium technology B.V). TECS electrochemical performance evaluation in different concentrations of NaCl (1-16 mM) was carried out using cyclic voltammetry (CV) and electrochemical impedance spectroscopic (EIS) analysis. The properties were evaluated through cyclic voltammetry (CV) analysis in the range of 50-500 $mV.s^{-1}$ at -0.8 to 0.8 V. Similarly, EIS measurements were performed over a frequency range of 10 mHz to 1 MHz with a voltage of 10 mV to assess the electrode/electrolyte interaction. The interference of the sensor with another major ion in sweat such as K^+ was evaluated.

III. Results and Discussion

A. Structural Characterization of TECS electrode

Fig. 2a and 2b depict the SEM images of MWCNT-coated cellulose cloth electrodes. The surface morphology of the electrode shows that, in this case, MWCNT coating on the top of cellulose cloth results in the formation of clusters of carbon tubes on the surface, as shown in Fig. 2a. Further magnification reveals the layered network of MWCNT on the top of cloth, as shown in Fig. 2b. This network-layered electrode is highly beneficial for sensing performances due to the interactions of individual nanotubes with ions in the electrolyte.

B. Sensing performance evaluation

The CV profiles of TECS at 100 $mV.s^{-1}$ for various concentrations of NaCl are shown in Fig. 3a. This observation highlights the ideal performance characteristics of the electrochemical capacitor. CV curves display a quasi-rectangular shape, with their nearly symmetrical profile signifying exceptional capacitive attributes. This characteristic behavior, commonly observed in EDL capacitors, indicates their impressive capacity for high-rate operation. The increase in the concentration of NaCl leads to the enhancement of the area under the curve and peak current for the developed device. The variation of peak current for the TECS is given in Fig. 3b. Here we can observe that the peak current increased with increasing concentration which could be due to the presence of more ions in the solution. The variation shows a linear behavior with a sensitivity of 0.29 µA/log [Na^+] as shown in Fig. 3c. The sensitivity of the sensor was also expressed in capacitance (6.9 $\mu F.cm^{-2}$)

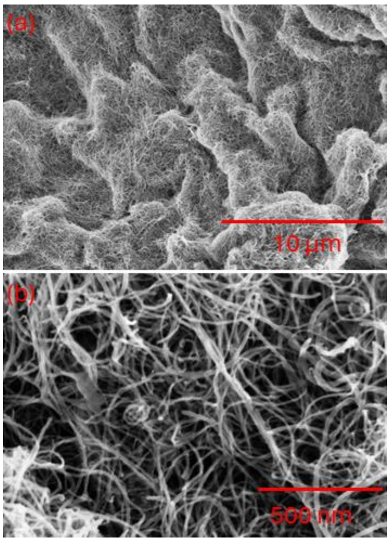

Fig. 2 (a) and (b) SEM images of MWCNT-coated cellulose cloth in different magnifications.

variation and is given in Fig. 3d. Here the capacitance was measured using previously reported works [11].

C. *Electrochemical Performances of the electrodes*

The interaction of ionic with electrode surface is highly important in electrochemical sensing performance. Here, the electrode/electrolyte interaction was investigated using EIS analysis. The Nyquist plot obtained using EIS for various concentrations of NaCl is shown in Fig. 4a. The Nyquist plot indicates the absence of a semi-circle arc in the high-frequency range, denoting the lack of charge transfer resistance. The increase in NaCl concentration enhances the conductivity of the solution. Here the equivalent series resistance or solution resistance (R_s) of the sensor is indicated at the location where it intersects the real impedance in the high-frequency zone, which is almost identical. This suggests excellent electrode/electrolyte interaction. However, in the low-frequency range, the impedance value varies significantly, indicating the influence of ionic concentration on the sensor. In low-frequency regions, ion diffusion occurs

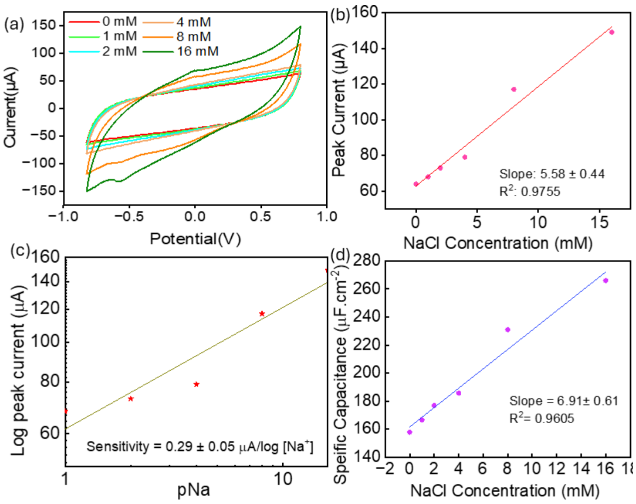

Fig. 3 (a) CV curves for TECS with change in NaCl concentration (b) The peak current variation of the sensor with concentration (c) peak current vs pNa plot shows the sensitivity of the sensor (d) the specific capacitance variation with NaCl concentration in the TECS.

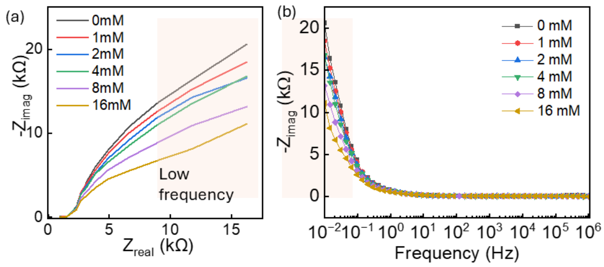

Fig. 4 (a) Nyquist plot of the TECS in various NaCl concentrations. (b) Variation of the imaginary component of impedance with frequency for the various concentrations of NaCl.

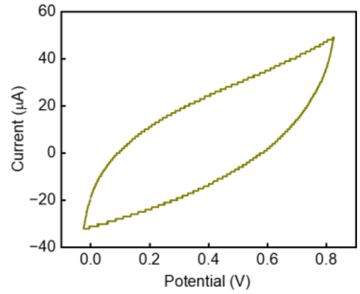

Fig. 5: CV plot of the TECS in 1 mM KCl solution.

on the electrode surface, and increasing the concentration of NaCl decreases the impedance value. This variation in impedance is further shown in the Bode impedance plot in Fig. 4b.

For a wearable application of the TECS, we investigated its influence on KCl concentration. We observed that a change in KCl concentration led to variations in peak current (48 µA at 0.8 V) as shown in Fig. 5 for 1 MM, which differed from the variations observed with NaCl (68 µA at 0.8 V for 1 mM). Furthermore, we prepared a sweat equivalent solution [11] and varied the NaCl concentration. In the sweat equivalent solution, TECS shows a capacitance of 116.17µF/cm^2. This value demonstrates the potential application of TECS for sweat monitoring. Additionally, the variation in specific capacitance of TECS in the sweat equivalent solution suggests its potential application as an energy storage device. Further detailed studies are required to implement TECS as self-powered sensors for epidermal electronics.

IV. Conclusion

In this work, we developed a new textile-based electrochemical capacitive sensor (TECS) using MWCNT-coated cellulose cloth. The CV analysis of the TECS shows that the fabricated sensor exhibited a sensitivity of 0.29 µA/log [Na^+] within the range of 0-16 mM concentration of NaCl. The device operates based on an electrochemical capacitive mechanism and exhibits a variation of specific capacitance of 6.9 µF.cm^{-2} in the range of NaCl 0-16 mM. The implementation of the proposed TECS as epidermal electronics for monitoring sweat chemicals presents a significant opportunity in healthcare.

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