Electrical Characterization of Graphene-based e-Tattoos for Bio-Impedance-based Physiological Sensing

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Abstract*— Bio-impedance (Bio-Z) is a promising method to measure a plurality of physiological observations from the human body. The principal challenge, however, remains in the electrodes. Wet-electrodes are inconvenient to wear and dry-contact electrodes do not provide sufficient robustness. The objective of this work is to demonstrate the feasibility of leveraging graphene-based electrodes to establish intimate contact with the skin while not introducing any discomfort to the user. Our proposed electrodes are ultrathin, soft, transparent, and can potentially remain on the skin at the same location over an extended period, while offering robust measurements. In this paper, we present the characterization of the proposed ultrathin and skin-conformable graphene-based electronic tattoos (GETs) in continuous Bio-Z measurements. Our bilayer GETs (biGETs) provide an average of 10 $k\Omega$ contact impedance with the skin at 10 kHz, improving the contact impedance acquired from the traditional dry electrodes. Moreover, Bio-Z measurements with the GETs show less variation (3.6 $m\Omega$ average standard deviation, 6.5 $m\Omega$ maximum standard deviation with biGET) due to its stable contact to the reference wet electrode measurements (4.1 $m\Omega$ average standard deviation and 7.5 $m\Omega$ maximum standard deviation with wet electrodes). Compared to the traditional electrode structures, our proposed GETs provide better contact impedance, good adherence to the skin, robustness in sensing, and additional comfort and breathability.

Keywords—graphene, bio-impedance, health monitoring, wearable, biopotential electrode, electrode-skin interface

I. Introduction

Cardiovascular diseases (CVDs) contribute to about 610,000 deaths in the USA alone [1]. Colossal efforts of scientific and biomedical communities are directed towards exploring the roots of the diseases [1]. It is important to monitor hemodynamic parameters in a continuous manner, in both affected and unaffected individuals, in order to provide more effective diagnostic and prognostic services. One principal challenge is the lack of truly unobtrusive sensors that users can wear over an extended period without discomfort and aesthetic implications.

Bio-impedance is a promising method that enables capturing various physiological parameters, including hemodynamic parameters (*e.g.* heart rate, heart rate variability, pulse wave velocity) [2]. In order to support extended wear for Bio-Z and other bio-potential instrumentation, the electrodes should be conformable, breathable, adherent, and non-invasive, offering a convenient experience to the end-user. Moreover, they should provide suitable contact quality, durability, and robustness to motion artifacts to ensure high fidelity sensing and signal acquisition. The traditional practices utilize either wet (gel) or dry electrodes that are obtrusive and invasive, resulting in skin irritation, redness, and skin necrosis from the long-term application of the electrodes on the skin [3]–[5]. Moreover, wet electrodes suffer from the drying out effect [6], whereas dry electrodes can result in dislocation of the electrodes and unstable contact with the skin, decreasing the consistency and reliability of the signal acquisition [7], [8].

We describe the first use of graphene-based electronic tattoos (GETs) in lieu of traditional electrodes for Bio-Z monitoring [9], [10]. We characterize the impedance of the single layer and bilayer GETs and provide a comparison to traditional electrodes. We demonstrate the ability to both inject an AC current into the epidermis as well as to record the AC voltage through two pairs of GETs as illustrated in Fig. 1. This is, up to our knowledge, the first reported usage of graphene for charge injection into the epidermis as well as usage of the graphene for Bio-Z monitoring.

Our contribution in this paper can be summarized as follows: we provided a novel method to establish electrical contact with the skin using an ultrathin graphene-based electronic tattoo (GET) structure. The proposed GETs are breathable, conformable, transparent, non-invasive and durable, where the e-tattoo is adhesive to the skin through Van der Waals forces. We showed that the Bio-Z measurements with GETs result in clear detection of periodic heart pulse signals with low noise, high fidelity and stability.

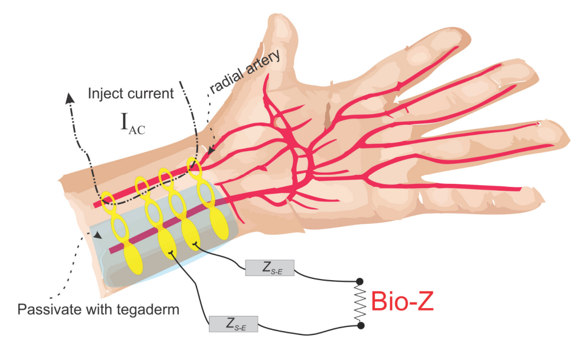

Fig. 1. Schematic of the system using the ultra-thin graphene electronic tattoo (GET) for physiological signal measurements. We injected AC signal into epidermis and measured Bio-Z with our proposed GETs, up to our knowledge, for the first time.

II. Materials and Methods

A. Graphene Tattoo Fabrication

Fabrication of graphene tattoos begins with chemical vapor deposition grown graphene on a copper foil. A 200 nm thick layer of polymethyl methacrylate (PMMA) is spin-coated on top of the graphene/Cu foil to serve as protection as well as further support the polymer. Following a hard bake of the

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PMMA at 200°C, the copper is etched in a 0.1M ammonium persulfate solution. The PMMA/graphene is then transferred into a beaker with fresh deionized water (DI) to clean the interface from the chemical residues. The process is repeated several times in order to ensure complete removal of any contaminants. Once ready, the PMMA/graphene is finally transferred onto the temporary tattoo paper [9]. The paper has a specific resin-based coating that is slippery and anti-adhesive whenever wet. Dried overnight, the graphene/PMMA/tattoo paper stack is loaded into a mechanical plotter that cuts a specific shape for the future GETs devices. After the cut is performed, the excess of the graphene/PMMA is removed and the ready tattoo can be transferred onto the skin.

In order to fabricate a bilayer GET (biGET), two graphene/copper pieces are used. PMMA is spin-coated onto the first piece and hard baked, while the second piece has no PMMA coverage. The first piece is then placed into copper etchant, and after the etching is done – transferred into clean DI water (similar to the described above). The floating PMMA/graphene(G) is then transferred on top of the second graphene/copper, resulting in the PMMA/G/G/copper stack, which is then dried overnight, and baked at 200°C. The second copper is etched away and the cleaning, transfer, and cutting procedures are performed as described above for monolayer case.

B. Preparation of Skin and Interconnecting Electrodes

An important measure of the contact quality established between the electrodes and the skin is the value of the contact impedance. A lower contact impedance allows for a higher current injection considering the supply power limitations with the circuits, increasing the SNR of the measurement system. In order to perform electrode-skin impedance measurements from the graphene tattoo and electrically isolate the skin from the tattoo connectors, the skin is prepared in the following manner. First, to insulate parts of the skin, a layer of Tegaderm is applied (see Fig. 2). On top of the Tegaderm we apply adhesive, conductive tape that is manufactured by evaporating 10 nm Ni and 60 nm of Au on top of an ultrathin adhesive tape. The softness and thinness of the Tegaderm and conductive adhesive tape are important to ensure good mechanical adhesion to the thin and soft graphene tattoo. However, in order to ensure a stable connection to the more rigid read-out electronics, an additional layer of adhesive copper tape is applied to the opposite end of the adhesive gold conductive tape. To ensure physical stability of the connector stack, it is later covered with a medical grade kind removal silicon tape (KRST). Image of the stack without KRST (for clarity) can be seen in Fig. 2.

C. Graphene-Skin Impedance Test

The graphene-skin impedance was pre-checked with a Keysight LCR meter U1732C allowing a frequency sweep from 100 Hz up to 100 kHz. Multiple data points were taken at each frequency in order to average the values. The measured values correspond to the electrode-skin impedance since the tissue bio-impedance is much smaller when compared to the typical electrode-skin impedance [11].

D. Bio-Impedance Sensing

The measure of impedance when the electrical current is passing through the cell membrane and surrounding body fluid is called bio-impedance. A non-invasive Bio-Z measurement can be done by injecting a small AC current and

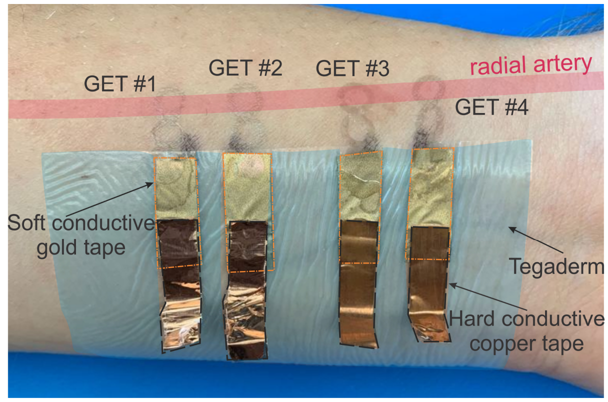

Fig. 2. Two pairs of GETs placed on the skin for current injection to epidermis and voltage sensing for Bio-Z measurements. Tegaderm is placed underneath both soft and hard conductive tapes and is highlighted in light cyan.

sensing the voltage difference using two separate pairs of electrodes. The changes in Bio-Z over time corresponds to the blood flow, lung movements, muscle contractions, and body fluid variations. By measuring this impedance change between two points on the body, it is possible to extract a plurality of physiological observations including but not limited to heart rate, heart rate variability, respiration rate, and hydration level. In this study, the injection and sensing biGET electrodes were placed on the radial artery to capture the periodic impedance change due to blood flow as shown in Fig. 2. The outer electrodes are used to inject a 0.2 mA sinusoidal signal at 10 kHz to carry the changes in the Bio-Z signal, also due to blood flow. We selected 10 kHz due to the low electrode-skin impedance at this frequency and to comply with the safety standards for 0.2 mA current injection [12]. Additionally, this choice on the frequency will mitigate the challenges with 1/f noise that exist at lower frequencies. The inner electrodes with a spacing of 4 cm are used for sensing the induced voltage due to the current flow on the radial artery and the surrounding tissue. To obtain a reference Bio-Z measurement, the same experiment was repeated with pre-gelled (wet) Ag/AgCl electrodes.

The amplitude of the Bio-Z variations due to the blood volume changes are very small at approximately 50 $m\Omega$, for the current 4 cm spacing of the sensing electrodes. Therefore, we developed low-noise Bio-Z sensing hardware using discrete components to capture blood volume changes from the wrist arteries with high sensitivity and fidelity. The overall Bio-Z sensing system is shown in Fig. 3. The hardware incorporates an ARM Cortex M4 MCU, which sends a digital waveform to a 16-bit DAC (DAC8811, Texas Instruments, USA) to drive the voltage-to-current converter. The converter utilizes a negative feedback loop on a low-noise operational amplifier (OPA211, Texas Instruments, USA) to generate a constant AC current signal, with programmable amplitude and frequency through the input voltage. In order to avoid injection of DC current into the human body, a series capacitor at the DAC output is used. The signal from the impedance sensing electrodes (middle two in Fig. 2) is sent through a high-pass filter to prevent source saturation caused by DC offset. This offset is generated by the skin-electrode interface due to the half-cell potential effect. Following, the signal is amplified with a low-noise instrumentation amplifier (IA). The IA output is provided to a high-precision ADC through an analog anti-aliasing low-pass filter. The ADC (ADS1278,

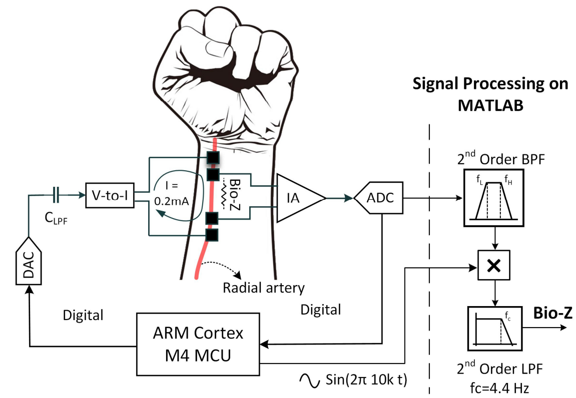

Fig. 3. Low noise Bio-Z sensing system. The hardware depends on the ARM Cortex M4 MCU. A controllable AC signal is generated at desired frequency and amplitude from DAC followed by V-to-I board for current injection. A pair of Bio-Z sensing electrodes were amplified with a low noise IA and sampled with high-precision ADC. MATLAB is used for digital signal processing of the recorded signals.

Texas Instruments, USA) samples the voltage at 93.75 kSPS with a 24-bit (0.3 μV) resolution, to provide sufficient precision.

The sampled data is sent to the MCU, which then forwards it to the PC through Hi-Speed USB Bridge for signal post-processing. The received signal is band-pass filtered by a second-order, Butterworth filter centered around the AC current frequency to remove the residual DC offset, 60 Hz interference and high-frequency noise. Then, the Bio-Z is extracted using synchronous demodulation by multiplying the filtered signal by the injection signal generated by the MCU. The multiplier output is filtered by a second-order, Butterworth low-pass filter with a cut-off frequency of 4.4 Hz to remove the image frequency and out of band noise, and to measure heart rates up to 180 beats per minute. The hardware was calibrated by measuring the impedance of a known resistor in order to convert the measured voltage to an accurate resistance value. The measurement system was capable of measuring impedance with a root mean square (RMS) error less than 1 mΩ, which is much lower than the target Bio-Z variations.

III. Results and Discussion

A. Contact-impedance Measurements

All our experiments were conducted on healthy participants under the IRB approval IRB2017-0086D by Texas A&M University at room temperature with the subjects being at rest. The graphene tattoos, fabricated as described in Section II, have a general structure of having two O-rings that go in contact with the skin and one that goes in contact with the conductive tape. The structure is selected based on a number of previous works, as it allows graphene to stay in direct contact with skin while it is under compression or strain [9], [13]. To compare the graphene-skin impedance, we performed the same measurements with pairs of dry Ag electrodes (30 mm^2), pre-gelled Ag/AgCl wet electrodes (100 mm^2) and similarly shaped tattoo-style Au electrodes (40 mm^2). The aforementioned sizes are selected due to availability (for wet and Ag dry electrodes) and fairness in comparison with the GETs. To establish good contact between the Ag and Au dry electrodes and the skin, we used soft conducting tape and a wrist band as described in Section II. Eight subjects have participated in the skin impedance measurements. One to four electrodes of each kind have been applied to each subject. At least five data points were taken for each frequency step, and averaged. The data from all subjects averaged and shown as median and standard deviation using error bars in Fig.4.

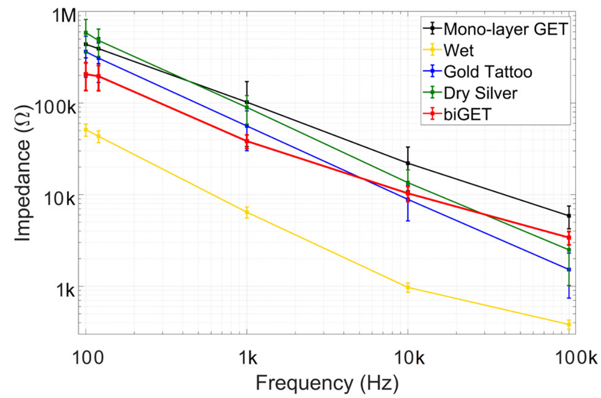

Fig. 4. Impedance over frequency plot for wet Ag/AgCl electrodes (yellow), dry silver electrodes (green), gold tattoos (blue), mono-layer GET (black), and biGET (red). The error bars are showing the SD.

We observe that wet electrodes provide the lowest contact impedance with the skin. This is due to the existence of free ions inside the Ag/AgCl gel supporting an ionic charge exchange between the electrode and the skin as well as the larger area compared to others. However, the dependency of the contact impedance on the Ag/AgCl gel causes degradation on the contact quality with time due to the drying of gel preventing long-term operations [6]. We also observe that the contact quality of biGET is similar to Au and better than Ag type dry electrodes at 10 kHz which is our mixing frequency for Bio-Z measurements. We noticed that applying a higher pressure on Au and Ag type dry electrode decreases the contact impedance with the trade-off of a decrease in convenience and an increase in skin redness [5]. On the other hand, due to adhesive nature of the GETs, the contact is established independently of the applied pressure, providing a stable and firm contact with the skin via van der Waals forces [9]. We observed that biGETs perform better than mono-layer GETs. We believe that the difference in the contact quality is caused by the fragileness of single-layer graphene, presence of microcracks, edge defects and grain boundaries of the graphene itself. Stacking graphene to be bilayer ensures uniformity of the material on a large scale, stabilizing its conductivity as well as interface impedance. Therefore, in Bio-Z measurements only biGET electrodes were used.

B. Bio-impedance Sensing

In order to observe the periodic arterial pressure pulse that can be used in extracting hemodynamic parameters, we looked into the changes in the Bio-Z over the radial artery for a single subject. For current injection and voltage sensing purposes, we placed two pairs of 40 mm^2 biGET on the radial artery with the separation of 40 mm between the sensing pair and 56 mm between the injection pair to mimic the form factor of wrist-worn jewelry or watches with enough signal quality within the enclosed sensing region. A sinusoidal signal with a 0.2 mA peak amplitude at 10k Hz is injected for one minute via the outer GET electrodes to obtain the voltage changes over time in between the inner GET electrodes due to blood flow. To ensure we can retain a similar signal morphology across various experiments, we followed the same procedure with pre-gelled Ag/AgCl wet electrodes in sequence to the GET experiment, where wet electrodes were placed at the exact same locations as the GET electrodes. Fig. 5 shows the change in Bio-Z signals for both electrode types due to the periodic blood flow in the radial artery. We observe that both the GET electrodes and the wet electrodes can successfully capture periodic activities due to the blood flow and heart rate.

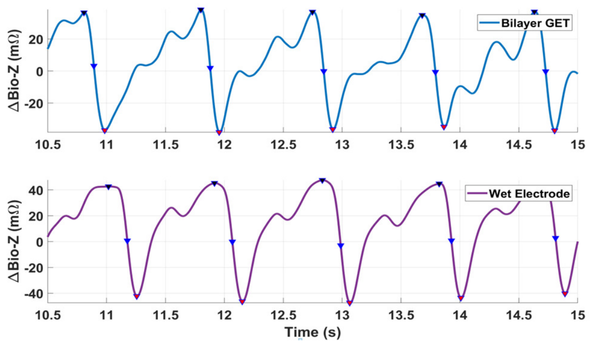

Fig. 5. Measured ΔBio-Z signals corresponding to the periodic blood flow in the radial artery using GET electrodes (top) and wet electrodes (bottom).

In order to evaluate the variations in the Bio-Z signal morphology for sequential heartbeats over a one-minute period, the samples were ensembled by selecting the maximum slope point found for each beat as the beginning of each window. We applied a five-window moving average (four-window overlap) to remove high-frequency disturbance. In order to compare the morphology of the signals, each window is normalized in time using the corresponding interbeat intervals (IBI). The results are shown in Fig. 6. We observe that Bio-Z measurements with biGETs give an average of 3.6 mΩ standard deviation (SD) and 6.5 mΩ maximum SD, less than the SD observed with the reference wet electrode measurements (4.1 mΩ SD_{avg} and 7.5 mΩ SD_{max}). This might be due to the fact that wet electrodes establish contact using the conductive Ag/AgCl gel having a gelatinous structure and causing slight movements/vibrations on the contact. This would create a divergence in the measured signal morphology when compared to the GET structure in which the e-tattoo establishes contact with the skin through Van der Waals forces, building a firm, seamless connection.

IV. Conclusion

In this paper, we introduced the sensing characterization of novel, ultrathin graphene-based electronic tattoos that provide robust electrical contact with the skin for continuous capturing of vital physiological signals from the human body and human tissues. Unlike other methods that are obtrusive and inconvenient for continuous long-term wear, our graphene-based tattoos can potentially provide non-invasive, conformable, robust, breathable and transparent electrical contact with the skin, offering convenience for wearable applications while not compromising on the robustness of signal acquisition [14]. For robustness and electrical contact quality investigations of the proposed GETs, we presented Bio-Z readings of high fidelity and stability for the first time in the literature, to our knowledge. Future investigations will include efforts to improve the mechanical stability of the contact between graphene-based electrodes and electronics to provide long-term operation and further characterization in the presence of motion artifacts.

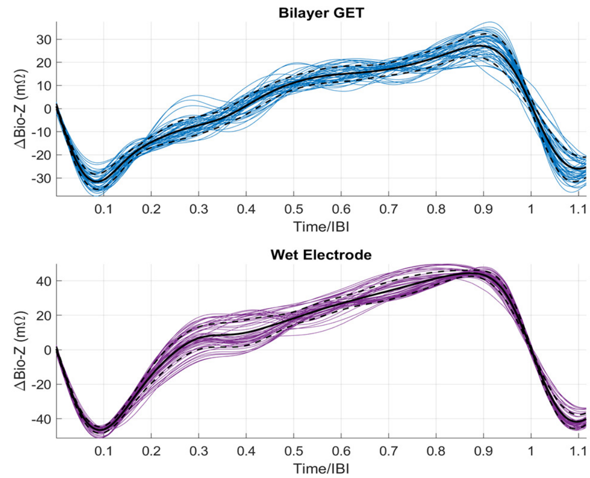

Fig. 6. Ensembled and time-normalized Bio-Z IBIs measured using GET electrodes (top, 3.6 mΩ STD_{avg}) and wet electrodes (bottom, 4.1 mΩ STD_{avg}).

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