The non-linear electrical properties of silver/silver chloride electrodes in sodium chloride solution

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Abstract
An electrical measurement is non-linear when it is affected by the applied stimulus, i.e. when the measured phenomenon changes with amplitude. If pinched hysteresis loops can be observed in the voltage current representation, the underlying tissue can be classified as a memristor. Several biological memristors have been published, like human skin and apples. However, changes in the polarization impedance of electrodes may also cause pinched hysteresis loops. The question whether the reported biological memristors are real or whether the results just reflect changes in the polarization impedance arises. If the impedance of the measured object is close to or smaller than the polarization impedance of the used electrodes, the latter may dominate the measurement.

In this study, we investigated the non-linear electrical properties of silver/silver chloride electrodes in a sodium chloride solution that has a similar concentration as human sweat and compared these to results from human skin. First of all, we found that silver/silver chloride electrodes in sodium chloride solution can be classified as memristors. However, the currents obtained from the sodium chloride solution are much higher than the currents recorded from human skin and there is a qualitative difference in the pinched hysteresis loops in both cases. We can conclude that the non-linear electrical measurements with silver/silver chloride on human skin are actually dominated by the skin and we can confirm that the human skin memristor really exists.

Keywords: Bioimpedance; non-linear electrical measurements; electrodes; cyclic voltammetry; memristor; human skin

Introduction
In 1971, Leon Chua presented the fourth basic electrical circuit element, the memristor (“memory resistor”) [1], the missing link between flux and charge. A memristor is characterized by its state dependent resistance (memristance), \( M \), and the voltage, \( v \), and current, \( i \), can be related via the state dependent ohm’s law

\[
v = M(x)i
\]

with \( x \) as the vector of the internal state variables. The change of \( x \) is described by the state equation

\[
dx/dt = f(x, i) \cdot i.
\]

Three fingerprints of memristors are defined: First, the voltage current (V-I) plots must show pinched hysteresis loops [2] for any periodic and non-periodic stimulus and different amplitudes. Secondly, the lobe area of the loop decreases with increased frequency. Thirdly, the hysteresis loop turns into a single-valued function as the frequency goes toward infinity [3].

It has been shown that human skin is a memristor [4]. The sweat is moved by electro-osmosis [5] towards the skin surface or towards deeper skin layers dependent on the polarity of the applied voltage. The change in sweating affects the (state-dependent) conductance of skin. In a previous study we demonstrated that electrode gel can affect the non-linear electrical measurements on human skin.
[6] since the ions of the electrode gel may also move by the applied voltage. The use of dry silver/silver chloride electrodes was recommended. However, electrochemical reactions on the electrode surface as in cyclic voltammetry [7] may also cause a non-linear relationship between voltage and current.

For example, it has been proposed that apples [8] and the aloe vera plant [9] are memristors. We demonstrated that similar results can be obtained from apples and apple juice and also from aloe vera and aloe vera extract and we concluded that the memristive properties actually originate from the change in polarization impedance [10].

Since we reported non-linear electrical properties from human skin [4], we are interested in whether these properties are real or whether these are also just caused by the change in polarization impedance of the used electrodes. We therefore did recordings with dry silver/silver chloride (Ag/AgCl) electrodes (same type that was used for the recordings on human skin) in sodium chloride (NaCl) solution that has a similar ion concentration as human sweat. In addition, we used the same instrumentation and similar test protocols as in the studies on human skin (see [4, 11]).

In a first experiment, we applied different low frequency alternating current (AC) voltages to investigate the voltage current relation. By doing so we can investigate whether silver/silver chloride electrodes in saline solution can be classified as memristors and we can directly compare with the results on human skin in [4]. In a second experiment we applied DC voltage pulses and measured the small signal admittance afterwards. We could show that the human skin memristor is non-volatile and that information can actually be stored inside (see [11]). We were interested here whether it is similar for the silver/silver chloride electrodes in sodium chloride solution. As a supplement we did measurements with stainless steel and aluminum electrodes in sodium chloride solution (see supplementary information Figs. S1 to S4). Finally, we did some additional measurements on the forehead of one test subject that allow for a direct comparison with the recordings in the sodium chloride solution.

Materials and methods
All measurements were done at the University of Oslo.

Instrumentation
The recordings were done by the use of a custom built measurement system (see Fig. 1b and [4]). The setup contains a DAQ card (NI USB-6356) which is connected to a computer and controlled by a custom made program based on LabVIEW 2018. A three electrode system was used with “M” as the measurement electrode, with “CC” as the current carrying electrode and a reference electrode (“Ref”). The resistance of the feedback resistor R fb was equal to 560 Ω and C fb was equal to 4.7 nF.

Electrodes and saline solutions
The dry, sintered silver/silver chloride electrodes were prewired, from the company Wuhan Greentek PTY LTD, and had and active area of 0.283 cm² (disk electrodes with a diameter of 0.6 mm). The stainless steel and aluminum disk electrodes were custom made and had a diameter of 5 mm (active area of 0.196 cm²). Wires were attached via conductive clue and non-conductive clue (3M™ Scotch-Weld™ Epoxy Adhesive 2216 B/A) was used to electrically isolate all parts from the electrodes except of the front plane.

The electrodes were placed inside a plastic bottle (see Fig. 1c), in which 120 ml of distilled water and 60 ml of a sodium chloride solution (9 g/l) were filled. The obtained saline solution (sodium chloride, 3 g/l) has a concentration of 51.33 mmol/l which is similar to the concentration of sweat at the forehead [12]. The measurements were repeated with a different solution concentration, namely 30.8 mmol/l (1.8 g sodium chloride per liter, obtained by using 120 ml distilled water and 30 ml sodium chloride solution with 9 g/l). The additional measurements with stainless steel and aluminum electrodes were also done in sodium chloride solution with a concentration of 51.33 mmol/l (3 g/l) and repeated in 180 ml of sodium chloride solution with a concentration of 154 mmol/l (9 g/l).

Experimental procedure
The measurements were done with different voltage waveforms (see Fig. 1a, triangular waveforms with amplitudes of 0.05 V, 0.1 V and 0.2 V without DC offsets and amplitude of 0.1 V with a DC offset of 0.05 V in addition, and sinusoidal with amplitude of 0.1 V) and two different frequencies each (0.01 Hz and 0.1 Hz). Different amplitudes were used for measurements on aluminum and stainless steel (triangular waveforms with amplitudes of 0.2 V, 0.4 V and 0.8 V without DC offsets and amplitude of 0.4 V with a DC offset of 0.2 V in addition, and sinusoidal with amplitude of 0.4 V). The sweep over the voltage waveform and the sweep over the frequencies were performed automated in randomized order. Reading and writing were done with 2000 samples per period.

The second conducted experiment consisted of three series of applied DC voltage pulses, each followed by small signal conductance measurements for about one minute. The voltage steps were always from 0 V to -0.1 V (first and third series) and 0 to + 0.1 V (second series). For the recordings on the stainless steel and aluminum electrodes, DC levels of -0.4 V and 0.4 V were used instead. Each single pulse had a duration of 5 seconds in high state, followed by 5 seconds in low state (0 Volts). Six pulses per series were applied and the total duration per series was exactly one minute. The small signal admittance measurement was done with a sinusoidal voltage with a frequency of 20 Hz and an amplitude of 100 mV.
The whole experimental procedure was done three times with the same silver/silver chloride electrodes on different days and two times on different days with each, the same stainless steel and aluminum electrodes, all in November 2018. Additional measurements (exact same silver/silver chloride electrodes, and same solution with 3 g/l and a volume of 180 ml) using triangular voltage waveform with amplitudes of 0.4 V and 0.8 V and sinusoidal voltage waveform, with 0.8 V amplitude, all with frequencies of 0.01 Hz, 0.05 Hz and 0.1 Hz were done once in December 2019. Voltage reading and writing was done with 500 samples per period within these additional measurements.

Additional measurement on human skin
The recordings were done in December 2019 on one test subject. Physical separation between the mains and the test subject was ensured (the personal computer, monitor and the DAQ were powered by an international medical isolation device (IMEdE 1000 from Noratel AG, Germany). The exact same dry silver/silver chloride electrodes that were used for the recordings in the sodium chloride solution were used for the measurements on the forehead. All three electrodes (M, Ref and CC) were taped to the skin. The measurement electrode was placed at the forehead above the iris of the left eye, at approximately the width of two fingers above the eyebrow (same placement as in [4] was used). The Ref and CC electrodes were placed at the left forearm central at approximately the width of two and four fingers away from the wrist, respectively. Different low frequency AC voltages (sinusoidal and triangular voltage waveform with an amplitude of 0.8 V and frequencies of 0.01 Hz, 0.05 Hz, and 0.1 Hz and triangular voltage with an amplitude of 1.5 V and frequency of 0.05 Hz) were applied and the corresponding current was measured, (reading and writing with 500 samples per period). A measurement (sinusoidal voltage with an amplitude of 2 V and frequency of 0.05 Hz) with stainless steel electrodes (exact same M electrode that was also used as M electrode for the sodium chloride solution measurements) was done and all three electrodes were placed in the same manner as it was for the silver/silver chloride electrodes.

Informed consent
Informed consent has been obtained from all individuals included in this study.

Ethical approval
The research related to human use has been complied with all relevant national regulations, institutional policies and in accordance with the tenets of the Helsinki Declaration, and has been approved by the authors' institutional review board or equivalent committee.

Results
Experiment 1
The obtained results (Fig. 2) from the silver/silver chloride electrodes in sodium chloride solution are non-linear for the used voltage stimuli. Pinched hysteresis loops can be observed for different amplitudes, shapes and frequencies of the applied voltage. The pinched point was located in the first quadrant if the voltage amplitude was 0.4 V and above. For voltage amplitude of 0.1 V the pinched point is located in the third quadrant. The two branches of the loop were always touching the pinched point with equal slopes.

The higher the amount of sodium chloride ions in the solution, the higher the amount of current that was recorded. However, the different ion concentrations had no noticeable effect on the shape of the voltage current plots.
Similar results were obtained when the measurements were repeated at another day.

The recordings with the stainless steel electrodes in sodium chloride solution are very non-linear (see Fig. S1). The recordings with the aluminum electrodes are slightly non-linear (see Fig. S3) and pinched hysteresis loops can be observed. The recordings with the aluminum electrodes exhibited a large DC offset, which may be an explanation for the shift along the y-axis.

The recordings on human skin (see Figs. 2e and 2f and results in [4]) exhibited pinched hysteresis loops in which the two branches of the loop crossed the pinched point with different slopes. This can be achieved for different amplitudes, frequencies and shapes of the applied voltage and also different electrode materials (see the recording with the stainless steel electrodes in Fig. S1h).

Experiment 2
The measured current was affected by the applied DC voltage pulses and slight changes from pulse to pulse were observed (see Fig. 3). The small signal conductance remains quite stable (see Fig. 3b) within the first minute after the last DC pulses. Different conductance states can be achieved- The conductance A1 in Fig. 3b, for example, is below 5 mS after negative pulses were applied for the first time (Series 1), above 6 mS after positive pulses (Series 2) were applied and around 5.5 mS after negative pulses were applied for the second time (Series 3).
Fig. 3: Results from the second experiment, recorded with the silver/silver chloride electrodes, A1, A2 and A3 reflect the measurements in the 3 g/L NaCl solution (first, second, and third time, respectively) and the B1 and B2 reflect the measurement results in 1.8 g/L NaCl solution. 

**a)** Non-linear electrical measurements with DC voltage pulses. Measured current, $i$, and applied voltage, $v$, plotted over time. **b)** Small-signal conductance measurements after each DC pulse series. The time is related to the end of the last pulse of the corresponding DC pulse series.

Within the recordings of stainless steel electrodes in sodium chloride solution, negative DC voltage pulses increased the overall conductance (see Fig. S2), while positive pulses decreased the conductance. Within the measurements with aluminum electrodes in sodium chloride solution, it seems like that the applied DC voltage pulses do not have any effect on the small signal conductance that was recorded afterwards (see Fig. S4).

**Discussion**

Pinched hysteresis loops have been shown for the silver/silver chloride electrodes in sodium chloride for different voltage stimuli and it is possible to classify the overall setup as a memristor. Shifts in pinched point position away from the origin of coordinates can be explained by parasitic capacitance and DC offsets [14].

The chosen concentration of the saline solution is similar to human sweat and the same type of dry silver/silver chloride electrodes as in [4] were used here, as well. With a given voltage, the currents obtained from the recordings in the sodium chloride solution are much higher than the currents that were obtained from human skin (up to 100 times). This is a first indication that human skin actually dominated the measurements in [4] while the measurements in the sodium chloride solution are dominated by the polarization impedance of the electrodes. However, there is the possibility that the polarization impedance from the electrodes to human skin is much higher than from the electrodes to saline solution since only parts of the...
measurement electrode may be in contact with the sweat. Another observation is that the quality of the pinched hysteresis loops here is different from the results from human skin (see Figs. 2e and 2f and [4]). For the sweat duct memristor in human skin, the two branches of the hysteresis loop cross the pinched point with different slopes (transversal memristor, see [14]). The orientation of the pinched hysteresis loop was always counter-clockwise in the first quadrant and clockwise in the third for the sweat duct memristor (see [4]). In contrast, the recordings from the silver/silver chloride electrodes in sodium chloride solution here exhibited pinched hysteresis loops in which the two branches were touching with equal slopes in the pinched point (tangential memristor) and the orientation of the loop was always clockwise in the first and third quadrant.

The sweat is moved by electro-osmosis in human skin [5, 15], which affects the ability the conduct current and results in the obtained pinched hysteresis loops. Here, electrochemical reactions on the electrodes themselves as in cyclic voltammetry [7] are the origin of the pinched hysteresis loops in the voltage current plots. Shifts in the equilibrium between silver and silver chloride at the measurement electrode with

\[ e^+ + AgCl \rightarrow Ag + Cl^- \]  

are likely to be the origin of the change in the polarization impedance at low voltage amplitudes (below 0.8 V). Redox reactions of water with

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]  

(Oxidation) \hspace{1cm} (4) \hspace{1cm} 

\[ 2H^+ + 2e^- \rightarrow H_2 \]  

(Reduction) \hspace{1cm} (5)

can be observed for a voltage amplitude of 0.8 V with the silver/silver chloride electrodes and already at an amplitude of 0.2 V for the stainless steel electrode recordings (see Fig. S2).

No redox reactions were observed from the recordings on human skin even though we tried higher amplitudes (1.5 V with silver/silver chloride, Fig. 2f, or 2 V with stainless steel, Fig S2h) which is another confirmation that the pinched hysteresis loops originates from the skin itself. If the polarization impedance was dominating, redox reactions should have been observed.

The three electrode system that was used here is suitable to measure the polarization impedance only under the measurement electrode since it neglects the polarization impedance under the current carrying electrode. If a bipolar system would have been used instead the results would have reflected the superposition of the polarization impedances of two electrodes.

We found that information can be stored in human skin [11]. However, here we found that information can be stored in the electrodes themselves since different conductance values can be set by applying DC voltage pulses (see Fig. 3).

It would be interesting to repeat this experiment with longer conductance measurements and also larger DC levels of the applied voltage. The changes in measured current here within the DC pulses are relatively small which is different from the recordings on human skin [11]. However, it is likely that the changes of the silver/silver chloride electrodes in sodium chloride solution would be larger with larger DC levels than 0.1 V. The current responses in series 2 were not periodic which is an indication that the electrodes exhibit non-volatile memory [11, 16]. However, the current responses in series 1 and 3 are quite periodic in most cases which might be due to the small DC levels.

**Conclusion**

We conclude that the non-linear electrical measurements on human skin in [4, 11] are actually dominated by the skin itself. Thus, we can confirm that human skin is a memristor. For low frequency AC and DC stimuli, the impedance of human skin is quite high in comparison to the polarization impedance of the silver/silver chloride electrodes that are commonly used for these kinds of measurements. However, as we have shown here, silver/silver chloride electrodes in sodium chloride solution also exhibit pinched hysteresis loops and the overall setup can be classified as a memristor.

One has to know which part of the experimental setup is dominating the measurement. If the test object has a low impedance, it is likely that the polarization impedance affects if not dominates the measurement.

**Conflict of interest**

Authors state no conflict of interest.

**Data and materials availability**

The recorded data have been deposited with figshare. These data can be obtained free of charge from: https://figshare.com/articles/_/11472585.

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Supplementary information

Fig. S1: Voltage current plots recorded with the stainless steel electrodes, always shown for the second period of each measurement and the two different solutions (results from the 3 g/l sodium chloride solution are presented in dark blue and results from the 9 g/l sodium chloride solution are presented in light blue). a) Applied triangular voltage with 0.4 V amplitude and frequency of 0.01 Hz. b) Repeated measurement with the same stimulus as in a) carried out one day later. c) Same stimulus as in a) but with an additional DC offset of 0.2 V. d) Applied sinusoidal voltage with 0.4 V amplitude and frequency of 0.01 Hz. e) Applied triangular waveform with a frequency of 0.1 Hz and an amplitude of 0.4 V. f) Applied triangular voltage with 0.2 V amplitude and a frequency of 0.01 Hz. g) Applied triangular voltage with 0.8 V amplitude and a frequency of 0.01 Hz. h) Result from a recording on human skin at the forehead of one test subject with sinusoidal voltage with an amplitude of 2 V and a frequency of 0.05 Hz.
Fig. S2: Results from the second experiment, recorded with the stainless steel electrodes, A1, A2 reflect the measurements in the 3 g/L NaCL solution (first and second time, respectively). a) Non-linear electrical measurements with DC voltage pulses. Measured current, i, and applied voltage, v, plotted over time. b) Small-signal conductance measurements after each DC pulse series. The time is related to the end of the last pulse of the corresponding DC pulse series.
Fig. S3: Voltage current plots recorded with the aluminum electrodes, always shown for the second period of each measurement and the two different solutions (results from the 3 g/l sodium chloride solution are presented in dark blue and results from the 9 g/l sodium chloride solution are presented in light blue). a) Applied triangular voltage with 0.4 V amplitude and frequency of 0.01 Hz. b) Repeated measurement with the same stimulus as in a) carried out one day later. c) Same stimulus as in a) but with an additional DC offset of 0.2 V. d) Applied sinusoidal voltage with 0.4 V amplitude and frequency of 0.01 Hz. e) Applied triangular waveform with a frequency of 0.1 Hz and an amplitude of 0.4 V. f) Applied triangular voltage with 0.2 V amplitude and a frequency of 0.01 Hz. g) Applied triangular voltage with 0.8 V amplitude and a frequency of 0.01 Hz.
Fig. S4: Results from the experiment applied DC pulses, recorded with the aluminum electrodes, A1, A2 reflect the measurements in the 3 g/L NaCl solution (first and second time, respectively) and B1 represents the result with the 9 g/L NaCl Solution. a) Non-linear measurements with DC voltage pulses. Measured current, $i$, and applied voltage, $v$, plotted over time. b) Small-signal conductance measurements after each DC pulse series. The time is related to the end of the last pulse of the corresponding DC pulse series.