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(Article begins on next page)

Impedance spectroscopy of conductive commercial hydrogels for electromyography and electroencephalography

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Abstract
In biomedical applications such as the electroencephalogram, electrocardiogram and electromyogram, usually conductive hydrogels are applied to the skin providing a skin–electrode layer, with the aim of lowering contact impedance and improving the signal/noise ratio. It is important to know the electrical behavior of these materials, obtaining reliable values of their conductivity. It can be extracted by the whole cell impedance, which is affected not only by the bulk but also by the surface properties. The aim of the present work is to characterize the impedance of some currently available conductive hydrogels in the frequency range 5 Hz–1 MHz. For this purpose we have designed a novel cell, with silver electrodes, optical detection of the gap and guard ring. In this paper the results are compared with those obtained by means of a commercial cell with stainless steel electrodes, without a guard ring. In order to extract the different contributions of the bulk and the interface, we fitted the experimental data with a very simple model: the bulk properties are described by a single RC-parallel, whereas the interface is represented by a constant phase element.

Keywords: electromyogram, hydrogel, bulk impedance, interface impedance, conductivity

1. Introduction

Biomedical screening of the population and patient check-in involves the widespread use of the electroencephalogram (EEG), electrocardiogram (ECG) and electromyogram (EMG). In all

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such applications the recording of signals at the skin surface allows physicians and scientists to extract neural information (Farina *et al* 2004). Of course, the complete signal recorded comprises a collection of electrical contributions, which consist of local microvoltages detected by electrodes placed on the skin and mainly come from the underlying tissues. The information extracted from EMG, for instance, is often considered a global measure of the activity of muscle motor units (MUs). In fact the features of the signal and its power spectrum depend on the membrane properties of the muscle fibres as well as on the timing of the MU action potentials, i.e. the surface EMG reflects both peripheral and central properties of the neuromuscular system. But, unfortunately, EMG is also influenced by many nonphysiological factors, emerging from the anatomy, geometry and physics of the body, and from the properties of the detection system. The relative importance and the features of most of the nonphysiological factors have been either evaluated or simulated (see references 22, 29, 30, 41, 49 and 71 in Farina *et al* (2004)). In any case, until now no result has been reported in the literature concerning the repeatability and stability of the electrical contact impedance between the skin and the electrode system. Since bioelectric signals need to be detected, skin contact electrodes have to be connected to signal amplifiers. To make the electrical contacts uniform and stable in time, biocompatible conductive hydrogels are normally applied between skin and electrodes. The contact electrode impedance consists of two parts: the hydrogel, and the interface impedance. It is important to establish a method for characterizing both contributions. In the following, we present our investigations on commercially available hydrogels currently used in EMG, where the relevant, most significant frequency range of signals goes from 5 Hz to 1 kHz.

For approximate conductivity analysis of liquids, commercial cells are available, allowing impedance detection with an accuracy not better than 10% as declared[4]. For obtaining more accurate results, a novel cell was designed by us, allowing an accuracy better than 2%, and a comparative study on two groups of conductive hydrogel mixtures (the first kind consisting of gels, the second one of creams) was performed with both types of cells. The bulk properties of the chosen hydrogels were extracted from the experimental data, obtaining the interface characteristics averaged in a frequency range from 5 Hz to 1 kHz and obtaining the bulk conductivity using as reference the plateau value at higher frequency (practically from 10 kHz to 1 MHz).

The skin–electrode contact—depending also on the geometry of the electrode system— affects the interface contribution to impedance, which mainly influences the frequency range below 1 kHz. This contribution decreases as the ratio between the electrode surface and the cell gap increases. We have to underline that if the conduction mechanism in gels is ionic, as in a salt aqueous solution, then, and only in such a case, the interface impedance would be essentially due to the Stern layer (Bockris and Reddy 1998) formed by the ions just nearby the electrodes and to the Gouy–Chapman layer diffused in the bulk. The Stern layer is in fact an electric double layer at the surface, consisting of the ions directly in contact with the metal electrode and of the ions compensating the previous ones, which are completely solvated (Barbero and Alexe-Ionescu 2005).

For these reasons, in general, the interface between a colloidal system and a metal is characterized by an impedance difficult to evaluate, either considering it as given by a parallel of infinite contributions, which differ point by point on the cell surface, or modeling a simple global passive circuit; hence, an interface equivalent mixed impedance (known as constant phase element—CPE) (Macdonald 1987, Bates *et al* 1988) is used here. In other words, in

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[4] Accuracy not better than 10% was declared by the workshop producing the commercial cell, but this was optimistic according to us, especially at low frequency (<100 Hz): the lack of a guard ring can give worse accuracy (usually up to 20% but in some cases up to 50%).

the case of an interface between a metal electrode and electrolyte, the frequency dispersion response cannot be described by a single finite circuit composed of ideal constant components such as resistors, capacitors and inductors. It is better to describe the surface impedance by a model implying an ad hoc complex parameter, defined as a CPE which is frequency dependent (Jorcin *et al* 2006, Grimnes and Martinsen 2008). It is necessary to realize that this is only an expedient for describing the experimental data in the range of frequency above 1 Hz, provided the impedance real part will not exhibit a peak at lower frequencies. In fact there is evidence to suggest that at about 10^{-2}, 10^{-3} Hz the bulk–surface interaction phenomenology is much more complicated (Macdonald 1987), and other models different from CPE should be introduced. Furthermore, the interface impedance turns out to be very sensitive to the changes of the whole conductive system, bulk included, since it is directly connected to the charge carrier size (Atkins 2004). In general, it is important to have a correct model of the interface contribution when the main part of the bioelectrical signals is in the very low frequency range (below 1 Hz), where the interface can play a critical role.

But in the case of EMG, only bioelectrical signals above 5 Hz are important; then in the following we use the CPE model for the metal–hydrogel interface.

In section 2 the hydrogels to be investigated are presented, and the commercial cell, the novel cell and the measurement protocol are described. In section 3 the experimental results are reported and discussed. In section 4 the conclusions of the investigation are pointed out.

## 2. Materials and methods

2.1. Investigated hydrogels

Hydrophilic polymers known as hydrogels (Farina *et al* 2004) and in particular their cross-linked forms are a class of biomaterials that have demonstrated great potential for biological and medical applications; they are appealing because of their biocompatibility, caused by their high water content. In fact, most of hydrophilic polymer networks have a high affinity for water, nevertheless do not dissolve into it, due to their chemically or physically cross-linked network; water molecules can only penetrate into the chains of the polymer network, subsequently causing swelling and formation of a hydrogel (Berger *et al* 2004). We decided to perform impedance measurement only considering two groups of hydrogel mixtures: gels and creams currently available in pharmaceutical market. The first kind of materials are by chance transparent (Cogel, Neurgel, Onegel and Zerogel), whereas the second kind of materials are opaque (ACcream, EC2, Ten20, Bionen and Onecream), providing some experimental problems. In fact, if the hydrogels are transparent, it is more easy to visually control and evaluate the capacitor gap in the cell than in the opposite case. The materials' manufacturers and their chemical compositions are listed as follows:

Gels

(1) *Cogel by Comedical*. Water, propylene glycol, sodium carbomer, lithium chloride, disodium ethylenediaminetetraacetic acid, methyl paraben.
(2) *Neurgel by Spes Medica*. Water, potassium chloride, hydroxyethylcellulose, propylene glycol, methylchloroisothiazolinone, methylsothiazolinone, bensyl alcohol.
(3) *Onegel by Ates Medica*. Chemical composition not declared.
(4) *Zerogel by Eurocamina*. Chemical composition not declared.

Creams

(1) *ACcream by Spes Medica*. Water, polyethylene glycol (25), cetyl/stearyl ether, glycerin, hydrated silica, calcium carbonate, potassium chloride, hydroxyethylcellulose, sodium
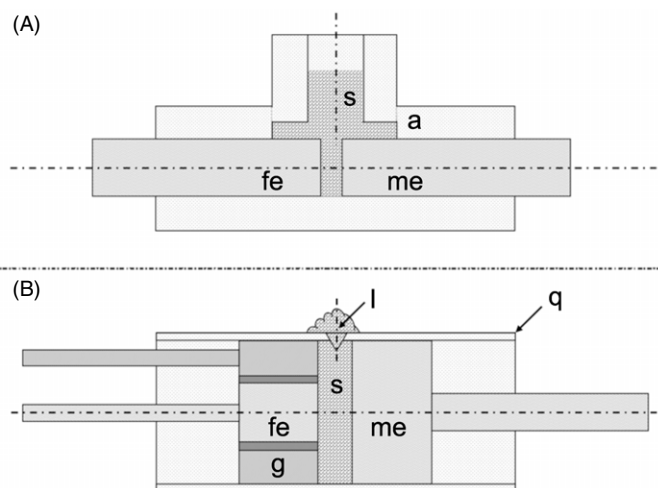
Figure 1. Scheme of the commercial cell and of the novel cell with supports. (A) refers to the commercial stainless steel electrode cell and (B) refers to the novel silver electrode cell with a guard ring. In both cases, **me** is the movable electrode and **fe** is the fixed one. **a** is the T-shape opaque acrylic holder in (A), whereas in (B) **g** is the guard ring, **l** is the gel leakage hole and **q** is the transparent quartz tube holder. The capacitor electrodes are in contact with the hydrogel sample **s**. The electric contacts of both electrodes are made through the metallic axial cylinders, whereas the guard ring contact is represented by the metallic cylinder drawn on the upper-left side of (B).

chloride, phenoxyethanol, ethyl methyl propyl butyl para-hydroxybenzoate (paraben), propylene glycol.
(2) *EC2 by Grass AstroMed.* Potassium chloride, sodium chloride and the rest chemical composition is not declared.
(3) *Ten20 by Weaver and Co.* Water, polyoxyethylene 20 cetyl ether, glycerin, calcium carbonate, propylene glycol, potassium chloride, gelwhite, sodium chloride, polysorbit 20 sorbitol, methyl propyl paraben.
(4) *Bionen by Ates Medica.* Chemical composition not declared.
(5) *Onecream by Ates Medica* Chemical composition not declared.

2.2. Commercial stainless steel electrode cell

The commercial cell has an opaque cylindrical acrylic holder in which the electrodes have to be inserted by opposite sides (figure 1(A)) and blocked with a fixing cap, in order to form a plane capacitor with a variable gap. In the correspondence of the cell gap, the sample reservoir is connected with the cell holder, forming a T-connection. The electrode diameter is (10.00 ± 0.02) mm. The electrode gap d can be varied by moving one of the two electrodes.

Due to the opacity of the cell holder, in the commercial cell there is no control of the possible presence of air bubbles inside the sample, and the uniformity of the electric field is not ensured at the border, in the absence of a guard ring. Moreover, the gap value can be detected only by a differential measurement with a calliper as follows. Before filling the cell with a sample, the total axial length of the system with both electrodes attached to each other has to be measured. It turns out to be (114.40 ± 0.02) mm. When the cell is filled, the gap value is obtained by subtracting the previous total axial length from the actual one. The uncertainty
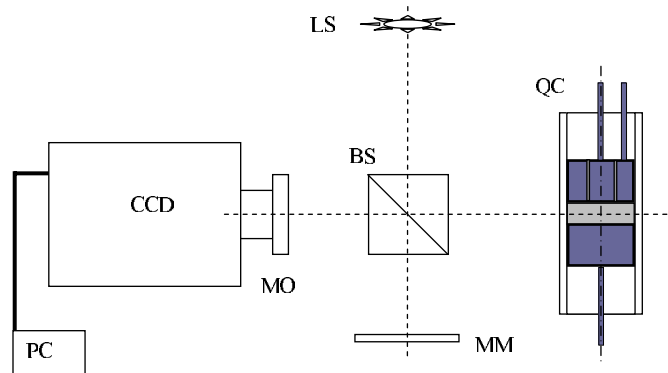
Figure 2. Scheme of the optical arrangement for the determination of the capacitor gap. LS is an extended light source; BS is a 50% beam splitter; MM is a 2.5 mm film divided into 500 parts; QC is the quartz cell with two electrodes, one of which has a guard ring; MO is the macro-objective in front of the CCD camera whose output can be sent to a PC.

(This figure is in colour only in the electronic version)

$|\delta d|$ is 0.04 mm and the gap measurement range is between 0.40 and 4.50 mm; this means that in the worse case the uncertainty source of R, X coming only from the gap accuracy is about 10%. But the whole accuracy, depending also on the field disuniformity and on the presence of bubbles, can be estimated only *a posteriori*, and in our measurements the uncertainty can be as large as 50%.

2.3. Novel silver electrode cell with guard ring

The novel cell was designed by us with the aim of solving the disadvantages of the commercial one. In particular, the transparency of the fused quartz holder allows us to see inside the sample checking the undesired presence of bubbles; the field uniformity is ensured by a proper guard ring and the gap value can be efficiently selected in advance and optically detected with a camera. Unfortunately, the gap can be directly measured only for transparent samples. For opaque ones it is necessary to mark two reference points drawn onto the lateral surface of both electrodes. The two reference points have to be distant enough not to be reached by gel leakage, exiting from gap by capillarity. The novel cell is designed with silver-plated electrodes, in order to deal surely with blocking ones. The low-voltage electrode (main electrode) has diameter equal to 8.00 ± 0.02 mm, whereas 14.00 ± 0.02 mm is the diameter of the high-voltage electrode. Both electrodes are inserted in a transparent quartz tube, whose surfaces are optically polished[5], the main electrode being surrounded by a guard ring (figure 1(B)). The space within the main electrode and the guard ring is filled by a thin teflon cylinder. The other electrode is axially moveable by means of a micrometer, so that the gap can be varied: the measurement range is between 0.02 and 2.00 mm. The gap value is given by comparison between two images acquired via a video camera (Hamamatsu C5985) with a macro-objective, transforming it into a long focus distance microscope with low magnification (4×). A beam splitter shows a quoting grid in the same plane of the image (see figure 2).

The camera, microscope, beam splitter and grid are fixed onto an optical table. Note that the minimum value of the gap (0.02 mm) can in principle be smaller than in the commercial

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[5] The quartz tube was supplied by SILO, Firenze.

cell due to the excellent sensitivity of the optical detection. If $d = 0.4$ mm, the accuracy due only to the cell geometry is about 0.4%, and the total accuracy estimated, due to residual bubbles, is about 2%.

Both commercial and novel cells comprise for the largest gap a small sample volume, about a few ml.

2.4. Experimental method

For all samples the same procedure is adopted for both cells. Before each measurement, the cell is cleaned with soap and water, and carefully rinsed with ultra-pure water. The hydrogel is applied onto both electrode surfaces overlooking each other by spatula; the first electrode is inserted into the cell holder and fixed in proper position; the second electrode (the moveable one) is introduced on the opposite side of the cell holder until the hydrogel layers come in contact, leaving the gap at its maximum value imposed for the measuring set. The air leakage occurs from a small hole made in the upper central part of the cell support. If necessary, during the filling procedure, more hydrogel is poured into the cell from the sample reservoir in contact with the upper leakage hole. Care has to be taken in order to avoid the appearance of air bubbles, which could strongly affect the measurements. The filling procedure has been standardized since the magnitude of the gel visco-elastic response is strongly dependent on the type of the imposed mechanical motion. Once impedance measurement is completed at a given gap value, it is necessary to reduce the gap carefully, approaching the next smaller value to be investigated, allowing the excess gel amount to exit from the cell through the upper leakage hole. In order to start a new detection, it is important to have the gel in the same initial condition; then, it is necessary to take into account that the time dependence and the magnitude of the applied stress determine the mechanical strain character, providing a bulk compression of the polymer molecule long chains, which can undergo visco-elastic—or visco-plastic behavior. The retention of the same initial condition is ensured only in the first case; thus, the stress application must be slow and small in magnitude.

After the cell filling, it is necessary to wait at least 15 min before starting the measurement, in order to allow the sample to reach the thermodynamic equilibrium. Moreover, after the gap variation, it is enough to wait a few minutes. Earlier measurements provide non-repeatable results.

The measurement implies the analysis of the cell impedance for a given sample at four different gap values (in our case $d = 2.0$ mm, $d = 1.5$ mm, $d = 1.0$ mm and $d = 0.5$ mm); per gap value the measurement of a set of at least three runs is made, to verify the repeatability with the same applied voltage. Each single run consists of 100 points in logarithmic scale between 5 Hz and 1 MHz. The time to complete a single run is about 15 min. Moreover, three different applied potentials ($V = 100$ mV, $V = 60$ mV and $V = 15$ mV) are investigated per gap value.

The measurements were made at room temperature (about 20 °C). In every measurement set, the time instability causing lack of repeatability was checked. The source of such time instability could be the variation of ambient temperature, pressure, humidity and sample aging. To ensure stable conditions, runs were performed again till the response was satisfactorily repeatable (within 1%).

The measurements were performed using the *HP-4192A* low- and middle-frequency impedance analyzer. This instrument was connected with a computer through an interface *GP-IB*, which receives the information by means of a data acquisition program prepared by us. All the measurements were made with the impedance meter in the *serial* mode, which refers to the separate detection of the real and imaginary parts (resistance R and reactance X) of the
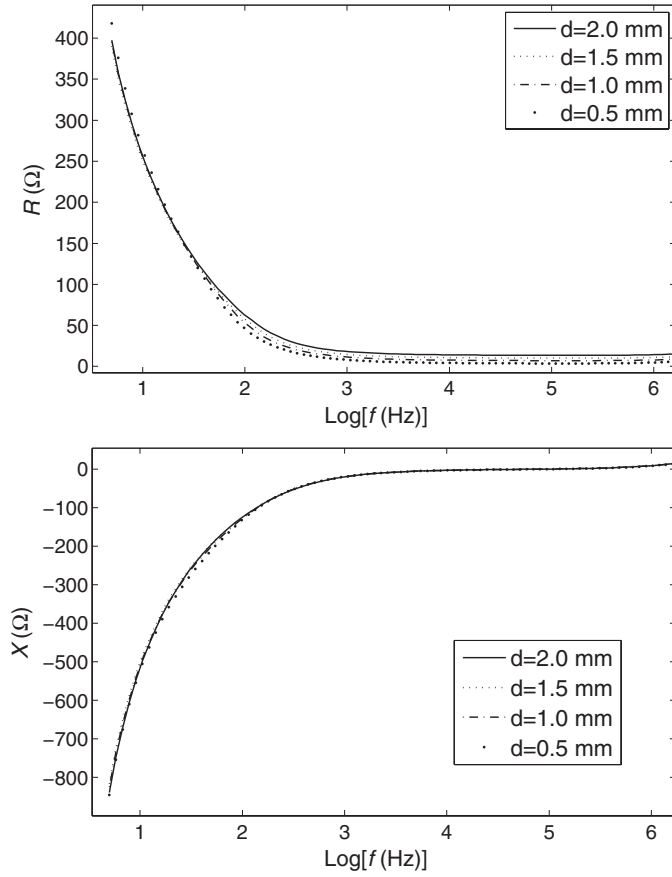
Figure 3. Real part (a) and imaginary part (b) of the experimental electrical impedance as a function of the frequency as measured with the novel cell at four different gap d values. The example of the novel cell filled by Cogel is reported, which illustrates the general trend of the R and X curves in both cells with all materials. At $f > 1$ kHz, R is proportional to d, whereas X is practically independent of it.

impedance Z. The serial mode is more convenient than the parallel mode, allowing a better separation of the bulk and surface impedance contribution, according to our model. The device calibration was performed on parallel and serial RC circuits, using high-precision standards ($\pm 1\%$): the values measured by us have accuracy consistent with the precision declared by the constructor (2%).

3. Results and discussion

In figure 3 the experimental data regarding the real and imaginary parts of the impedance of the novel cell filled by Cogel are shown, for different gap values. The data represent the typical behavior of all hydrogels investigated. Only when $f > 1$ kHz, R is proportional to the gap d, whereas X is practically independent of it.

The total cell impedance in general can be described as a series of bulk and interface contribution, $Z = Z_{\text{int}} + Z_B$ (Becchi *et al* 2007). In the hypothesis that the bulk term is

Table 1. Conductivity (σ) and CPE parameters. The values reported are relevant to the commercial stainless steel electrode cell and to the novel silver electrode cell with guard ring in each column (symbol with star).

Hydrogel	σ (S m^{-1})	σ^* (S m^{-1})	A ($10^4\ \Omega/s^\nu$)	A^* ($10^4\ \Omega/s^\nu$)	ν	ν^*
Cogel	2.02	3.13	0.90	2.87	0.73	0.77
Neurgel	4.18	6.39	2.38	1.38	0.64	0.71
Onegel	0.37	0.36	1.31	4.28	0.72	0.76
Zerogel	0.30	0.39	1.05	1.09	0.74	0.70
Accream	1.41	1.65	2.44	1.84	0.79	0.80
T20	0.54	0.89	2.60	1.43	0.79	0.79
Onecream	0.088	0.099	1.99	1.20	0.68	0.77
Bionen	0.063	0.091	6.47	1.17	0.67	0.76
EC2	2.35	3.18	2.41	1.23	0.74	0.76

given by a simple parallel of a capacitor and a resistance, its contribution in the series mode corresponds to a more or less constant term in the real part of the impedance below the relaxation frequency; in the imaginary part, this provides a peak around the same critical frequency, whereas in the whole remainder of the frequency range it approaches zero and can be neglected. Any deviation from this behavior is caused by the interface contribution. Then, the experimental series impedance, resulting from the sum of the interface and bulk contributions, can be expressed as a function of the sample bulk resistance and capacitance, i.e.

$$Z_B = R_B \frac{-\mathrm{i}/(\omega C_B)}{R_B - \mathrm{i}/(\omega C_B)}, \tag{1}$$

and

$$Z_{\text{int}} = A(\mathrm{i}\omega)^{-\nu} = A\omega^{-\nu}\left[\cos\left(\frac{\pi}{2}\nu\right) - \mathrm{i}\sin\left(\frac{\pi}{2}\nu\right)\right]. \tag{2}$$

Z_{int} is a phenomenological model, termed *Constant Phase Element* (CPE) (Macdonald 1987, Barbero *et al* 2008). In (1) R_B is the bulk parallel resistance, C_B is the parallel bulk capacitance, $\omega = 2\pi f$ is the angular frequency and i is the imaginary unit. In (2) A is the amplitude of the mixed surface impedance and ν is a parameter related to the phase-approximated shift. This model is suitable for describing the interface behavior in the frequency range (1 Hz, 1 kHz), provided we are interested to reach a precision not higher than 1%.

Hence only the mean bulk conductivities can be extracted from the experimental data with reasonable accuracy: they are reported in table 1 for both the commercial and silver electrode cell. As we can see, the first set of data have the same order of magnitude than the second one: this means that for general purpose it is acceptable to use the commercial cell, whereas, for metrological purpose or for comparing two models or for testing a theory, the more precise cell designed by us must be used.

As is evidenced in figure 3, the interface impedance contributes to the total impedance only in the low-frequency range (below 10^3 Hz), as expected (Becchi *et al* 2007). Moreover, all samples have relaxation frequencies much greater than 1 MHz; for this reason the peak in the X curve is absent and the dielectric constant cannot be determined. Note that this is also a consequence of the fact that the reactance X versus f is independent of the cell thickness; this means that the cell reactance at high frequencies, which is essentially a bulk contribution, is much lower than the resistance, i.e. almost negligible with respect to it. Furthermore, in
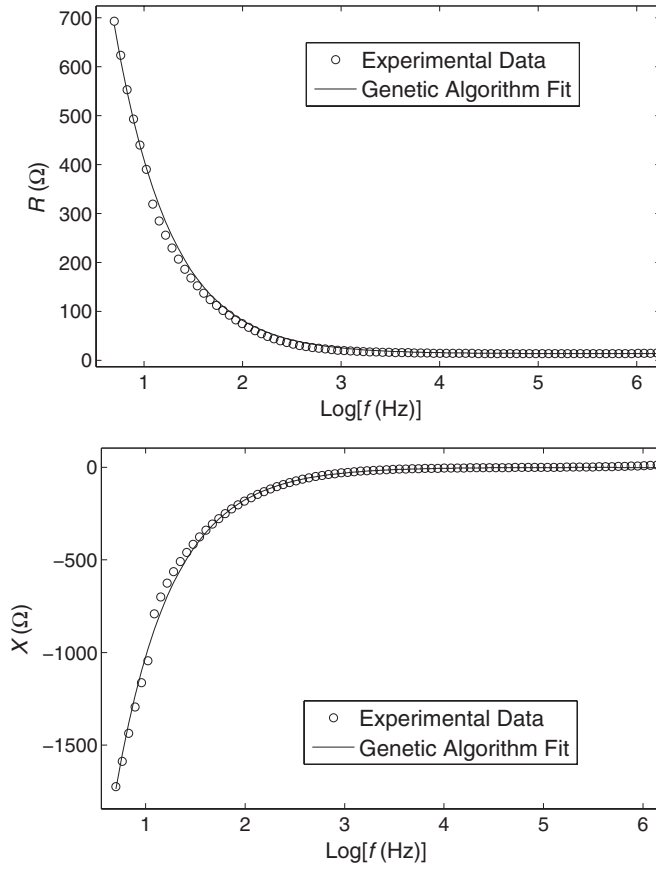
Figure 4. Fit with the genetic algorithm of the data of the novel cell filled by Cogel reported in figure3 for $d = 0.5$ mm, according to the CPE model.

figure 3 the cell resistance is shown to depend on the cell thickness only at high frequency ($f > 1$ kHz); this means that at lower frequency the cell resistance is affected only by the interface contribution, whereas at higher frequency it is mainly determined by the bulk:

$$R(f < 1 \text{ kHz}) \simeq \text{Re}(Z_{\text{int}})$$
$$R(f > 10 \text{ kHz}) \simeq \text{Re}(Z_B). \tag{3}$$

The conductivity of all samples determined by best fit is shown in table 1.

As shown in figure 4, concerning data elaboration from the novel cell, and in figure 5, concerning data elaboration from the commercial cell, the fit sensitivity is very good. In all cases we measured, the fits in the present model (sample impedance as a parallel of bulk capacitance and conductance in series with a CPE-surface) were performed according to the genetic algorithm[6] (Vose 1999). It describes the experimental data with very high resolution (within 1%) for both cells. The main difference between them concerns the estimated

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[6] A genetic algorithm is a method of optimization which iterates candidate encoded solutions forming a set (called population) of strings (called phenotypes) evolving to better solutions. Each iteration (generation) is randomly chosen and its fitness to the requested property is checked. The iterations stop when a satisfactory fitness is reached.
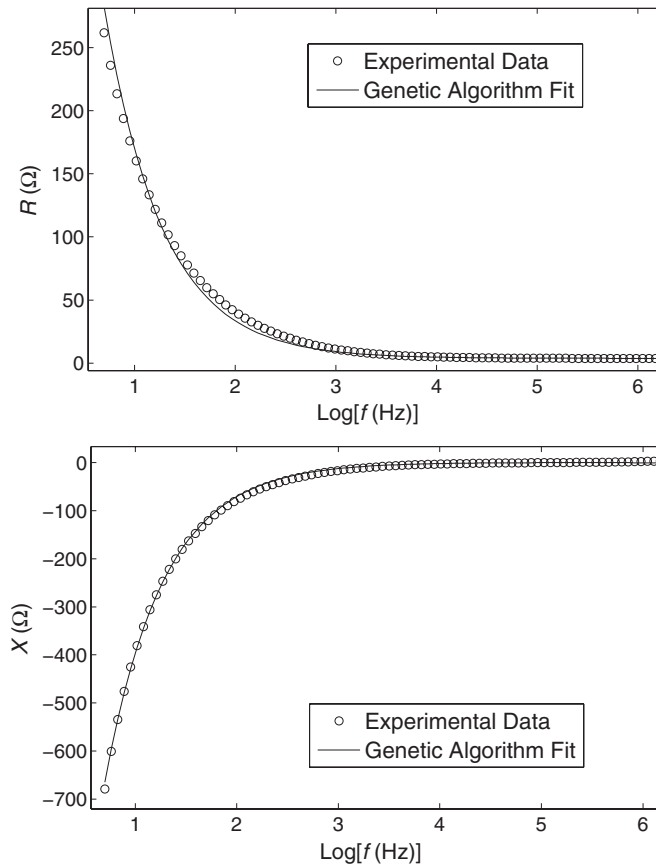
Figure 5. Fit with the genetic algorithm of the data of a commercial cell filled by Cogel for $d = 0.69$ mm, according to the CPE model.

accuracy, which is about 50% for the commercial cell and about 2% for the cell designed by us.

4. Conclusion

The cell we have designed is able to measure the bulk conductivity of either a transparent or an opaque hydrogel mixture commonly used in EMG applications with an estimated accuracy of about 2% due to its following features: silver-coated electrodes, presence of a guard ring, optical measurement of the gap, requiring only a camera observation during impedance detection. These characteristics are necessary for obtaining reliable repeatable data. In contrast, if for practical purpose it is enough to have only an order of magnitude of the gel conductivity, then the commercial cell with stainless steel electrodes is acceptable, giving results within 50% of those obtained with the more precise cell. This happens since the commercial cell needs to measure two lengths having very closed values, evaluating their difference to calculate the gap, which turns out to be known with high uncertainty. In this paper we have for the first time reported the conductivity of hydrogels currently applied for matching skin and electrodes contact in the frame of EMG.

Acknowledgments

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