

Article

Electrochemical Characterization of Commercial Electroencephalography Bioelectrodes in Isotonic Saline Solution

Alexandra C. Alves ^{1,2}, Patrique Fiedler ^{3,*} and Carlos Fonseca ^{1,2,*}

¹ Department of Mechanical Engineering, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal; alexandra.alves@fe.up.pt

² LAETA/INEGI, Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

³ Institute of Biomedical Engineering and Informatics, Technische Universität Ilmenau, Gustav-Kirchhoff-Str. 2, 98693 Ilmenau, Germany

* Correspondence: patrique.fiedler@tu-ilmenau.de (P.F.); cfonseca@fe.up.pt (C.F.)

Abstract

The electrochemical performance of eight commercially available bioelectrodes for electrophysiological measurements was systematically evaluated in isotonic saline solution. The studied bioelectrodes included sintered Ag/AgCl pellet, cup and ring, an Ag/AgCl multipin, tin (Sn) ring and disc, a gold cup, and a stainless-steel needle. Open circuit potential (OCP) and drift rate, electrochemical impedance spectroscopy (EIS), and electrochemical noise (ECN) measurements were performed to assess interfacial stability, impedance behavior, and generated noise in time and frequency domains. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were used to study the morphology and chemical composition of the bioelectrodes. Ag/AgCl-based bioelectrodes exhibited the highest OCP stability and potential reproducibility, lowest impedance, and electrochemical noise, attributed to the fast and reversible Ag/AgCl electrochemical equilibrium, and high area related to roughness and porosity. EIS analysis showed predominantly low-resistance charge-transfer behavior and high capacitance for Ag/AgCl bioelectrodes, while tin, gold, and stainless-steel bioelectrodes displayed higher impedance and mixed capacitive/resistive responses associated with passive oxide films and slower interfacial kinetics. Tin, gold, and stainless-steel bioelectrodes also presented substantially higher low-frequency noise and OCP drift rate. Among all tested bioelectrodes, sintered Ag/AgCl bioelectrodes demonstrated the most favorable electrochemical characteristics for electrophysiological signal acquisition, particularly for low-amplitude and low-frequency biosignals.

Keywords: bioelectrodes; electrophysiological signals; electrochemical impedance spectroscopy; electrochemical noise

Academic Editor: Dimitrios Tasis

Received: 3 June 2026

Revised: 25 June 2026

Accepted: 27 June 2026

Published: 30 June 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Electrophysiological potentials are generated by neural activity in the human body and can be measured at the tissue or body surface. They provide the foundation for clinical diagnostics, neurotechnology, biomedical research, and human–machine interaction applications [1,2]. These signals reflect the electrical activity of neuronal cell groups in real

time, providing a direct window into physiological function, enabling monitoring of e.g., the brain, heart, muscles, or ocular systems. Clinically, electrophysiological measurements support a wide range of applications. In neurology, electroencephalography (EEG) is used to diagnose epilepsy and sleep disorders, as well as to develop brain–computer interfaces [3]. In cardiology, electrocardiography (ECG) is essential for detecting arrhythmias and myocardial ischemia. Similarly, electromyography (EMG) supports the diagnosis of neuromuscular disorders, prosthetic limb control, and rehabilitation monitoring, while electrooculography (EOG) is used for eye-movement analysis and sleep stage classification [2]. Each of these signals differs in amplitude and frequency characteristics, see Table 1, but they all rely on the same underlying biophysical principles of ionic current flow and volume conduction [1,2]. More recently, advances in wearable technologies have expanded the use of bioelectrodes toward continuous, ubiquitous, and remote monitoring, enabling applications in personalized healthcare, fitness tracking, and long-term physiological assessment [4].

At the cellular level, electrophysiological potentials arise from ionic gradients across cell membranes. The synchronized activity of large populations of excitable cells produces extracellular field potentials that propagate through biological tissues and can be detected with appropriate bioelectrodes, either invasively or non-invasively on the body surface. As a result, surface-recorded signals represent the spatial and temporal average of the signals from a large number of underlying sources [2].

Table 1. Electrophysiological signal characteristics.

Technique	Typical Amplitude/ μV	Frequency Range/Hz
EEG	2–100	DC to >1000
ECG	1000–10,000	0.05 to 100
EMG	50–5000	2 to 500
EOG	50–5000	DC to 10

Electrophysiological potentials provide a real-time assessment of functional activity in related tissues. However, accurate recording requires careful selection of the bioelectrode material, control of the bioelectrode–tissue interface properties, particularly impedance and intrinsic noise, and appropriate amplifier design [3,5]. This is essential, especially when the signals have amplitudes in the microvolt range and/or include frequency components extending down to DC. In the case of non-invasive bioelectrodes, a gel is often used to optimize the signal conduction at the bioelectrode/tissue interface [6,7].

Bioelectrical signals (biopotentials) are acquired by transducing ionic charge transport within biological tissues into electronic conduction in the measurement system. This process occurs at the bioelectrode–tissue interface, where the bioelectrode enables electrochemical coupling for signal transfer. Consequently, the bioelectrode–tissue interface must facilitate efficient and accurate ionic-to-electronic transduction by maintaining low interfacial impedance and minimizing susceptibility to external electrical noise.

Major noise contributions are commonly associated with high skin–bioelectrode impedance, often resulting from inadequate hydration of the stratum corneum or poor bioelectrode–skin coupling [8–11]. Increased impedance—particularly when unbalanced between bioelectrodes—reduces common-mode rejection, increases susceptibility to electromagnetic interference, and exacerbates motion-induced artifacts due to time-varying interface impedance [8,12]. While this problem has been reduced due to advances in amplification electronics components, it is still evident in clinical practice. Furthermore, mechanical deformation of the bioelectrode–skin interface alters polarization potentials and contact impedance, generating additional voltage fluctuations superimposed on the physiological signal [13,14].

A bioelectrode must efficiently transduce ionic currents into electronic currents while introducing minimal distortion, baseline drift, or noise [5,7,11,15]. To achieve this, the bioelectrode should exhibit non-polarizable behavior, enabling fast and reversible electrochemical reactions. Additionally, it should maintain a stable half-cell potential to prevent DC drift, which can contaminate low-frequency signal components and may even saturate the amplifier. A high double-layer capacitance is also desirable, as it enhances low-frequency stability and reduces sensitivity to potential fluctuations at the bioelectrode–electrolyte interface. Deviations from the ideal behavior may be related to corrosion processes, slow charge-transfer kinetics, ionic adsorption/desorption at the metal surface, or passive film formation [16].

In this paper, eight commercially available bioelectrodes, primarily designed for EEG recording, were electrochemically evaluated in contact with isotonic saline solutions. However, owing to the diversity of tested materials, these bioelectrodes represent a broad spectrum of the most commonly used bioelectrode types across electrophysiological measurements and application scenarios. Ag/AgCl bioelectrodes are considered the gold standard for electrophysiological signal recording, and are known to provide the best signal quality, especially for low-frequency signal components [17]. Sn- and gold-coated bioelectrodes are cheaper than Ag/AgCl bioelectrodes and are suitable for most routine electrophysiological exams. Multipin Ag/AgCl bioelectrodes were developed specifically for dry EEG, and are usually used when rapid application, repetitive application, or avoiding consumables is a priority. Stainless-steel needle bioelectrodes are used percutaneously for invasive electrophysiological exams, which is a common application for neonatal EEG over extended periods like neonatal intensive care. The selected electrode materials and shapes, therefore, cover the most widely used electrode types and EEG applications to date.

The novelty of the present work lies in providing a systematic and controlled comparison of Ag/AgCl, Sn, gold, and stainless-steel bioelectrodes using a comprehensive electrochemical characterization protocol. To the authors' knowledge, this is one of the few studies to directly compare electrode materials under controlled experimental conditions. Beyond confirming the superior performance of Ag/AgCl electrodes, the study quantifies the extent to which alternative materials differ from Ag/AgCl in parameters relevant to electrophysiological recordings.

2. Materials and Methods

The studied bioelectrodes were purchased from different medical manufacturers except for the Multipin Ag/AgCl bioelectrode, which was produced according to prior work of some of the present authors on dry bioelectrodes [18,19]. Details for all bioelectrodes are listed in Table 2. The bioelectrode photos are shown in Figure 1.

Table 2. Studied commercial bioelectrodes.

Material	Shape	Manufacturer
sintered Ag/AgCl	Pellet bioelectrode	eemagine Medical Imaging Solutions GmbH, Berlin, Germany
sintered Ag/AgCl	Cup bioelectrode	BioMed Products Inc., Truckee, CA, USA
sintered Ag/AgCl	Ring bioelectrode	BioMed Products Inc., Truckee, CA, USA
Ag/AgCl on PU	Multipin bioelectrode	produced according to Fiedler et al. [18]
Sn	Ring bioelectrode	eemagine Medical Imaging Solutions GmbH, Berlin, Germany
Sn	Disc bioelectrode	eemagine Medical Imaging Solutions GmbH, Berlin, Germany
Au	Cup bioelectrode	Natus Medical Inc., Middleton, WI, USA
Stainless-steel	Needle bioelectrode	Natus Medical Inc., Middleton, WI, USA

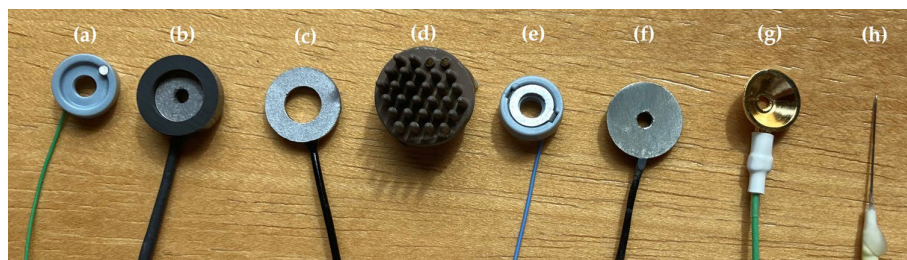


Figure 1. Macro-images for the studied bioelectrodes: (a) Ag/AgCl pellet, (b) Ag/AgCl cup, (c) Ag/AgCl ring, (d) Ag/AgCl Multipin, (e) Sn ring, (f) Sn disc, (g) gold cup, and (h) stainless-steel needle.

2.1. Bioelectrode Samples and Solution Preparation

Five samples of each bioelectrode type were tested for open circuit potential (OCP), and electrochemical impedance. Three bioelectrode couples were tested for electrochemical noise. The electrical wire connections of the bioelectrodes were cut to a similar length of about 10–15 cm. In the case of Sn ring bioelectrodes, where the wire connections were too short, new wires were welded to the original ones, and the electrical connections were insulated with Araldite™ glue (Huntsman Corporation, Salt Lake, UT, USA). For the Ag/AgCl multipin bioelectrodes, a 15 cm insulated electrical wire was soldered to the bioelectrode back plate using high-silver-content solder (ChipQuik, Ancaster, ON, Canada), and the contact was insulated with Araldite™ glue.

The test solution was prepared by dissolving 0.90 g sodium chloride (Merck KGaA, Darmstadt, Germany) per 100 mL of solution. The solution was freshly prepared for each bioelectrode type and discarded when it presented any signs of precipitates, color or cloudiness. Before the testing procedure, each sample was first cleaned by ultrasonication with 2-propanol (Merck KGaA, Darmstadt, Germany) for five minutes. Afterward, it was thoroughly rinsed with water. Before starting each experiment, each sample was equilibrated for 10 min in the solution. Finally, all experiments were carried out with the electrochemical cell inside a Faraday cage to minimize interference from external electromagnetic fields.

2.2. Secondary Electron Microscopy and Energy Dispersive Spectroscopy

The SEM/EDS exam was performed using a High-resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: FEI Quanta 400 FEG ESEM/EDAX Genesis X4M (Thermo Fisher Scientific, Waltham, MA, USA). Each sample was examined in 2–3 different regions to confirm the consistency of the observed features.

2.3. Open Circuit Potential Measurements

The Open Circuit Potential (OCP) was recorded for each bioelectrode for 3600 s, relative to an Ag/AgCl reference bioelectrode (XR 300, Radiometer Analytical, Villeurbanne, France). A Gamry G300 potentiostat/galvanostat (Gamry Instruments, Warminster, PA, USA) controlled by the Gamry software was used to monitor the electrochemical potential. The sampling rate was 0.5 Hz. The mean OCP curve and the 95% confidence interval were calculated for each bioelectrode.

2.4. Electrochemical Impedance Measurements

Prior to electrochemical impedance spectroscopy (EIS), the OCP evolution was monitored to warrant the stability of the system (bioelectrode/electrolyte interface), and the system was considered stable when $\Delta E < 60$ mV/h.

Electrochemical impedance spectroscopy (EIS) data was acquired with the Potentiostat/Galvonostat/ZRA (Model Interface 1000, Gamry Instruments, Warminster, USA) in the potentiostatic mode from 10^5 to 10^{-1} Hz (7 point per decade of frequency, avoiding multiples/sub-multiples of the network frequency), with a sinusoidal, 5 mV (RMS) signal amplitude. The DC potential was kept at the OCP during acquisition. An Ag/AgCl (3 M, XR 300) and a Platinum wire (Radiometer Analytical, Villeurbanne, France) were used as reference and counter electrodes, respectively. All the EIS results were normalized by the geometric exposed area of each bioelectrode to the electrolyte, even though the geometric-area normalization does not account for variations in electrode roughness, porosity, or electrochemically active surface area. Therefore, using the EIS results normalized by the geometric area should be interpreted as reflecting the overall electrode-level performance, including contributions from morphology and mass transport effects, rather than the intrinsic activity of individual electrochemically active sites. Thus, the exposed geometric areas of the Ag/AgCl based bioelectrodes are 0.07, 3.44, 1.78, and 12.66 cm² for pellet, ring, cup, and multipin bioelectrodes, respectively. Regarding the other bioelectrodes the exposed areas were 1.18, 4.28, 1.83, and 0.17 cm² for Sn ring and disc, gold and stainless-steel bioelectrodes, respectively.

The EIS experimental data was fitted using Z-view software (version 3.1) and the fitting quality for all electrodes was evaluated by chi-square (χ^2) values, being always $<10^{-3}$, together with fitted parameters obtained through the used electrical equivalent circuits (EECs).

2.5. Electrochemical Noise Measurements

Electrochemical potential noise was measured for three pairs of bioelectrodes of each type, for 15 min at a 1000 Hz sampling frequency. The Gamry Interface 1000 potentiostat was controlled by the Gamry ESA 410 electrochemical signal analyzer module. The Power Spectral Density (PSD) was calculated using the ESA 410 software's PSD calculation function with a Hanning smoothing window. The RMS value of the noise was calculated after detrending the data with a 4th-degree polynomial function. Two principal noise measurements were performed: (i) measurement of the respective bioelectrodes noise exposed to the electrolyte solution, and (ii) noise of the measurement device, achieved by short-circuiting the equipment's input cables [7].

3. Results and Discussion

3.1. SEM Analysis

3.1.1 Ag/AgCl pellet, Ag/AgCl ring and Ag/AgCl cup

These bioelectrodes exhibited comparable microstructural features and chemical compositions. Their production involves sintering, i.e., compacting and thermally consolidating silver powder, or a blend of silver and silver chloride powders, within a mold defining the targeted bioelectrode shape [15]. Figure 2 shows the bioelectrode's surfaces together with EDS spectra. The secondary electron (SE) images show a quite smooth and porous surface, and the back-scattered electron (BSE) images present grey brighter (Z2) and darker grey (Z1) areas corresponding to AgCl and Ag, respectively.

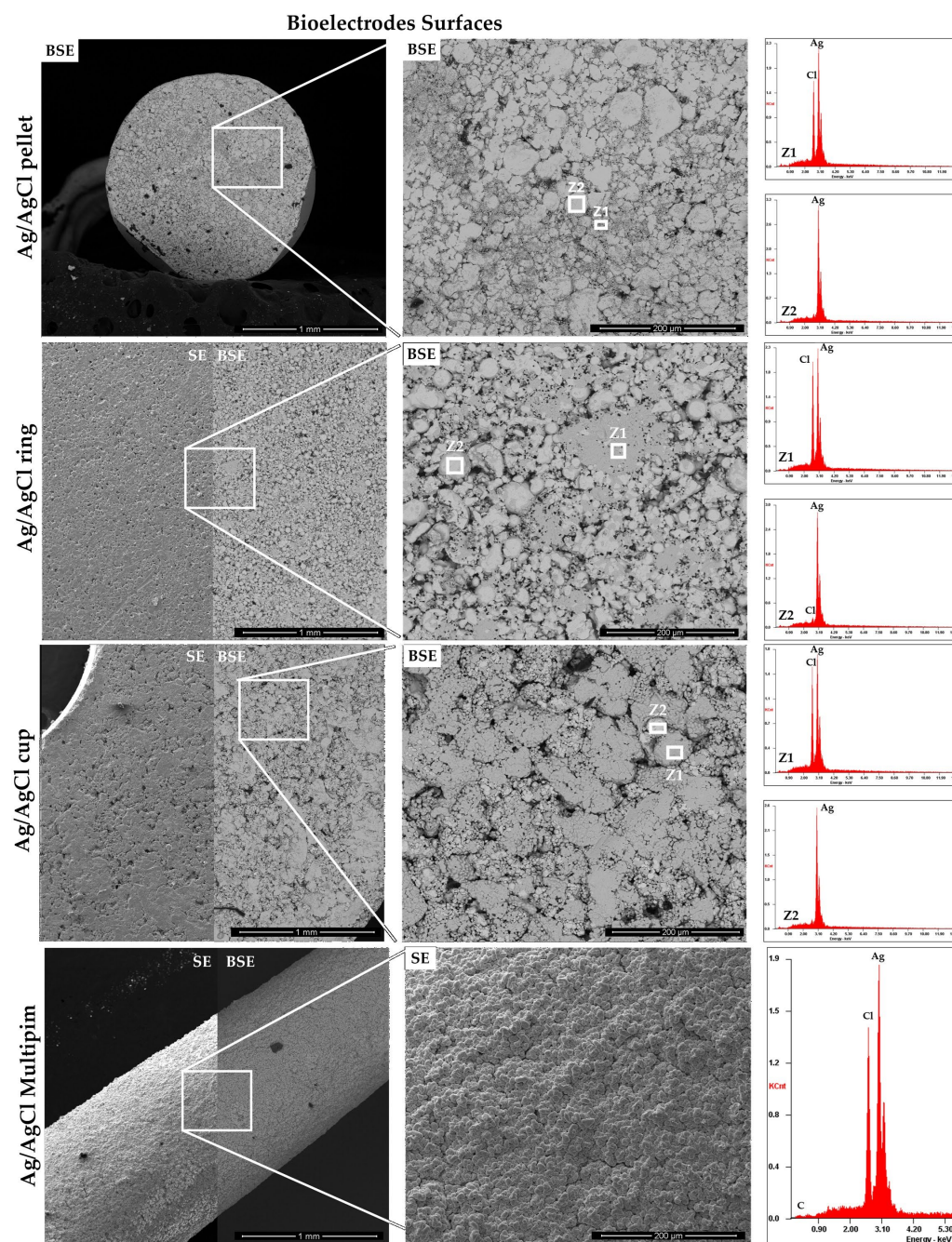


Figure 2. SE/BSE SEM images of the Ag/AgCl pellet, Ag/AgCl ring and Ag/AgCl cup bioelectrodes surfaces together with EDS spectra obtained in the marked zones.

3.1.2 Ag/AgCl Multipin

Multipin bioelectrodes are fabricated by first depositing silver via electroless plating, followed by chemical oxidation of the silver in the presence of chloride ions [20]. The morphological examination of a single pin sectioned from the electrode revealed a highly irregular surface composed of aggregated micrometer-scale silver particles, with occasional cracks and pores. The inset in Figure 3a shows signs of wear from repeated use, and the surface composition indicates a homogeneous AgCl coating (Figure 3b).

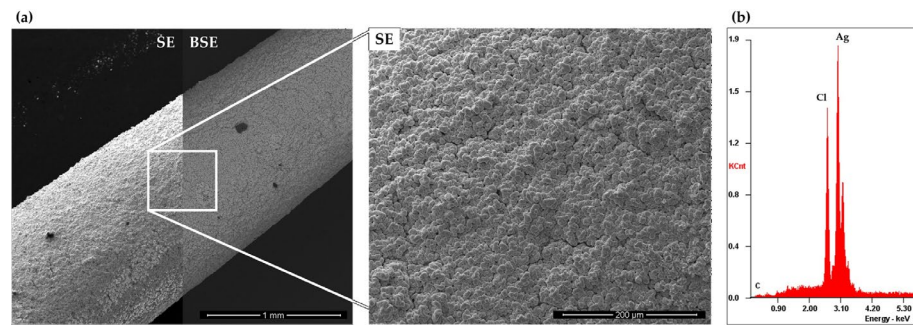


Figure 3. (a) SE/BSE SEM images of the Ag/AgCl multipin bioelectrodes surface and (b) respective EDS spectrum of the overall chemical composition.

3.1.3 Sn ring

The surface characteristics of the Sn ring bioelectrode are presented in Figure 4, highlighting the rough morphology resulting from the fabrication process (Figure 4a). The BSE micrograph reveals distinct darker areas. EDS performed on brighter areas (Z1) showed the presence of mainly Sn, while the darker regions consistently detected lead (Pb) (Z2), along with substantial oxygen levels, suggesting an increased concentration of metallic oxide species, either from Sn or Pb (Figure 4b).

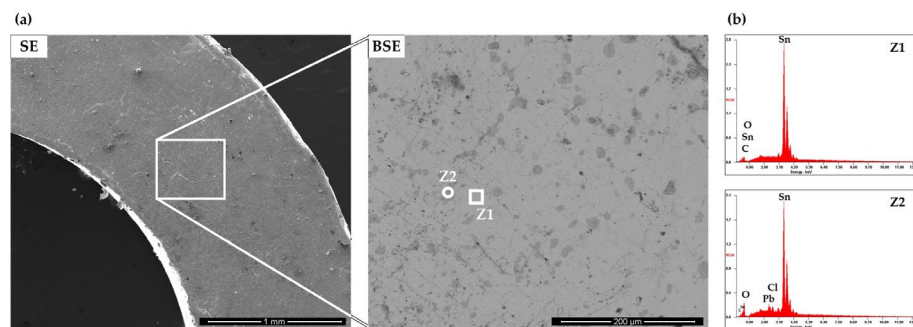


Figure 4. Analysis of the ring Sn bioelectrode: (a) SE/SEM topography and BSE micrograph with highlighted EDS analysis zones; (b) EDS spectra of marked regions (Z1 and Z2).

3.1.4 Sn disc

The Sn disc bioelectrode did not exhibit the distinct regions identified in the Sn ring. Likewise, the chemical analysis did not detect the presence of Pb, Figure 5b.

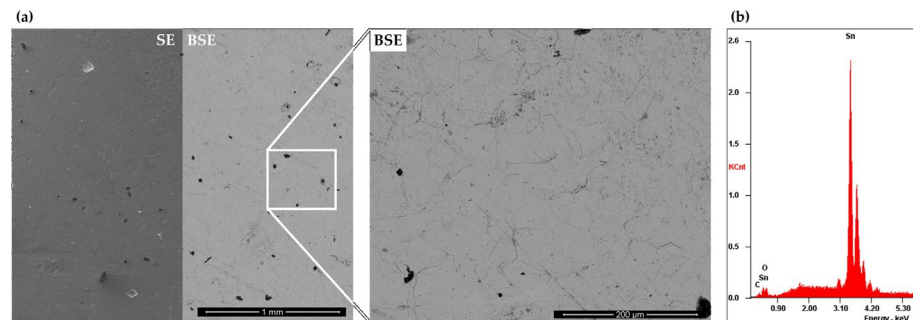


Figure 5. Analysis of the Sn disc bioelectrode: (a) SE/SEM images of the surface topography and BSE micrographs and (b) EDS spectra of the overall area of the inset area.

3.1.5 Gold cup

SEM of the gold bioelectrode showed a topography characterized by inherent irregularities arising from the manufacturing process, as shown in the SE/SEM image in Figure

6a. Intentional scratching presented in the SE/BSE SEM image in Figure 6b exposed an underlying Ag substrate, confirming that a thin gold coating was deposited on the substrate, see EDS spectra of regions Z1 and Z2 marked in Figure 6c.

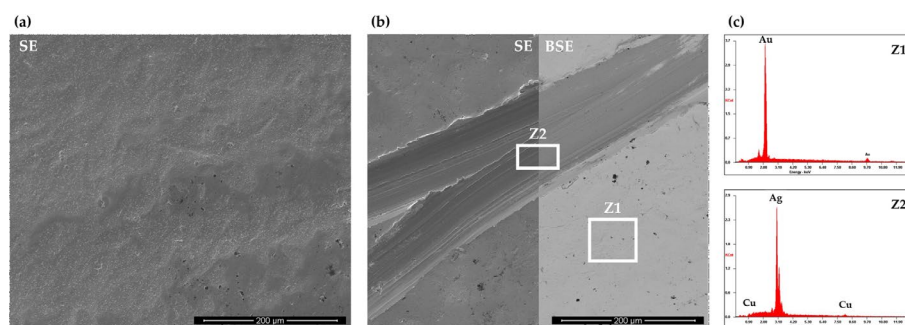


Figure 6. Analysis of the gold cup bioelectrode: (a) SE SEM image of topography, (b) SE/BSE SEM images with the scratch uncovering the presence of the Ag substrate and highlighted with the marked zones for (c) EDS analysis of regions Z1 and Z2.

3.1.6 Stainless-steel needle

The SEM image showed the presence of a smooth surface, and the chemical composition identified the presence of chromium, iron, nickel, and silicon, all usually associated with the composition of stainless-steel, Figure 7.

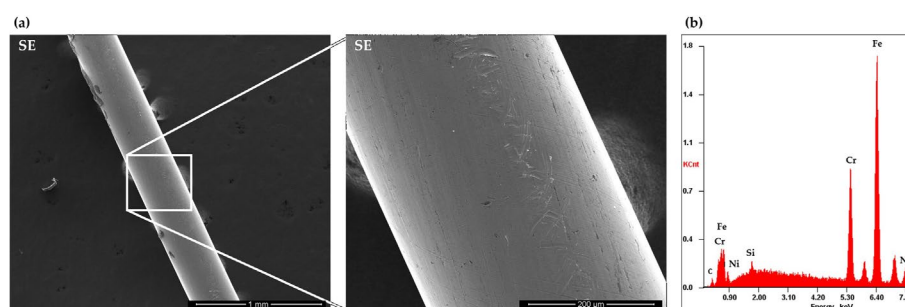


Figure 7. Analysis of the stainless-steel needle bioelectrode surface: (a) SE/SEM image of surface topography and (b) EDS spectrum of the overall area of the inset image.

3.2. Open Circuit Potential

The OCP is a key parameter that reflects the electrochemical interaction between a metal and the electrolyte or tissue. Temporal variations in OCP suggest interfacial modifications, such as the growth of a passive layer, corrosion processes, or ionic adsorption/desorption. Significant OCP drift can adversely affect physiological signal acquisition, hindering the detection of low-frequency potential fluctuations and ultimately leading to amplifier input saturation [21]. An isotonic saline solution was used to simulate the body fluids. Even if it does not fully reproduce the complexity of the electrode–skin interface found in electrophysiological recordings, it enables the intrinsic electrochemical behavior of the bioelectrode materials to be evaluated under simplified, but controlled and reproducible conditions. The use of a saline solution eliminates subject-to-subject variability and minimizes skin-related influences, enabling a direct comparison of the electrochemical characteristics.

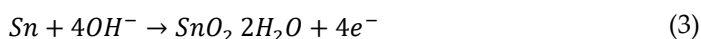
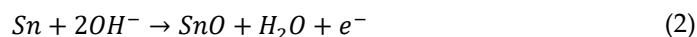
Figure 8 shows the average OCP value (left axis) and drift rate (right axis), with the shaded regions representing the standard deviation of five samples. It can be concluded that the Ag/AgCl bioelectrodes display the best reproducibility and the lowest drift rates ($<2 \mu\text{V/s}$) among all bioelectrodes. This behavior is attributed to the stable electrochemical

equilibrium established between metallic silver, chloride ions, and the AgCl layer at the electrode surface, according to Equation (1):

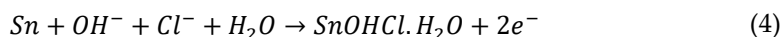


This reaction is characterized by a high exchange current density, which stabilizes the interfacial potential near its equilibrium value and minimizes sensitivity to small current perturbations [21]. Nevertheless, some differences in reproducibility were observed among the Ag/AgCl bioelectrodes, likely related to differences in fabrication processes. In the Ag/AgCl multipin bioelectrode (Figure 8d), the silver layer is deposited by electroless plating, followed by chemical chlorination to form the AgCl layer [18,19]. In contrast, the thermo-electrolytically manufactured bioelectrodes commonly used in commercial systems (Figures 8a–c) exhibit a porous sintered Ag/AgCl structure [12,15,17,22]. Minor differences among the sintered Ag/AgCl bioelectrodes may additionally arise from variations in geometry and surface microstructure [23].

For the Sn bioelectrodes (Figure 8e,f), the OCP stability was inferior to that of the Ag/AgCl bioelectrodes, particularly for the Sn disc, as evidenced by the significantly larger potential fluctuations, with the average OCPs in the range reported in the literature under similar conditions [24]. The lower OCP stability of Sn bioelectrodes has also been reported by Tallgren et al. [21]. It is caused by the gradual oxidation of Sn according to reaction Equations (2) and (3) with the formation of a porous oxide film:



or the formation of an oxychloride Sn compounds, according to reaction Equation (4)



The higher drift rate (5–25 $\mu\text{V/s}$) and lower reproducibility among bioelectrodes observed in the OCP for the Sn/chloride systems may be attributed to the formation of a blocking oxide film, followed by its permeation by the solution, or to the appearance of localized corrosion spots on the bioelectrode surface, possibly related to the presence of chloride. It is also important to note that the electrochemical behaviors of Sn ring and Sn disc bioelectrodes are quite different, with the Sn disc bioelectrodes displaying a higher OCP variability and offset than Sn ring bioelectrodes, Figure 8e,f. EDS analysis of the Sn ring bioelectrodes revealed Pb, O, and Cl, which may correspond to the formation of Pb oxychloride deposits. The micro-galvanic effect between Pb-rich phases (cathode) and the surrounding Sn matrix (anode) may accelerate the oxidation of Sn and promote the formation of a more stable mixed potential, less sensitive to tin oxide changes, which can contribute to improved OCP stability. To note that the average OCP of the Sn-ring bioelectrodes is more cathodic than the OCP of the S-disc, further supporting a mixed potential mechanism on the electrochemical behavior of these bioelectrodes. Sn-based bioelectrodes are straightforward to manufacture, exhibit sufficient mechanical durability to withstand repeated cleaning cycles, and represent a cost-effective alternative to Ag/AgCl systems [15].

The gold cup and stainless-steel needle bioelectrodes (Figures 8g,h) displayed significantly higher OCP drift rate and offset than the other bioelectrodes, reaching 20 $\mu\text{V/s}$ for gold and 100 $\mu\text{V/s}$ for stainless-steel. This behavior is attributed to the absence of a predominant faradaic process at the bioelectrode/solution interface and to their lower effective interfacial area. Consequently, the interfacial potential is primarily governed by the charging and discharging of the electrical double layer and slow adsorption/desorption processes. In the case of stainless-steel, a compact, insulating, passive film forms on the

surface, and the asymptotic potential increase may also be attributed to further thickening of the oxide layer in contact with the electrolyte.

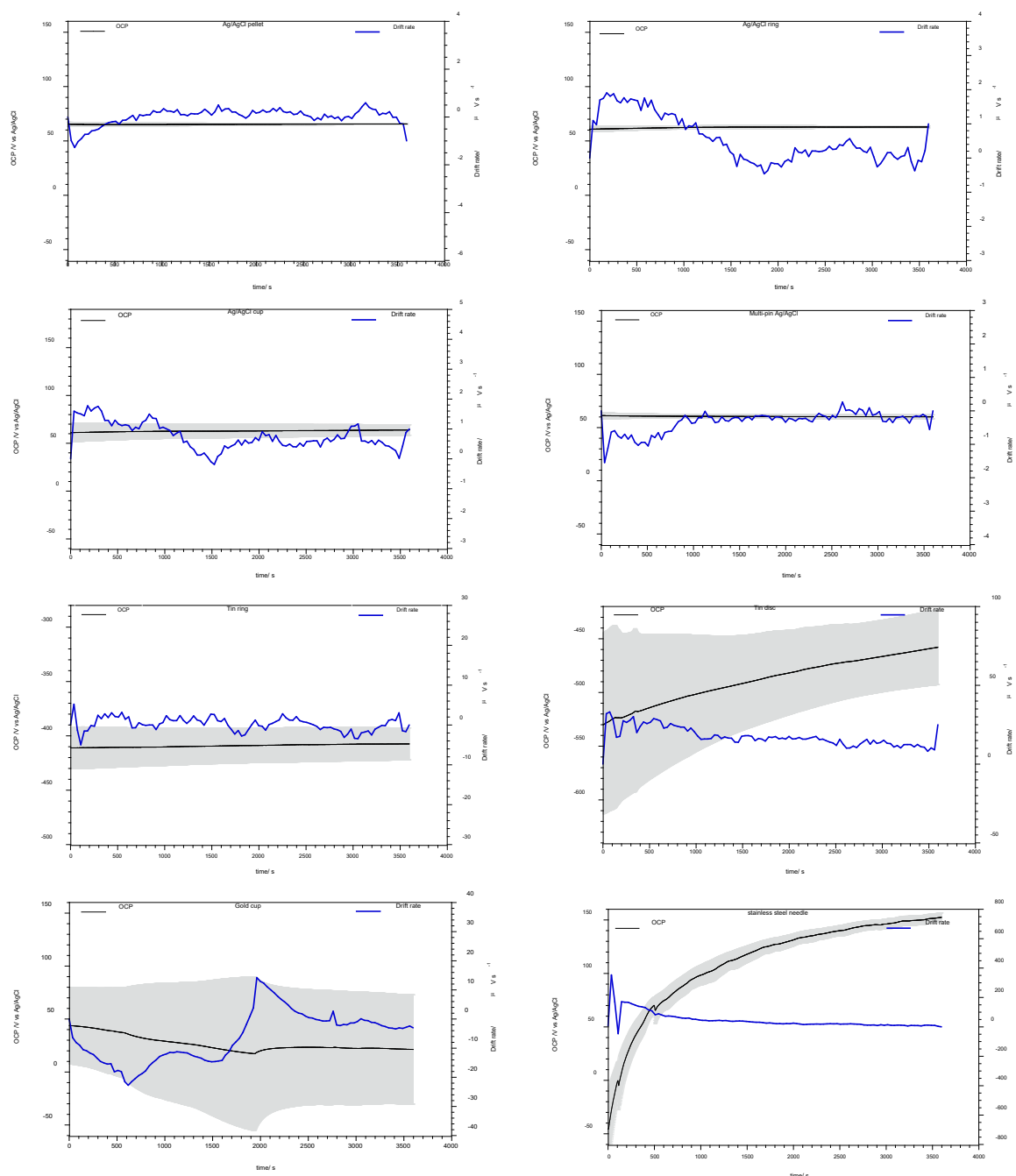


Figure 8. OCP of the bioelectrodes: (a) Ag/AgCl pellet, (b) Ag/AgCl ring, (c) Ag/AgCl cup, (d) Multipin Ag/AgCl, (e) Sn ring, (f) Sn disc, (g) Gold cup, and (h) stainless steel needle bioelectrodes, respectively. The black area represents the standard deviation for five bioelectrode samples.

3.3. Electrochemical Impedance Measurements

Electrochemical impedance spectroscopy (EIS) is a valuable technique for assessing the suitability of metallic electrode materials for electrophysiological signal acquisition, as it characterizes the electrical behavior of the electrode–conductive medium interface over a broad frequency range. EIS provides information on the resistive, capacitive, and, in some cases, inductive contributions to the impedance as a function of frequency. By fitting the impedance spectra with appropriate equivalent electrical circuit (EEC) models, it is

possible to associate the impedance response with electrochemical phenomena occurring at the interface, such as charge-transfer resistance, double-layer capacitance, and diffusion-related processes.

A high-quality bioelectrode for electrophysiological recordings should exhibit low impedance, high capacitance, and low polarization. Indeed, a low charge-transfer resistance reduces susceptibility to electromagnetic interference and motion artifacts, and a high interfacial capacitance is also desirable since it reduces low-frequency impedance and attenuates polarization-induced voltage fluctuations.

3.3.1. Ag/AgCl Based Bioelectrodes

The EIS spectra, presented as Bode diagrams for the Ag/AgCl-based bioelectrodes is shown in Figure 9 and EECs used to fit the EIS data are shown in Figure 10, while the fitting results are summarized in Table 3. Two types of EECs were proposed to describe the Ag/AgCl–electrolyte interface, accounting for the different microstructures of the bioelectrodes. In the Ag/AgCl pellet, cup, and disc bioelectrodes, the porous structure originates from the sintering of Ag/AgCl powders, whereas in the multipin bioelectrode it results from the silver electroless plating and electrochemical chlorination of the Ag surface (Figures 2 and 3) [25].

According to Figure 10, CPE_1 represents the capacitive behavior of the compact coating layer while the R_2/CPE_2 branch describes the resistive/capacitive behavior associated with the Ag/AgCl interfacial reaction given by Equation (1), occurring at the innermost surface. R_1 corresponds to the resistance encountered by ions as they move through the porous structure, and R_s represents the electrolyte resistance, Figure 10. The two EECs differ in whether a diffusion-related element accounting for ion transport in the deeper regions of the complex porous structure is included, depending on the bioelectrode architecture. Tjon et al. [26] and Polk et al. [20] proposed alternative EECs for the Ag/AgCl–electrolyte interface; however, these EECs did not provide satisfactory fits to the present experimental results, eventually because the AgCl coatings were produced by different methods.

All Ag/AgCl bioelectrodes display low impedance values ($100\text{--}300\ \Omega\text{-cm}^2$) and a relatively smooth phase response in the low-frequency region, both of which are indications of a good bioelectrode performance, Figure 9. The presence of a diffusion-related element in the pellet and multipin bioelectrodes, Table 3, indicates limitations in ionic transport at the electrode–electrolyte interface, likely associated with deep, narrow pores, Figures 2 and 3.

The multipin architecture is specifically designed to penetrate the hair layer and establish stable contact with the scalp. The core of the bioelectrode is composed of flexible thermoplastic polyurethane (TPU) coated with an electrochemically formed AgCl layer. This bioelectrode exhibits a capacitance approximately 30 times higher than that of the sintered bioelectrodes (Table 3), which may be attributed to the surface microstructure and pseudo-Faradic processes. This high charge-storage capacity will “absorb” small potential variations, contributing to bioelectrode stability. The CPE exponent (“ n ”) values, ranging from 0.7 to 0.8, indicate non-ideal capacitive behavior associated with significant interfacial heterogeneity, roughness, porosity, and distributed electrochemical time constants.

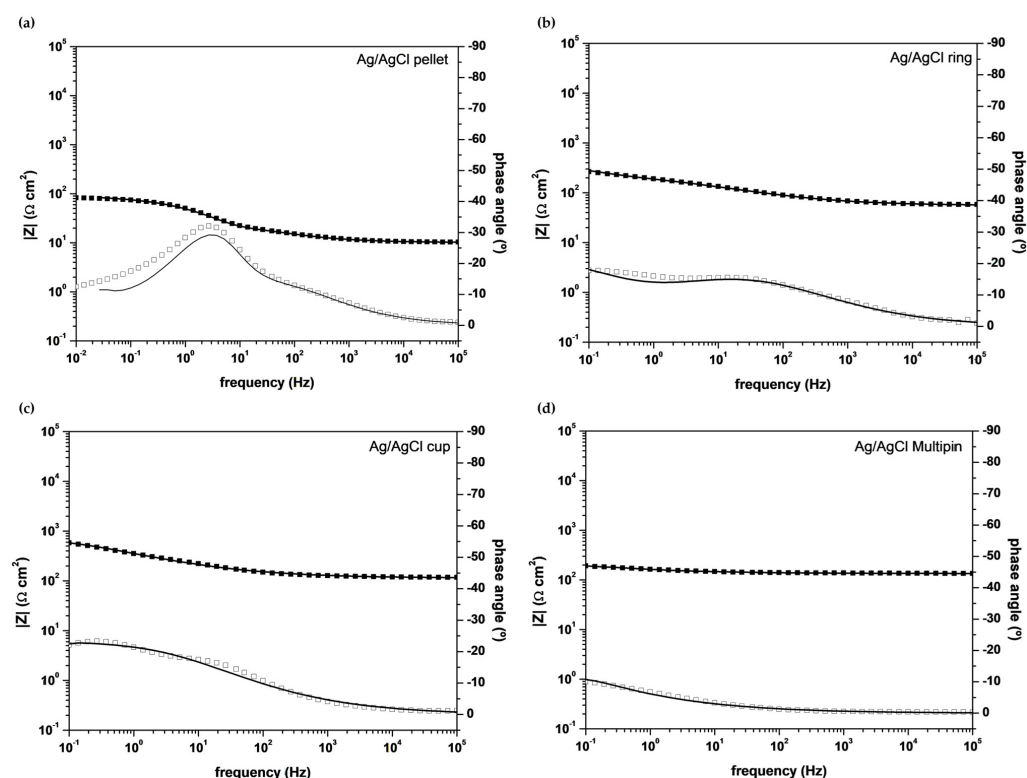


Figure 9. EIS spectra in the form of Bode diagrams for (a) Ag/AgCl pellet, (b) Ag/AgCl ring, (c) Ag/AgCl cup, and (d) Ag/AgCl multipin bioelectrodes (scattered—experimental data, straight line—fitted data, ■ — $|Z|$, and □ — phase angle).

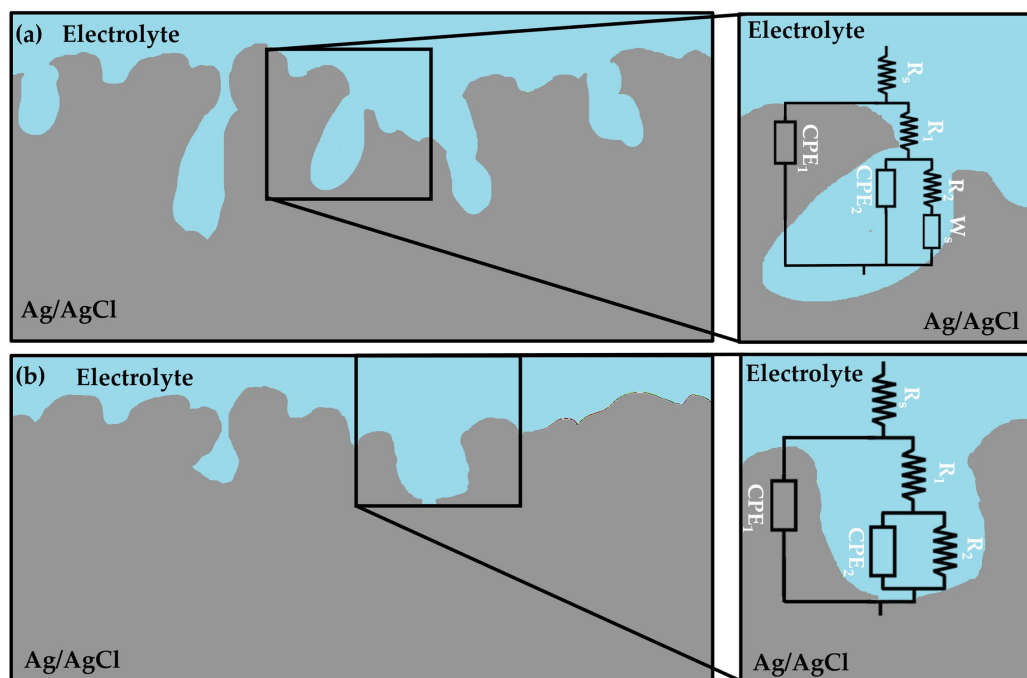


Figure 10. Schematic representation of the bioelectrode/electrolyte interface and corresponding EECs for the (a) pellet and multipin Ag/AgCl bioelectrodes, and (b) ring and cup Ag/AgCl bioelectrodes.

Table 3. Electrochemical parameters obtained from the proposed EECs for Ag/AgCl based bioelectrodes.

	R_1 ($\Omega \text{ cm}^2$)	R_2 ($\Omega \text{ cm}^2$)	CPE_1 ($\times 10^{-3} \text{ S s}^n \text{ cm}^{-2}$)	n_1	CPE_2 ($\times 10^{-3} \text{ S s}^n \text{ cm}^{-2}$)	n_2	W_{s-R} ($\Omega \text{ cm}^2$)	W_{s-T}	W_{s-P}	χ^2
Ag/AgCl pellet	19.18	61.02	1.01	0.79	4.07	0.72	81.30	53.40	0.51	$<10^{-2}$
Ag/AgCl ring	183.02	510.01	1.26	0.74	8.66	0.69	—	—	—	$<10^{-2}$
Ag/AgCl cup	139.61	411.00	1.58	0.74	3.37	0.80	—	—	—	$<10^{-2}$
Ag/AgCl multipin	136.60	138.50	29.95	0.73	15.81	0.74	107.86	136.60	0.55	$<10^{-3}$

3.3.2. Sn, Gold and Stainless-Steel Bioelectrodes

Although stainless-steel needle (invasive) bioelectrodes and surface (non-invasive) bioelectrodes are both used for bioelectrical signal acquisition, their fundamentally different interfaces (invasive vs. non-invasive) introduce differences in impedance, spatial selectivity, and signal transmission pathways. Therefore, the comparison presented in this study should be interpreted with consideration of these methodological differences.

The EIS spectra in the form of Bode diagrams for Sn, gold, and stainless-steel bioelectrodes in contact with saline solutions are reported in Figure 11, together with the EECs used to fit the data reported in Figure 12. The optimized EECs parameters are reported in Table 4.

According to Figure 12, CPE_1 corresponds to the capacitive behavior of the metal interface (gold), or to the non-porous areas of the oxides (Sn and stainless-steel), CPE_2/R_2 represents the capacitive and resistive behavior of the Faradic processes occurring within the pores, and R_1 corresponds to the electrolyte resistance within the pores in Sn bioelectrodes. The resistance values R_1 and R_2 are clearly higher than those for the Ag/AgCl-based bioelectrodes, which may be related to deeper/narrower pores (R_1) and a higher resistance to charge transfer (R_2).

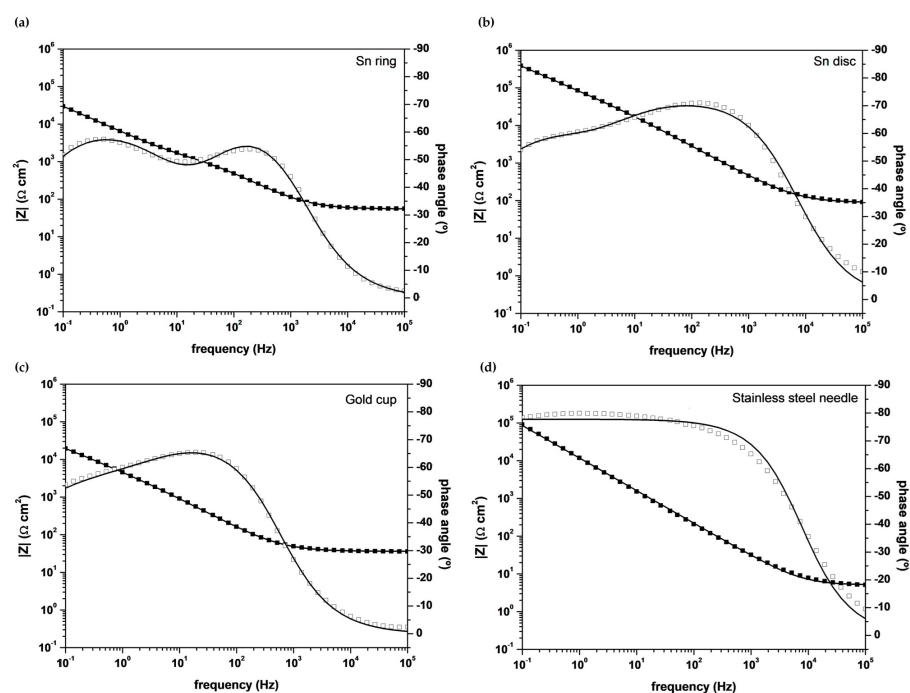


Figure 11. EIS spectra in the form of Bode diagrams for (a) Sn ring, (b) Sn disc, (c) gold cup, and (d) stainless-steel needle bioelectrodes together with the respective EECs used for fitting the experimental data (scattered—experimental data, straight line—fitted data, $\blacksquare$ — $|Z|$, and $\square$ —phase angle).

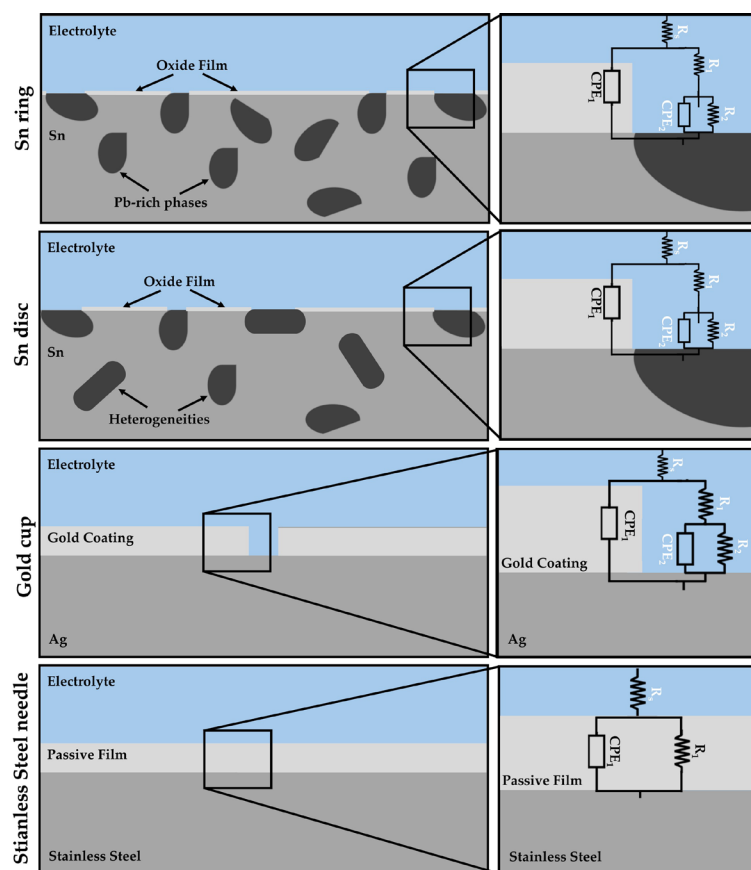


Figure 12. Schematic representation of the bioelectrode/electrolyte interface and corresponding EECs for the Sn ring, Sn cup, gold, and stainless-steel needle bioelectrodes.

Table 4. Electrochemical parameters obtained from the proposed EECs for Sn, Gold, and Stainless-steel bioelectrodes.

	$R_1 (\times 10^3 \Omega \text{ cm}^2)$	$R_2 (\times 10^5 \Omega \text{ cm}^2)$	$CPE_1 (\times 10^{-5} \text{ S s}^n \text{ cm}^{-2})$	n_1	$CPE_2 (\times 10^{-5} \text{ S s}^n \text{ cm}^{-2})$	n_2	χ^2
Sn ring	1.75	1.16	1.11	0.80	3.17	0.81	$<10^{-3}$
Sn disc	108.26	21.52	0.19	0.81	0.18	0.84	$<10^{-3}$
Gold cup	6.11	1.63	3.85	0.80	3.67	0.75	$<10^{-3}$
Stainless-steel needle	638.48	—	1.74	0.86	—	—	$<10^{-3}$

Furthermore, the presence of Pb in the Sn ring bioelectrode fundamentally influences its corrosion kinetics by creating microgalvanic cells within the metal matrix, as stated in Section 3.2. Because Pb and Sn have slightly different standard bioelectrode potentials, Pb tends to act as a cathode, while the surrounding Sn matrix functions as an anode and undergoes preferential dissolution (see Figure 4). This internal galvanic interaction accelerates the overall degradation of the bioelectrode in Cl-rich saline environments, resulting in higher corrosion current densities than in pure Sn.

In an EIS profile, this behavior typically manifests as a decrease in charge-transfer resistance (R_2 , Table 4), indicating that the electrochemical reactions at the interface occur more rapidly [27]. On the other hand, Pb-rich phases disrupt the natural passive oxide film (SnO/SnO_2) that typically protects Sn surfaces [28]. These disruptions create structural discontinuities in the protective layer, which serve as entry points for aggressive chloride ions, allowing active corrosion to initiate. Unlike the uniform passive layer found on pure Sn, the corrosion products formed in the presence of Pb are often more porous and less stable, preventing the bioelectrode from maintaining a high-resistance barrier.

The EIS behavior of the gold cup bioelectrode is best described by the proposed hierarchical EEC because microscopic defects in the gold coating expose the underlying silver substrate, Figure 12, creating a dual-layer interface where both materials contribute to the overall electrochemical response.

The stainless-steel needle bioelectrode is fitted with a significantly simpler EEC, known as a modified Randles circuit, where an R_s is in series with a pair R_1/CPE_1 , Figure 12. A single loop where the current splits between a resistive path (R_1) and a capacitive path (CPE_1). The physical significance of this EEC indicates that the stainless-steel needle forms a much more uniform protective film on the bioelectrode surface, lacking the multi-layered or deep-pore complexity that requires a nested EEC.

All in all, the Ag/AgCl-based bioelectrodes display resistance values two orders of magnitude lower and capacitance values two orders of magnitude higher than their Sn, gold, and stainless-steel counterparts, both of which contribute to better signal-recording performance, especially in the DC and low-frequency range.

3.4. Electrochemical Noise Measurements

The electrochemical reactions and adsorption phenomena at the bioelectrode–electrolyte interface produce fluctuations in the interfacial potential, generating electrical noise that can interfere with the accurate recording of electrophysiological signals. The electrochemical noise (ECN) technique is based on the analysis of small (μV range) voltage and/or current fluctuations recorded in open circuit conditions [29].

The average RMS noise values recorded for three couples of each bioelectrode type are plotted in Figure 13. The “Gamry short” represents the noise measured when the equipment’s terminals are short-circuited. It can be concluded that the Ag/AgCl bioelectrode types exhibit the lowest noise levels (5–12 μV). No statistical differences were detected between the “Gamry short” and the Ag/AgCl bioelectrodes ECN, according to the one-way ANOVA test ($p > 0.05$). The Sn, gold, and stainless-steel bioelectrodes display noise values 1–2 orders of magnitude higher, with the Sn bioelectrodes displaying the highest values, 306 μV and 637 μV , and the gold cup, and stainless-steel needle bioelectrodes displaying average noise values of 198 μV and 311 μV , respectively. No statistical differences were perceived between the ECN of these electrodes ($p > 0.05$). On the other hand, significant differences were found among the Ag/AgCl group and the Sn, gold, stainless-steel groups ($p < 0.05$).

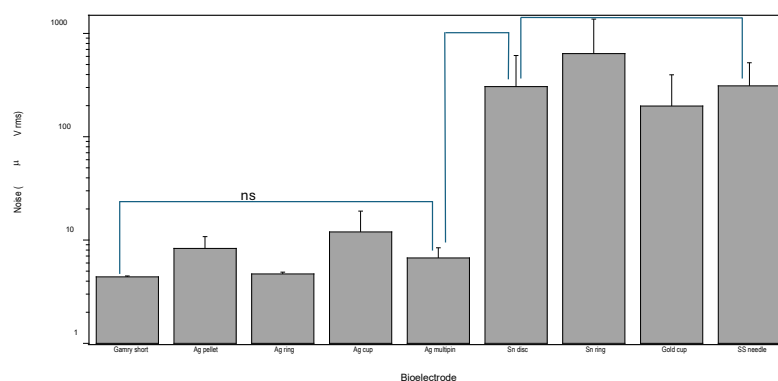


Figure 13. RMS values of ECN for three couples of each bioelectrode type. The bars represent the standard deviation. Statistical significance was assessed using one-way ANOVA test: asterisk and “no significance” (ns) indicate statistical significance (*: $p < 0.05$ and ns: $p > 0.05$, respectively).

The same ECN results are presented in the frequency domain as Power Spectral Densities (PSD) in Figure 14. All PSD curves display the same shape, characterized by a low,

constant noise of 10^{-13} – 10^{-15} V²/Hz from 10 Hz–100 Hz, followed by an increase of noise according with a $1/f^\alpha$ function [6,7] for frequencies below ~ 10 Hz. The higher ECN observed for the Sn, gold, and stainless-steel bioelectrodes is consistent with the higher OCP variability and drift rate of these bioelectrodes and the EIS results, as noise has been shown to increase with electrochemical potential instability and interfacial impedance [29,30]. The results confirm that the Ag/AgCl bioelectrodes exhibit the lowest PSD in the <10 Hz region, making them the most suitable for low-frequency and DC recording of electrophysiological signals.

However, the excellent performance of Ag/AgCl electrodes cannot be attributed to the Ag/AgCl equilibrium solely. Although the excellent reversibility and high exchange current of Ag/AgCl redox couple plays a fundamental role in stabilizing the interfacial potential and reducing drift, the bioelectrode microstructure is also important. Surface roughness and porosity increase the electrochemically active area, leading to a higher interfacial capacitance, lower impedance, and reduced total current. All in all, the overall performance of Ag/AgCl electrodes arises from the interplay between the intrinsic electrochemical properties of the Ag/AgCl equilibrium and the structural characteristics of the bioelectrode, including roughness, porosity, and effective surface area.

It is also important to note that a 15-min recording duration enables reliable assessment of electrode stability at frequencies down to approximately 0.01 Hz (100 s per cycle), which corresponds to the lowest frequency represented in the spectra. This frequency range encompasses most conventional EEG and DC-EEG recordings. However, the characterization of ultra-slow phenomena, such as the slowest cortical potential and long-term electrode drift, would require longer ECN acquisition times.

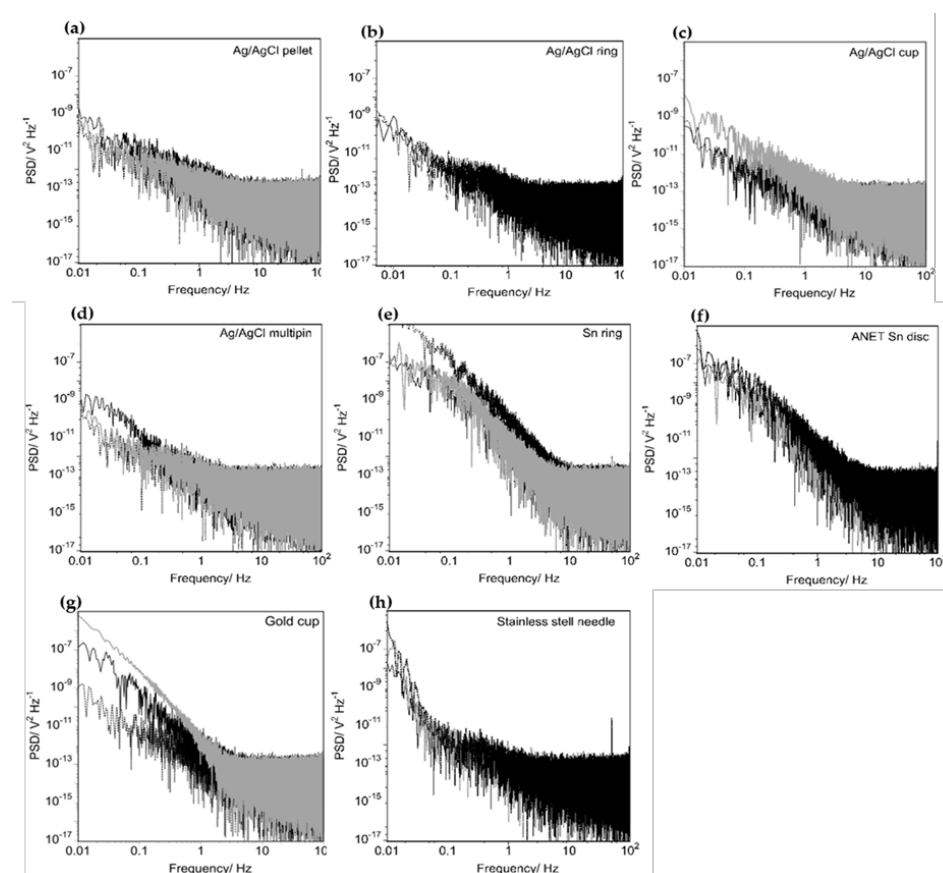


Figure 14. Power Spectral density as a function of frequency (Hz) of the bioelectrode couples: (a) Ag/AgCl pellets, (b) Ag/AgCl ring, (c) Ag/AgCl cup, (d) Ag/AgCl multipin, (e) Sn ring, (f) Sn disc, (g) gold cup, and (h) Stainless steel needle.

4. Conclusions

The electrochemical behavior of eight commercially available bioelectrodes for electrophysiological recordings was evaluated in isotonic saline solution using OCP, EIS, and ECN measurements, complemented with SEM/EDS analysis. The results demonstrated that the electrochemical performance of the bioelectrodes is strongly dependent on the nature of the bioelectrode/electrolyte interface, particularly the interfacial electrochemical reactions, surface morphology, and oxide film characteristics.

Ag/AgCl-based bioelectrodes exhibited the best overall electrochemical performance, characterized by excellent OCP stability, low interfacial impedance, high capacitance values, and low ECN, particularly at low frequencies.

Sintered Ag/AgCl bioelectrodes, particularly the pellet and ring configurations, displayed the lowest noise levels and the most stable low-frequency behavior, making them especially suitable for the accurate recording of low-amplitude and low-frequency bio-signals.

In contrast, Sn, gold, and stainless-steel bioelectrodes presented higher impedance, larger potential drift, and significantly increased low-frequency noise. Their electrochemical behavior was dominated by passive oxide films, slower charge-transfer kinetics, and interfacial heterogeneity, which compromise signal stability and increase susceptibility to baseline fluctuations. The stainless-steel needle bioelectrode exhibited highly capacitive behavior associated with a compact passive film, while Sn bioelectrodes showed evidence of unstable oxide formation and corrosion processes.

Overall, from the point of view of the bioelectrode/isotonic solution interface, and excluding the influence of the skin contact, the results confirm that Ag/AgCl bioelectrodes remain the most suitable choice for high-fidelity electrophysiological recordings with wet and semi-dry electrodes, particularly in applications requiring low noise, stable DC behavior, and accurate acquisition of low-frequency physiological signals.

Author Contributions: Conceptualization, C.F., P.F.; Methodology, C.F., P.F.; Validation, C.F., P.F., A.C.A.; Formal analysis, C.F., P.F., A.C.A.; Investigation, A.C.A., C.F.; Data curation, A.C.A., C.F.; Writing—original draft preparation, C.F.; Writing—review and editing, C.F., A.C.A., C.F.; Supervision, C.F.; Project administration, C.F.; Funding acquisition, P.F. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT) for its financial support to LAETA via the project UID/50022/2025 (DOI: <https://doi.org/10.54499/UID/50022/2025>), the German Federal Ministry for Economic Affairs and Energy, grant number KK5358202CR3; the German Federal Ministry of Research, Technology and Space, grant numbers 01QE2316C and 13GW0721C. We acknowledge support for the publication costs by the Open Access Publication Fund of the Technische Universität Ilmenau.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Acknowledgments: The authors would like to acknowledge CEMUP (Centro de Materiais da Universidade do Porto) for SEM analysis.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BSE	Back-scattered electrons
ECG	Electrocardiography
ECN	Electrochemical noise
EDS	Energy-dispersive X-ray spectroscopy
EEC	Equivalent electrical circuit
EEG	Electroencephalography
EIS	Electrical Impedance Spectroscopy
EMG	Electromyography
EOG	Electrooculography
OCP	Open Circuit Potential
PSD	Power Spectral Density
RMS	Root-Mean-Square
SE	Secondary electrons
SEM	Scanning Electron Microscopy

References

1. Maltzahn, W.W. Medical Instruments and Devices. In *The Biomedical Engineering Handbook Medical Devices and Systems*; Bronzino, J.D., Ed.; Taylor & Francis: Oxfordshire, UK, 2006.
2. Clark, J.W., Jr. The Origin of Biopotentials. In *Medical Instrumentation: Application and Design*; Webster, J.G., Ed.; Wiley: Hoboken, NJ, USA, 2009.
3. Qin, Y.; Zhang, Y.; Zhang, Y.; Liu, S.; Guo, X. Application and Development of EEG Acquisition and Feedback Technology: A Review. *Biosensors* **2023**, *13*, 930. <https://doi.org/10.3390/bios13100930>.
4. Surantha, N.; Atmaja, P.; David; Wicaksono, M. A Review of Wearable Internet-of-Things Device for Healthcare. *Procedia Comput. Sci.* **2021**, *179*, 939–943. <https://doi.org/10.1016/j.procs.2021.01.083>.
5. Kim, K.; Jeong, J.Y.; Shin, J.H.; Kim, T.-i. Materials and Structures of Skin-Interfaced Electrodes for Reducing Motion Artifacts in Neural Recording. *Small Methods* **2025**, *10*, e01718. <https://doi.org/10.1002/smt.202501708>.
6. Huigen, E.; Peper, A.; Grimbergen, C.A. Investigation into the Origin of the Noise of Surface Electrodes. *Med. Biol. Eng. Comput.* **2002**, *40*, 332–338.
7. Fernández-Chimeno, M.; Pallas-Areny, R. Ag-AgCl Electrode Noise in High-Resolution ECG Measurements. *Biomed. Instrum. Technol.* **2000**, *24*, 125–130.
8. Habibzadeh Tonekabony Shad, E.; Molinas, M.; Ytterdal, T. Impedance and Noise of Passive and Active Dry EEG Electrodes: A Review. *IEEE Sens. J.* **2020**, *20*, 14565–14577. <https://doi.org/10.1109/JSEN.2020.3012394>.
9. Xiong, F.; Fan, M.; Feng, Y.; Li, Y.; Yang, C.; Zheng, J.; Wang, C.; Zhou, J. Advancements in Dry and Semi-Dry EEG Electrodes: Design, Interface Characteristics, and Performance Evaluation. *AIP Adv.* **2025**, *15*, 040703. <https://doi.org/10.1063/5.0228644>.
10. Tam, H.W.; Webster, J.G. Minimizing Electrode Motion Artifact by Skin Abrasion. *IEEE Trans. Biomed. Eng.* **1977**, *207*, 134–138.
11. Merletti, R. The Electrode-Skin Interface and Optimal Detection of Bioelectric Signals. *Physiol. Meas.* **2010**, *3*, S157. <https://doi.org/10.1088/0967-3334/31/10/e01>.
12. Bayat, M.; Safaie, J.; Beidokhti, S.M.; Wallois, F. A Comprehensive Review of EEG Electrode Technologies: Advancements, Applications, and Future Directions. *Sens. Actuators A Phys.* **2026**, *399*, 117396. <https://doi.org/10.1016/j.sna.2025.117396>.
13. De Talhouet, H.; Webster, J.G. The Origin of Skin-Stretch-Caused Motion Artifacts under Electrodes. *Physiol. Meas* **1996**, *17*, 81–93.
14. Edelberg, R. Local Electrical Response of the Skin to Deformation. *J. Appl. Physiol.* **1973**, *34*, 334–340.
15. Newman, M.R. Biopotential Electrodes. In *Medical Instrumentation: Application and Design*; Webster, J.G., Ed.; Wiley: Hoboken, NJ, USA, 2009.
16. Hassibi, A.; Navid, R.; Dutton, R.W.; Lee, T.H. Comprehensive Study of Noise Processes in Electrode Electrolyte Interfaces. *J. Appl. Phys.* **2004**, *96*, 1074–1082. <https://doi.org/10.1063/1.1755429>.
17. Lito, M.J.G.; Camões, M.F. Meeting the Requirements of the Silver/Silver Chloride Reference Electrode. *J. Solut. Chem.* **2009**, *38*, 1471–1482. <https://doi.org/10.1007/s10953-009-9462-8>.

18. Fiedler, P.; Pedrosa, P.; Griebel, S.; Fonseca, C.; Vaz, F.; Supriyanto, E.; Zanow, F.; Haueisen, J. Novel Multipin Electrode Cap System for Dry Electroencephalography. *Brain Topogr.* **2015**, *28*, 647–656. <https://doi.org/10.1007/s10548-015-0435-5>.
19. Mota, A.R.; Duarte, L.; Rodrigues, D.; Martins, A.C.; Machado, A.V.; Vaz, F.; Fiedler, P.; Haueisen, J.; Nóbrega, J.M.; Fonseca, C. Development of a Quasi-Dry Electrode for EEG Recording. *Sens. Actuators A Phys.* **2013**, *199*, 310–317. <https://doi.org/10.1016/j.sna.2013.06.013>.
20. Polk, B.J.; Stelzenmuller, A.; Mijares, G.; MacCrehan, W.; Gaitan, M. Ag/AgCl Microelectrodes with Improved Stability for Microfluidics. *Sens. Actuators B Chem.* **2006**, *114*, 239–247. <https://doi.org/10.1016/j.snb.2005.03.121>.
21. Tallgren, P.; Vanhatalo, S.; Kaila, K.; Voipio, J. Evaluation of Commercially Available Electrodes and Gels for Recording of Slow EEG Potentials. *Clin. Neurophysiol.* **2005**, *116*, 799–806. <https://doi.org/10.1016/j.clinph.2004.10.001>.
22. Patrick, E.; Ordonez, M.; Alba, N.; Sanchez, J.C.; Nishida, T. Design and Fabrication of a Flexible Substrate Microelectrode Array for Brain Machine Interfaces. *Conf. Proc. IEEE Eng. Med. Biol. Soc.* **2006**, *2006*, 2966–2969.
23. Brewer, P.J.; Brown, R.J.C. Effect of Structural Design of Silver/Silver Chloride Electrodes on Stability and Response Time and the Implications for Improved Accuracy in pH Measurement. *Sensors* **2009**, *9*, 118–130. <https://doi.org/10.3390/s90100118>.
24. Al-Mayouf, A.M.; Al-Suhybani, A.A. The Behaviour of Tin Electrode in Aqueous Solutions. *Mater. Sci. Eng. Technol.* **1994**, *25*, 292–299.
25. Ha, H.; Payer, J. The Effect of Silver Chloride Formation on the Kinetics of Silver Dissolution in Chloride Solution. *Electrochim. Acta* **2011**, *56*, 2781–2791. <https://doi.org/10.1016/j.electacta.2010.12.050>.
26. Tjon, K.C.E.; Yuan, J. Impedance Characterization of Silver/Silver Chloride Micro-Electrodes for Bio-Sensing Applications. *Electrochim. Acta* **2019**, *320*, 134638. <https://doi.org/10.1016/j.electacta.2019.134638>.
27. Zohdy, K.M.; El-Sherif, R.M.; El-Shamy, A.M. Corrosion and Passivation Behaviors of Tin in Aqueous Solutions of Different PH. *J. Bio Tribocorros.* **2021**, *7*, 74. <https://doi.org/10.1007/s40735-021-00515-6>.
28. Fan, Z.; Wang, X.; Zhou, H.; Shi, J.; Chen, J.; Song, J.; Xiao, K. Study on the Corrosion Mechanisms Evolution of Dual-Phase Tin-Lead Bronze. *Corros. Sci.* **2025**, *252*, 112975. <https://doi.org/10.1016/j.corsci.2025.112975>.
29. Mansfeld, F.; Sun, Z.; Hsu, C.H. Electrochemical Noise Analysis (ENA) for Active and Passive Systems in Chloride Media. *Electrochim. Acta* **2001**, *46*, 3651–3664.
30. Cottis, R.A. Interpretation of Electrochemical Noise Data. *Corrosion* **2001**, *57*, 265–285.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.