Saline solution impedance sensor based on Poly Methyl Methacrylate and graphite: preliminary results

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Abstract. This paper shows a preliminary study of behaviour comparison in NaCl and KCl saline solutions of three screen printed bipolar electrodes with a coating mixture of Poly Methyl Methacrylate (PMMA) and graphite. Results indicate greater selectivity of the coating electrodes with partial ring geometry compared with concentric and spiral bipolar, cover mixture allows eliminating electrolyte electrode interface in low frequencies. The benefits of using this electrode are: optimize sample measurements; low-cost manufacturing; integration feasibility into a mobile device. Upcoming research requires including test with other ionic solutions and new doped graphite composes.

1. Introduction
Monitoring methods of saline concentration in aqueous solutions are based in laboratory equipment as UV-Vis measurements, mass spectrometry, ion-sensitive electrodes and amperometric sensors [1]. The amperometric sensors as screen-printed electrodes (SPE) can be adapted in impedance spectroscopy measurements. These electrodes are constructed with several shapes, configurations and surface modifications to obtain information of cells in suspensions [2], biomarker detection [3] and toxic detection with microfluidic [4].

The SPE are based on thick-film technology with a fabrication process relatively simple and applicability in tiny aqueous samples due portability [5], the main advantage of this technique is low cost and minimized error as real time method to detect chemical profile [1,6]. Such advances permit favorable and easy procedures as monitoring system due time reduction of sample collection and avoid transport to a central laboratory [6].

SPE surface modified are made with nanoparticles of metals (gold, platinum, titanium oxide, cooper) [7], but also using carbon based materials as nanotubes, nanofibers, graphene and graphite [4]. The capacities of carbon based materials as electro-activity, biocompatibility, chemical stability, large potential window, marginal polluting of biological samples [8,9], Surface contact is improved due to electrical properties of semiconductor/electrolyte interface and the effects as dielectric relaxation in the depletion layer, deep donor levels and roughness of electrode surface [10].

In this paper, we propose a saline concentration electrode using three geometries of cooper bipolar SPE with modified surface of PMMA and graphite powder. The objective is to reduce the electrode electrolyte interface at lower frequencies for electrical impedance spectroscopy applications.
2. Methodology

2.1. Bipolar screen printed electrode geometries
The bipolar electrodes were constructed using three patterns; first pattern was a partial ring with 8 mm of inner diameter and 10 mm of outside diameter, and a center diameter of 1 mm (figure 1a). Second electrode shape is an Archimedes spiral with three turns, 10 mm of diameter and 1 mm in both thickness and separation (figure 1b). Third shape was a concentric interdigitated electrode with 10 mm of diameter, and 1 mm of thickness and separation (figure 1c).

![Figure 1](image1.png)

Figure 1. Electrode geometry shapes (a) Partial ring; (b) Archimedes spiral; (c) Concentric.

2.2. Surface preparation
Two sets of three electrode geometries were manufactured by a standard printed circuit board technique using copper clad laminate Bakelite. The first set remained with the copper exposed (figure 2a), while the second was covered with a 100 µm thickness layer of PMMA (62% weight) and graphite powder (38% weight). The polymerization of the mixture was in situ (figure 2b).

![Figure 2](image2.png)

Figure 2. Electrode surface (a) cooper (b) modified with PMM-graphite.

2.3. Impedance measurements
Impedance measurements of saline solution was made using HF2IS (Zürich Instruments), setting a voltage unity gain which was injected in the sample and collecting 80 discrete frequency point between 10 Hz to 1 MHz. The experiments were performed using NaCl and KCl saline solutions of two different concentrations (93.7 mM/ml and 3 M/ml) with a volume of approximately 0.5 ml. Before each experiment, both copper and PMM electrodes were cleaned with isopropyl alcohol in order to eliminate the oxidation and salt particles, and then the electrodes were dried for further experiments.
3. Results

Figure 3 shows the Nyquist curves of the electrodes without PMM-graphite at 3 different geometries. It can be seen that the effect of the electrode electrolyte interface appears at low frequencies. Also, it can be observed that electrical impedance is sensitive to NaCl and KCl concentration changes. However, it is less sensitive at higher concentration of NaCl when using concentric and spiral electrodes whereas moderate for KCl at low frequencies. In all curves of figure 3, the corner frequency was reduced in higher concentration. The corner frequency was related with change between negative (low frequencies) and positive (high frequencies); the reactance values were considered as absolute value in figures 3 and 4.

![Figure 3](image)

Figure 3. Nyquist curves of saline solution without modified PMM-graphite electrode.

Figure 4 shows the Nyquist curves of the modified electrodes with PMMA. It can be seen a reduction of the electrode electrolyte interface at low frequencies for all electrode geometry. However, both spiral and concentric electrodes showed both very low selectivity and sensibility. The partial ring electrode showed a better sensitivity for impedance change by presenting a semicircle in terms of resistance and reactance. For the case of NaCl solution, the semicircle diameter increased from 4.9 $\Omega$ at 93.7 mM/ml to 9.7 $\Omega$ at 3 M/ml, resulting in a change of 4.8 $\Omega$. On the other hand, the impedance change was 6.6 $\Omega$ for the case of KCl over the same solution concentration. It was also observed that the corner frequency had a significant change either for different salt or different concentration of it inside de solution.

4. Discussions and Conclusion

Metallic electrodes measurements in saline solution showed lowest values in impedance compared with electrodes with PMMA. The difference might be explained due to the concentration of PMMA and graphite mixture, which may change the resistance electrode surface [11]. The electrodes without PMMA of 93.7 mM/ml (see figures 3a and 3c) showed an electrode electrolyte interface at lower
frequencies by presenting a similar behavior. However, at higher concentrations, this process presents irregular characteristics (see figures 3b and 3d). In the case of electrodes with PMMA, this last introduces a larger electro-active surface, which is directly related to the roughness [12], reducing electrode electrolyte interface at lower frequencies.

Electrodes with PMMA showed the advantage of being easy to make in a laboratory and stable measurements. The partial ring electrode depicts a more sensibility to detect saline solutions compared to concentric and spiral electrodes.

The screen printed electrode with modified surface of PMMA and graphite mixture might be recommended for human applications [13], such as aqueous electrolyte like urine and sweat. Also, this type of electrode may be used in industrial application, such as saline concentration of drinking water.

![Nyquist curves of saline solution using electrode with PMM-graphite.](image)

**Figure 4.** Nyquist curves of saline solution using electrode with PMM-graphite.

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