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Characterization of gold electrodes in phosphate buffered saline solution by impedance and noise measurements for biological applications

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Abstract—**Impedance spectroscopy and noise measurements have been used to study gold electrodes of three different surface areas in phosphate buffered saline (PBS) solution. The gold-PBS solution interface can be modeled by a charge transfer resistance in parallel with an interfacial constant phase element (CPE) which are in series with the solution resistance. The voltage noise fluctuations were analyzed using the Fast Fourier Transform (FFT) method. It is found that the voltage noise power is characterized by a $1/f^{\alpha}$ spectrum in the low frequency range. The value of α is observed to be double that of the CPE coefficient β. The authors suggest a link between the interface impedance and the measured noise.**

I.INTRODUCTION

Noise levels are found to be much higher than the expected thermal noise [1]-[2] in a wide range of systems (electrodes, tissues etc.). It may contribute to the distortion of signals in biomedical measurements. This creates a serious problem in medical diagnostics. An understanding of the mechanism of noise generation is therefore of significant scientific and practical interest.

Thermal noise, also termed Johnson noise or Nyquist noise, arises from the random thermal motions of charge carriers in a conducting material. The thermal noise voltage across a resistance is given by

$$V_n(rms) = \sqrt{4k_bTR\Delta f}$$

where k_b is the Boltzmann constant, T is the absolute temperature, R is the resistance and Δf is the bandwidth.

Shot noise arises from the statistical fluctuations of a discrete number of particles carrying energy. The strength of this noise increases with the average magnitude of signal intensity. Electrochemical noise occurs due to random fluctuations in voltage or current which occur during an electrochemical process. Electrochemical noise measurements [3]-[4] do not involve external perturbations to the system and have been widely applied in studies of corrosion systems [5]-[7].

Characterization of electrode-solution interfaces by impedance spectroscopy [8]-[11] offers a powerful tool in the study of interfacial processes. An equivalent circuit can be built with each element representing a physical process relating to the interface. By modeling the impedance spectrum, information about each individual interfacial process can often be obtained. Impedance measurements are utilized in a wide array of biosensing techniques.

In this work, impedance spectroscopy and electrochemical noise measurements are used to study the gold-phosphate buffered saline (PBS) solution interface. We have chosen PBS because it is the physiological medium for most biological studies. This will help in order to get a detailed understanding of the interfacial process and also to find a correlation between noise and impedance.

II.EXPERIMENTAL

Gold electrodes were prepared by evaporating gold onto polyimide substrate containing a titanium layer and subsequent patterning. The thickness of the gold was 200 nm. Gold electrodes of three different areas 6mm^2, 2mm^2 and 0.05 mm^2 were studied respectively. The electrolyte was a solution of 0.01 M phosphate buffered saline (PBS) (Sigma) prepared in Millipore water of pH 7.4. All experiments were carried out at room temperature. The gold electrodes were cleaned with piranha solution before immersion into PBS solution. Two identical gold working electrodes of the same area and a Ag/AgCl reference electrode were used for electrochemical noise measurements which were carried out using a Solartron 1287 Electrochemical interface. Voltage and current noise were measured simultaneously. Data acquisition was carried out at a sampling interval of 0.5 s for one hour. Data was analyzed in the frequency domain by the fast fourier transform (FFT) algorithm using Microcal Origin software. Impedance measurements were carried out with the Solartron 1287 Electrochemical interface coupled to the Solartron 1260 Impedance analyzer. A platinum wire was used as the counter electrode with Ag/AgCl being the reference electrode. All impedance experiments were carried out at open circuit potential. The ac excitation voltage was 10 mV with a frequency range of 0.1Hz to 100 kHz. All measurements were carried out after an equilibration time of 5 minutes. Modeling of impedance

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data was carried out using Z view software.

III.RESULTS AND DISCUSSION

Figure 1 shows the Bode plot for gold electrodes of different areas in 0.01M PBS solution. The solution resistance dominates at very high frequencies, while at lower frequencies the behaviour is capacitive in nature. It can be observed that as the area of the gold working electrode decreases its impedance increases in magnitude.

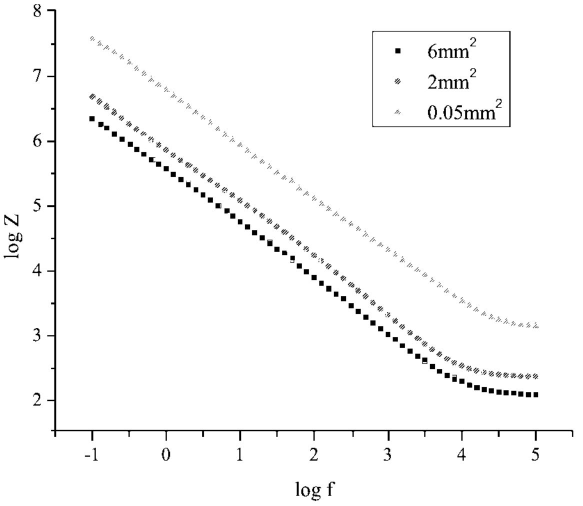

Fig.1. Bode plot of the log of impedance modulus as a function of log of frequency for gold electrodes of three different areas in 0.01M phosphate buffered saline solution.

The equivalent circuit for the gold-PBS solution interface can be modeled as a constant phase element (CPE) [($Z_{CPE} = 1/K(j\omega)^{\beta}$,K being the magnitude of the CPE] in parallel with the charge transfer resistance R_{ct} which are then connected to the series resistance R_s . (Figure 2)

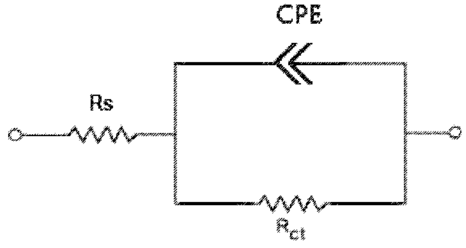

Fig.2.Equivalent circuit for the Gold-PBS solution interface.

The values of the individual circuit elements obtained after modeling the impedance data for the three different electrode sizes are given in Table I.

Note: Given the limited frequency range used, the accuracy of the calculated values of R_{ct} is not high. The calculated values are presented to show the orders of magnitude involved and the trends observed.

TABLE I

VARIATION OF K, β, R_{ct} AND R_s WITH ELECTRODE AREA

Electrode Area (mm^2)	K (μF s$^{\beta-1}$)	β	R_{ct} (MΩ)	R_s (Ω)
6	0.544	0.85	8.04	110
2	0.258	0.86	27.8	203
0.05	0.036	0.83	209	1137

As the area of the electrode decreases the value of CPE decreases while that of R_{ct} and R_S increase respectively. The value of coefficient β indicates the deviation of the CPE from pure capacitive behaviour. Figure 3 shows the voltage and current noise as a function of time while Figure 4 shows the plot of power spectral density (PSD) of voltage noise as a function of frequency for gold electrode (2 mm^2) in PBS solution respectively.

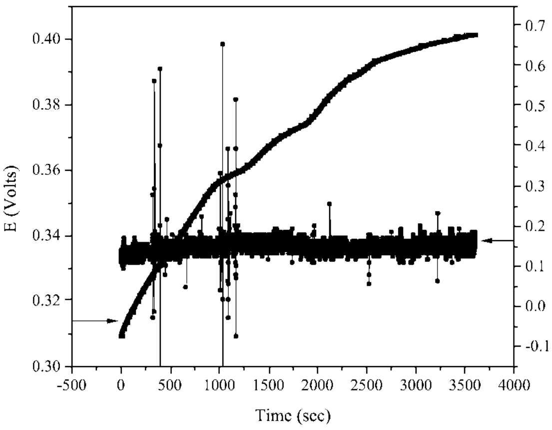

Fig.3. Potential and current noise – time record for gold electrode (2 mm^2) in 0.01M phosphate buffered saline solution.

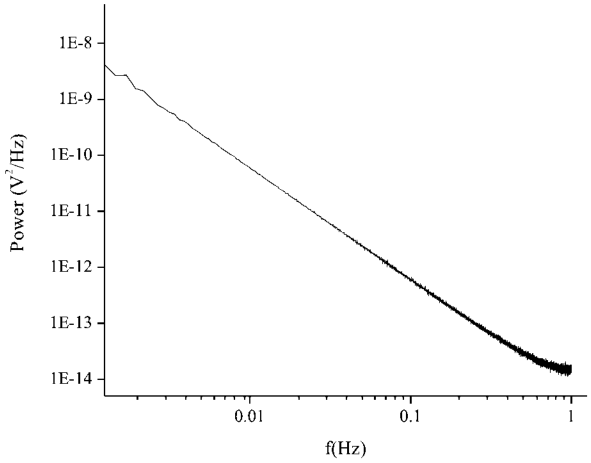

Fig.4. Power spectral density of voltage noise as a function of frequency for gold electrode ($2mm^2$) in 0.01M phosphate buffered saline solution.

There was a drift of about 100 mV of the dc voltage during the experiment. Measurement of root mean square (RMS) voltage noise with background correction was used to offset this change. The noise resistance R_n can be calculated by dividing the RMS voltage noise by the RMS current noise. The standard way of analyzing electrochemical noise data is to transform the data from the time domain to the frequency domain using the fast fourier transform (FFT). The voltage noise PSD was obtained by carrying out the FFT of the voltage-time plot using the Hanning window. The spectrum can be fitted on a logarithmic scale by a $1/f^{\alpha}$ function. Table II shows the values of α and R_n for the three different electrode areas.

TABLE II

VALUE OF α AND R_n FOR DIFFERENT ELECTRODE AREAS

Electrode area (mm^2)	α	R_n (MΩ)
6	1.8	83.56
2	1.82	256.9
0.05	1.81	314.26

The noise resistance is thus inversely related to the electrode area. Electrochemical noise and impedance are intimately related to each other [12]. There exists a direct correlation between noise and the real part of the impedance. We suggest that the source of this noise is due to the charge transfer resistance R_{ct} and that the frequency dependence is due to R_{ct} being connected in parallel with the frequency dependent CPE. The voltage noise PSD across R_{ct} is given as,

$$\bar{S}_{VCT} \square 4kTR_{ct}$$

The fact that the expression for voltage noise PSD in a charge transfer resistance is similar to the general expression of thermal noise in a resistor indicates why noise in electrode-electrolyte interfaces has often been referred to as thermal noise. The frequency response of a CPE is given by,

$$Z_{CPE} = \frac{1}{K(j\omega)^{\beta}}$$

where, K is a measure of the magnitude of the CPE and β is the fractional exponent. For a pure capacitor, $\beta = 1$ and Z_{CPE} represents a pure capacitive element. We argue that the CPE does not produce noise due to the fact that R_{ct} in parallel with CPE accounts for the conduction process at the interface. It can be shown from the above equation that the reactance of the equivalent circuit passes by a maximum magnitude at a frequency given by,

$$(2\pi f_0)^{\beta} = \frac{K}{R_{ct}}$$

It follows that the power spectral density of the voltage noise for the equivalent circuit can be given as,

$$\bar{S}_{VCT} = \frac{4kTR_{ct}}{1+\left(\frac{f}{f_0}\right)^{2\beta}+2\left(\frac{f}{f_0}\right)^{\beta}\cos\left(\beta\frac{\pi}{2}\right)}$$

where $\bar{S}_{VCT}$ is the PSD, β is the coefficient of the CPE, k is the Boltzmann constant, T is the absolute temperature. The above equation predicts that for frequencies above f_0, the power spectral density of interfacial noise tends to decrease as proportionally to $f^{2\beta}$. We find from our results that the value of α from the plot of voltage PSD with frequency is approximately twice that of the CPE exponent obtained from impedance measurements. The excess noise indirectly confirms the validity of the CPE element in the equivalent circuit model of electrode-electrolyte interface.

IV.Conclusion

The gold-PBS electrolyte interface has been characterized by electrochemical noise and impedance spectroscopy measurements. The effect of electrode area on impedance has been elucidated. Smaller electrodes are found to have greater noise. This result could help in better design of micro and nanoscale electrochemical sensors. The electrodes are shown to have $1/f^{\alpha}$ noise spectrum in addition to thermal noise. It is also inferred that electrode noise and impedance are intimately connected to each other and that the slope of the noise spectrum α is double the coefficient of the CPE β. Further work will help in a better understanding of noise processes at electrode interfaces.

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