Use of the radiofrequency-intermodulation distortion technique to investigate intrinsic nonlinearity at the electrode-electrolyte interface

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We report on investigations of nonlinear radiofrequency responses of electrolytes with Na^+ and Cl^- ions placed within gold electrodes of a capacitor. The sample was part of a frequency-adjustable inductance-capacitance-resistance (LCR) parallel resonant circuit, and measurements were carried out using the two frequencies intermodulation distortion technique. We employed double layer model to analyze the observed nonlinearities and their dependence on ionic concentration. Electrode-electrolyte interface polarization was found to be a predominant cause of this intrinsic nonlinearity and to be dependent on electrolytic ion concentration. We also measured and calculated coefficients of resistive and capacitive components of the observed nonlinearity. © 2012 American Institute of Physics. [doi:10.1063/1.3683477]

Efficient characterization of biochemical systems has gained tremendous significance in both the clinical and research domains of biomedicine. Dielectric spectroscopy is amongst the most powerful non-invasive techniques for such characterization. These biosystems are quite complex and their dielectric responses are not easy to interpret. The measurements are frequently further distorted and convoluted by generation of harmonics that can appear in the transfer function of the measured systems.

The nonlinear effects in biological cells¹ have been reported already as markers of important phenomena like activities of membrane-embedded proteins and enzymes,² ion channels,³ and processes such as electroporation and electrofusion.^{4,5} The nonlinear responses from suspensions of yeasts, etc.^{6,7} have been measured and used to estimate cells' growth phase and intramembranous fields.^{8,9}

Besides the nonlinearities originating from biomatter, there are also known nonlinear effects from rectification and generation of harmonics from Faradaic and non-Faradaic processes at the electrode-electrolyte interface in electrochemical systems.^{10–13} Schwan was first to analyze the harmonic response of an electrochemical system after a sinusoidal excitation was applied, and he pointed out the rectifying role of electrodes.¹⁴ Geddes mentioned use of Zener diodes to represent rectification at the electrical double layer (EDL) at electrode-electrolyte interface.¹⁵ EDL's unique properties including non-linearity play important role in supercapacitors such as electrochemical double layer capacitors (EDLCs), which have emerged recently and have demonstrated significant advances in capacitive energy storage. EDLCs use non-Faradaic processes for charge storage mechanisms, where charges are distributed on surfaces by physical processes that do not involve building or cleavage of chemical bonds. Such supercapacitors show non-linear

behavior due to dependence of their capacity and electrical series resistance on voltage level and frequency.^{16,17}

Despite the potential importance of such nonlinear measurements in determining signatures for biochemical phenomena and induced-charge electro-kinetic phenomena, no sensitive technique for such measurements has yet been developed. In addition to improved sensitivity, experimental methods should have the ability to clearly distinguish the effects of the electrode-electrolyte interface from those of biological entities. The conventional technique for studying such nonlinearities is the measurement of total harmonic distortion, in which the system is driven by a single-tone input signal¹⁸ and, because of the nonlinear characteristics of the transfer functions, higher order spectral components are present in the output signals. Such signals, when Fourier transformed, appear to also contain second-, third-, and higher order harmonics. Because higher order harmonics have decreasingly small amplitudes and are buried under the vector analyzer's noise, total harmonic distortions become difficult to detect and study.

In the present work, we realized a very sensitive setup based on detection of intermodulation distortion (IMD) peaks. This technique has already been widely accepted as a comprehensive method to study radiofrequency and microwave nonlinearities in electronic circuits¹⁸ and also in superconductors.¹⁹ The idea is to drive the system with a signal containing two frequencies f_1 and f_2 and to study the resulting mixed intermodulation products (IMPs). Typically, in the case of nonlinearity, an IMD spectrum contains many higher order peaks; to conserve bandwidth, however, only the fundamental (f_1 and f_2) and third-order IMP peaks ($2f_1-f_2$ and $2f_2-f_1$) are measured, in our case as a function of the input power. An important additional advantage of the IMD technique, related to its sensitivity, is its capability of probing nonlinearities at very low power levels, which allows avoidance of thermal effects. In this letter, we focus only on characterization of the intrinsic nonlinearity of the electrodes submerged in solutions. Such characterization is necessary

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prior to any extraction of actual biosample-induced nonlinear components. The nonlinear response of yeast to oxygenation level will be a subject of a separate publication.

A current-voltage response represented by the transfer function $i = H(v)$ can be expanded into a power series: $i = a_1 v + a_2 v^2 + a_3 v^3 + \dots$. For excitation by a two-tone signal of the same amplitude: $v = v_{in}[\cos(\omega_1 t) + \cos(\omega_2 t)]$, the linear output power (P_{linear}) at the fundamental frequency is proportional to the input power (P_{in}) and can be expressed as

$$P_{linear} = \frac{1}{2} a_1^2 v_{in}^2 = k P_{in}. \quad (1)$$

The third-order IMP's output power (P_{3IMP}),¹⁸ using Eq. (1), can be written as

$$P_{3IMP} = \frac{9}{32} a_3^2 v_{in}^6 = \frac{9}{4} \left(\frac{k}{a_1^2} \right)^3 a_3^2 P_{in}^3, \quad (2)$$

where a_1 and a_3 are expansion coefficients and k is a parameter of the measuring system.

From Eqs. (1) and (2), one can infer that for each dB rise in the input power, the fundamental and third-order IMPs increase by 1 dB and 3 dB, respectively. Therefore, the output power, when plotted against the input power, should follow the 1-dB/dB slope line for fundamentals (f_1 and f_2) and 3-dB/dB slope line for the third-order IMP sidebands ($2f_1 - f_2$ and $2f_2 - f_1$).

The IMD setup was constructed for liquid samples (Fig. 1). An ultra-low distortion function generator DS-360 (Stanford Research Systems) operated in two-tone mode was used to drive an LCR parallel circuit resonator (Fig. 2(a)). The input and output power signals of the resonator were monitored by an Agilent power meter N1912A. The output frequency response was measured by a spectrum analyzer (SR785; Stanford Research Systems).

The sample container was built as a capacitor, an RC component of an LCR resonator, and consists of parallel plate gold electrodes (Fig. 2(b)). Capacitor electrodes were made of a gold layer (2000 Å) deposited on a glass substrate with a Cr adhesion layer. These planar electrodes of size 17.5 mm × 15 mm were patterned using optical lithography and spin-coated at about 1000 rpm with a thin Teflon (DuPont-AF) layer for protection and insulation. Teflon on the electrodes ensures the absence of any net Faradaic current through the capacitor cell, thus making the resistive

component of the resonator relatively large. Spacers of neoprene rubber were used to separate the two plates of electrodes by 0.5 mm. An equivalent circuit of such sample container comprises of five capacitances connected in series: two for the insulating layer, two for the interface double layers, and one for the solution. We assumed that the nonlinearity comes only from the capacitance and resistance of the double layers at the electrode interface with the solution. Other components such as the bulk electrolyte, Teflon layer, and inductance (L) were assumed to be linear.

When the LCR circuit is tuned to the resonant frequency f_r , the impedance of the parallel resonator is equal to the resistance R of the sample capacitor. It results in proportionality of the input and output power at resonance and makes the coefficient k in Eq. (1) equal to 1. Any deviation from this k value will be a function of the resistive R component in the capacitor, which is large in our case because of the Teflon electrode coating.

For each measured sample, we first tuned the setup to the resonant frequency f_r of the LCR resonator using a network analyzer. The resonance frequency can be selected from a wide kHz range by changing the separation between the ferrite cores, as shown in Fig. 2(c). Once the f_r value was known, we selected two tone signals at equal power to drive the resonator. These signals have two fundamental tones: f_1 and f_2 centered around the resonance peak, with a difference between f_1 and f_2 frequencies of approximately 100 Hz. The third-order IMPs $2f_1 - f_2$ and $2f_2 - f_1$ were observed where all the output signal frequencies f_1 , f_2 , $2f_1 - f_2$, and $2f_2 - f_1$ were within the pass-band of the resonator. By adjusting input power, we were able to plot 1-dB and 3-dB slope lines and analyze nonlinearity. To identify the intermodulation spectrum of each sample, the power levels of the fundamental tone and the third-order IMPs at frequencies $2f_1 - f_2$ and $2f_2 - f_1$ were measured in the spectrum analyzer as a function of the resonator input power. At each input power, the frequency was adjusted to the resonant frequency and the third-order IMD sidebands peaks were monitored for the output power maximum.

The first measurements were done with the sample capacitor filled with deionized water Nanopure Systems at 18 MΩ-m resistivity. No third-order IMPs were observed above the noise limit of -65 dBm, implying that there are no nonlinear effects in pure water in this power range. Next, we measured the IMD spectra for 0.01M, 0.1M, and 1M sodium chloride aqueous solutions. As shown in Fig. 3, for all concentrations of ions, the output power followed the standard 1-dB/dB slope line and 3-dB/dB slope line behavior between the fundamental and third-order IMP sidebands, respectively. The two plots of slopes 1 and 3 for each sample were then extrapolated to determine the intersection points, called the third-order intercept points (IP_3), which can be treated as a figure of merit of the degree of nonlinearity. We found the IP_3 values to be dependent on ion concentration. The IP_3 values for concentrations of 1M, 0.1M, and 0.01M are noted in Table I. From Eqs. (1) and (2), we found the relation between IP_3 and a_3 to be $a_3 = (2/3)a_1^3/IP_3$. We could have estimated the coefficient a_3 from the extrapolated IP_3 value,¹⁸ but we instead used Eq. (2) to calculate a_3 since it involves more reliable interpolated IMP data. Rearranging

FIG. 1. (Color online) Two-tone intermodulation distortion measurement setup.

FIG. 2. (Color online) (a) LCR resonator showing adjustable ferrite core-based inductor. (b) Expanded view of the sample capacitor. (c) Resonant frequency sweep versus distance between the ferrite cores for different sample capacitances.

Eq. (2), and substituting constants $k = 1$, $a_1 = 1$, and using dBm units, a_3 can be expressed as

$$a_3 = \frac{2}{3} 10^{\frac{P_{3IMP}(\text{dBm}) - 3P_{in}(\text{dBm})}{20}}. \quad (3)$$

To analyze data, we selected three P_{3IMP} points for each molarity corresponding to the input power P_{in} of 25.48 dBm

FIG. 3. (Color online) Output power for the fundamental and third-order intermodulation product vs. input power.

from Fig. 3; a_3 values were calculated using Eq. (3) and are presented in Table I. These three a_3 values are plotted versus molarity as circular dots in Fig. 4.

An electrical double layer model²⁰ was used to interpret the results. We derived expressions for polarization and capacitive currents, which are related to the resistive and capacitive nature of the double layer, respectively. The third-order coefficient of the Taylor's expansion of the resistive ionic current, which flows against the electrode and polarizes the sample between the two electrodes, was derived as

$$a_{3cond} = \alpha^3 D e \left(\frac{A}{\epsilon h} \right) \cosh(\alpha \psi_s) n_{\infty}. \quad (4)$$

It can be seen that this coefficient is proportional to the ion concentration, n_{∞} , or molarity M , defined as $M = n_{\infty} / 1000 N_A$. Here, ψ_s is the surface potential, $\alpha = e/k_B T$, e is the electron charge, A and h are the area and distance between the electrodes, ϵ is the dielectric constant of the electrolyte, and D is the ionic diffusion coefficient in m^2/s units.

TABLE I. P_{3IMP} and a_3 for respective molar concentrations.

Molarity	IP_3 (dBm)	P_{3IMP} (dBm)	a_3
0.01M	47.5	-47.2	4.384×10^{-7}
0.1M	59.6	-31.26	2.747×10^{-6}
1.0M	69.2	-13.32	2.173×10^{-5}

FIG. 4. (Color online) Plot of Eq. (6) (black curve) and experimental data (red dots).

The third-order coefficient of the capacitive current is expressed as

$$a_{3cap} = j \frac{\omega \alpha^3 A}{8} [2\epsilon k_B T]^{1/2} \cosh\left(\frac{\alpha}{2} \psi_s\right) \sqrt{n_\infty}. \quad (5)$$

The capacitive component coefficient is proportional to the square root of ion concentration. Capacitive and conductive components of nonlinear mechanisms appear at the same electrode/electrolyte interface: one at the electrode surface and the other in the double layer side of the interface. It is equivalent to capacitors connected in parallel and they both experience the same electric potential, v . As a result, the two response currents can be added and all the corresponding expansion coefficients of the two power series can be added as well, as shown in Eq. (6). These two expressions allow us to use the following equation for fitting the experimental data:

$$a_3(M) = aM + bM^{0.5}. \quad (6)$$

The nonlinear function of double layer conductivity has a factor proportional to the electrolyte concentration M (mole/l), and thus all coefficients of the power expansion of the nonlinear part of the function are also proportional to M , as shown in Eq. (4). Similarly, the nonlinear capacitance of the double layer, where the nonlinear part of the function represents the surface charge (whose change with respect to potential is its capacitance), has a factor proportional to the square root of concentration, $M^{1/2}$ (Eq. (5)). We formed three equations by substituting the three experimental points into Eq. (6), and solve for “ a ” and “ b ” using the least squares method. The obtained results are as follows: $a = 1.910 \times 10^{-5}$ and $b = 2.626 \times 10^{-6}$. Using Eq. (6), we plotted a curve representing

these two parameters (Fig. 4). As can be seen, the curve is a perfect fit with the three experimental data points.

In conclusion, we measured the contribution of the insulator-coated gold electrode-electrolyte interface to the observed nonlinearity in an aqueous electrolyte solution. It was confirmed that the measured nonlinear effect, which interferes with the nonlinear signal coming from the bio-electrolytes, is intrinsic and originates from the electrode-electrolyte interface. Using the double layer model approach, we obtained the third-order coefficients of the power series of the nonlinear response function of the electrical double layer. These coefficients, related to capacitive and conducting components of nonlinearity, can be used to differentiate the nonlinear signal of the biosample contained in a two-electrode capacitor. The intermodulation distortion technique used in this work turned out to be sensitive enough for future investigation of biological samples in a two-electrode configuration. This technique can also be used to characterize the working and mechanisms of supercapacitors and thus could be used for their electrolytic optimization.

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