Effect of parasitic capacitances on impedance measurements in microsensors structures: a numerical study

Nicolás H. Beltrán [a,*], Ricardo A. Finger [a], Jorge Santiago-Aviles [b], Patricio Espinoza-Vallejos [c]

[a] *Electrical Engineering Department, University of Chile, Casilla 412-3, Santiago, Chile*
[b] *Electrical and Systems Engineering Department, University of Philadelphia, Philadelphia, PA, USA*
[c] *Agere Systems, Allentown, USA*

Abstract

The use of solid electrolyte cells to detect specific gases is widely applied in the electronic control systems. Ionic conduction in this type of sensors is normally studied through impedance spectroscopy, since the data obtained with this technique provide valuable information about the electrical properties of the solid electrolyte and electrode behavior. This work addresses the influence of inter-electrode capacitance on the impedance characterization of small structures. Parasitic capacitance was determined by solving Laplace equation and integrating the potential over a Gauss surface including the electrode. Computer simulations of electrode impedance behavior of a solid cell were carried out using a well-known electronic simulator. It is concluded that parasitic capacitances introduce a small distortion on the high-frequency portions of Nyquist plot that are important when miniaturized sensor are electrically characterized.

Keywords: Gas sensors; Impedance spectroscopy; Electrochemical cells; Thin-ceramic films

1. Introduction

Impedance measurements or impedance spectroscopy is an adapted technique from liquid electrochemical cells to characterize solid-state cells used in sensor applications. This characterization has proven useful in determining the behavior of a particular cell during gas detection. There is also an increasing interest for microsensors devices, especially if they are compatible with silicon technology, because they could be located close to the signal-processing circuit in the semiconductor chip. This arrangement minimizes signal-processing times and reduces signal interference, which could be introduced along transmission path. Furthermore, the use of thin-ceramic films, a requirement for small dimension gas sensors could give faster response since the gas ions have to cover a shorter path than in conventional ceramic electrolytes fabricated by pressing and sintering. Thin-ceramic films have been deposited by different techniques [1–5].

A great deal of work has been done in interpreting the solid electrolytes impedance spectra, mainly relating the real and imaginary part at different frequencies and obtained from three-point impedance measurements. To carry out this task on solid cells, Hsieh et al. [6], list some considerations that should be taken into account when the technique is used, such as the lower conductivities of solid electrolytes cells as compared to liquid electrolytes, and the high impedance of the reference electrode (RE) contacts. Some authors have reported spurious arcs and high-frequency artifacts [7] during impedance measurements carried out on liquid electrolytes with high resistivity reference electrodes. These distortions are attributed to the high resistance of the electrode. When impedance measurements are carried out on solid cells, a similar behavior is explained by the electrode resistance [8]. However, the inter-electrode capacitance present in systems where high-frequency electric fields are applied, has not been considered in the equivalent circuit. The effect of parasitic capacitance becomes important when sensor miniaturization is used. In this paper we address the influence of these capacitances on the impedance spectra of a particular sensor structure suitable for gas detection. The structure was reported by Hsieh et al. [6] and uses an inserted reference electrode into the ceramics known as a Luggin type-probe.

When sensor dimensions are scaled down, inter-electrode parasitic capacitance should be taken into account when

* Corresponding author. Tel.: +56-26784193; fax: +56-26953881.
E-mail address: nicolas.beltran@die.uchile.cl (N.H. Beltrán).

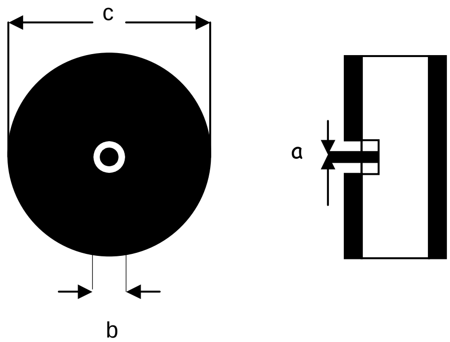

Fig. 1. Sensor structure used for impedance simulations.

modeling the sensor. The effect of this parasitic capacitance on impedance spectroscopy for the structure shown in Fig. 1 was simulated by means of the equivalent circuit proposed by Bauerle [9] and using a well-known electronic simulator package, SPICE. Mutual capacitance is determined by applying Gauss law to the electrode structure as to calculate the enclosed charge and solve for all involved capacitances. The impedance response is obtained from SPICE simulation of the equivalent circuit when a variable frequency signal is applied.

To get some insight of the effect parasitic capacitance may have on the impedance, we compare our results to measurements and electrical models published. With this purpose in mind, we have considered the results obtained by Hsieh et al. [6] of yttria-stabilized zirconia (YSZ) including a reference electrode concentric with the counter electrode, and inserted into the electrolyte as to form an equivalent of the Luggin probe-type reference electrode. According to Hsieh et al., there is no noticeable difference between the actual and the apparent impedance responses with this structure.

2. Parasitic capacitance

The relationship between charge Q and potential V for a system of m electrodes is given by

$$Q = CV \tag{1}$$

where C is an $m \times m$ matrix. This matrix has columns determined by setting the potential on the ith electrode to unity while other electrodes are set to zero. The charge on each of the electrodes, yields capacitance terms from the equation

$$C_{ij} = \frac{Q_j}{V_i} \tag{2}$$

Therefore, to determine capacitance between electrodes the potential distribution must be found as well as the accumulated charge for each one. Laplace equation $\nabla^2 \Phi = 0$ is numerically solved in cylindrical coordinates assuming that the electrolyte is not polarized, this is, the charge density is concentrated in the electrodes which is a reasonable assumption when small voltages are applied. The potential Φ is determined by using two types of boundary conditions:

- Dirichlet on the electrodes for $0 < r < a$ and $b < r < c$.
- Newmann on the other surfaces limiting the region at $z = 0$ where the equation is solved.

Considering the symmetry of the problem, the Laplace equation is solved for $\rho > 0$ and $z > 0$. The independence respect to the azimuthal angle ϕ reduces the problem to a two-dimensional equation:

$$\partial_\rho^2 \phi + \frac{1}{\rho} \partial_\rho \phi + \partial_z^2 \phi = 0 \tag{3}$$

Applying a mesh to the region of interest with a side equal to h, and using the following form for the discretization of the derivatives:

$$\partial_i \phi_{i,j} = \frac{\phi_{i+1,j} - \phi_{i-1,j}}{2h};$$
$$\partial_i{}^2 \phi_{i,j} = \frac{\phi_{i+1,j} - 2\phi_{i,j} + \phi_{i-1,j}}{h^2} \tag{4}$$

Eq. (3) takes the form

$$\phi_{i,j} = \frac{1}{4}\left[\left(1 + \frac{h}{2i}\right)\phi_{i+1,j} + \left(1 - \frac{h}{2i}\right)\phi_{i-1,j} + \phi_{i,j+1} + \phi_{i,j-1}\right] \tag{5}$$

The mesh is updated by using relation (5) until $\phi_{i,j}$ converge to a value that satisfy an error criterion. Once the potential is determined, integration over a Gauss surface that includes the electrodes gives their charge.

3. Results

Equipotential lines calculated in a structure having the reference electrode reported by Hsieh et al., with a wire of 0.254 mm diameter, 0.4 mm of separation with counter electrode and 17.6 mm diameter of the working electrode (WE), are shown in Fig. 2.

The enclosed charge determined after integration over a Gauss surface for the structure defined above, is shown in Fig. 3.

Inter-electrode capacitance calculated for the small structure resulted in capacitance values of the order of 0.03 pF between reference and counter electrode and of the order of 5 pF between counter and working electrode. Here, we use for zirconia, the electrolyte ceramic of our model sensor structure, with an average value of 22 for the electric permittivity [1]. Fig. 4 shows a Nyquist plot obtained from the results of impedance simulation with SPICE, taking into account inter-electrode capacitance connected between the reference, the counter and working electrodes for the structure of Fig. 1. On the same plot, also shown are the results of impedance simulation using configuration 4 as reported

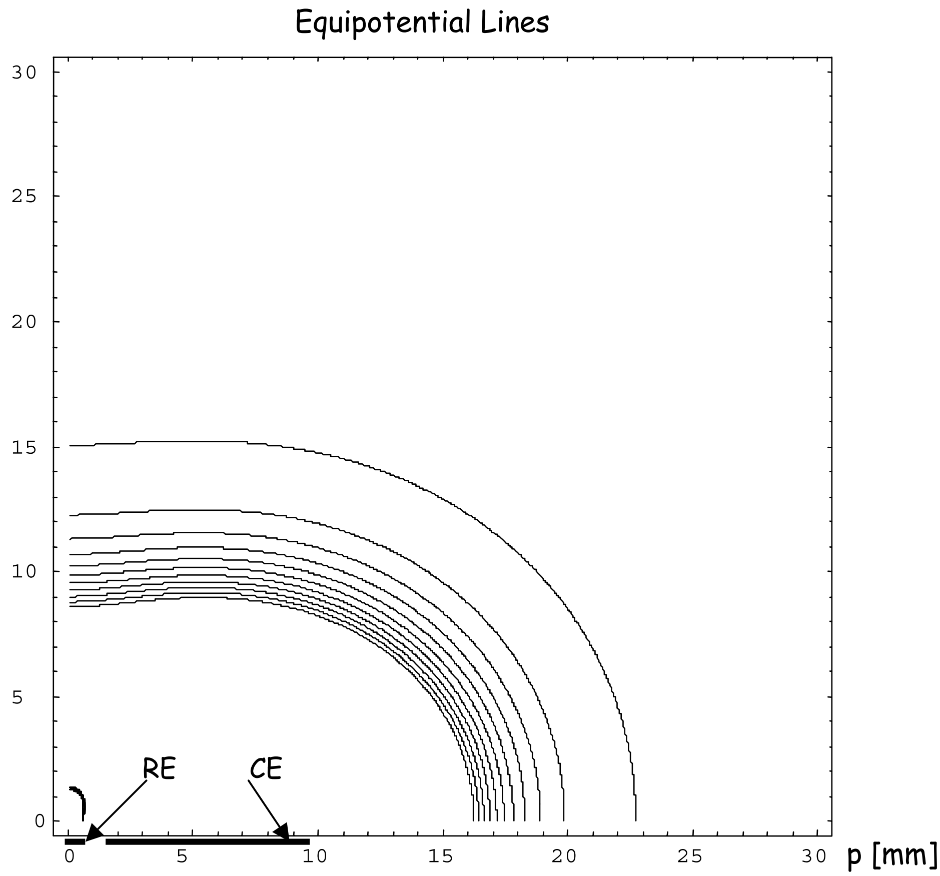

Fig. 2. Equipotential lines obtained in a sensor with dimensions $a = 0.25$ mm, $b = 0.8$ mm and $c = 16.8$ mm. Location of reference and working electrodes are shown in the ρ-axis of the plot.

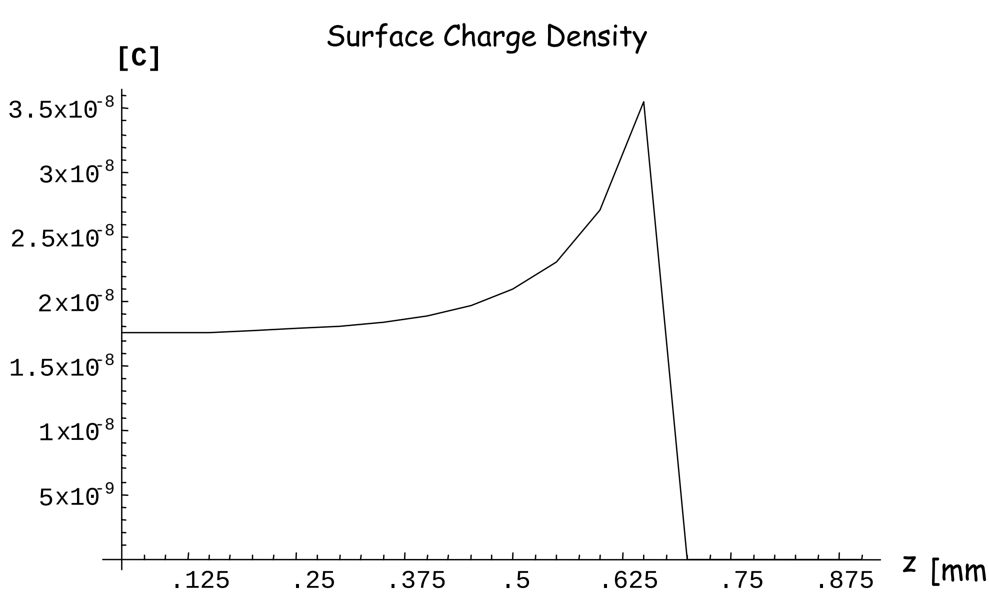

Fig. 3. Charge density on the reference electrode of the sensor structure of Fig. 1.

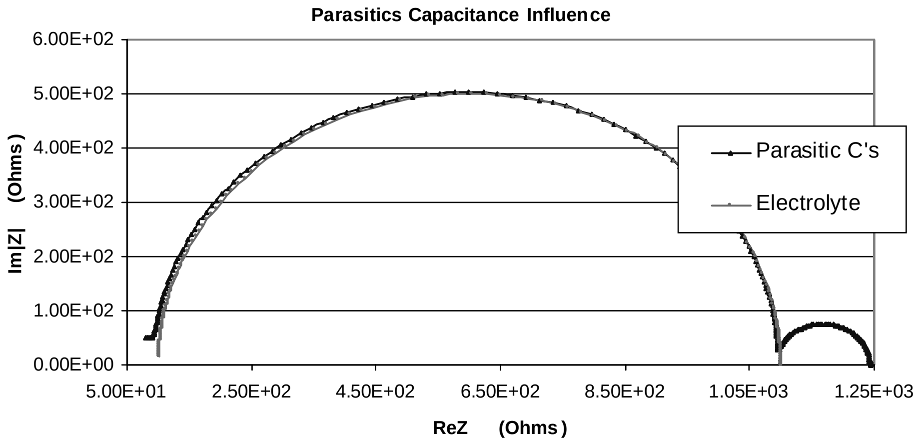

Fig. 4. Distortion of the electrolyte impedance due to inter-electrode parasitic capacitances simulated on the structure of Fig. 1. The small semicircle in the low-frequency portion corresponds to the working electrode. Note that 50 Ω offsets the Re Z-axis.

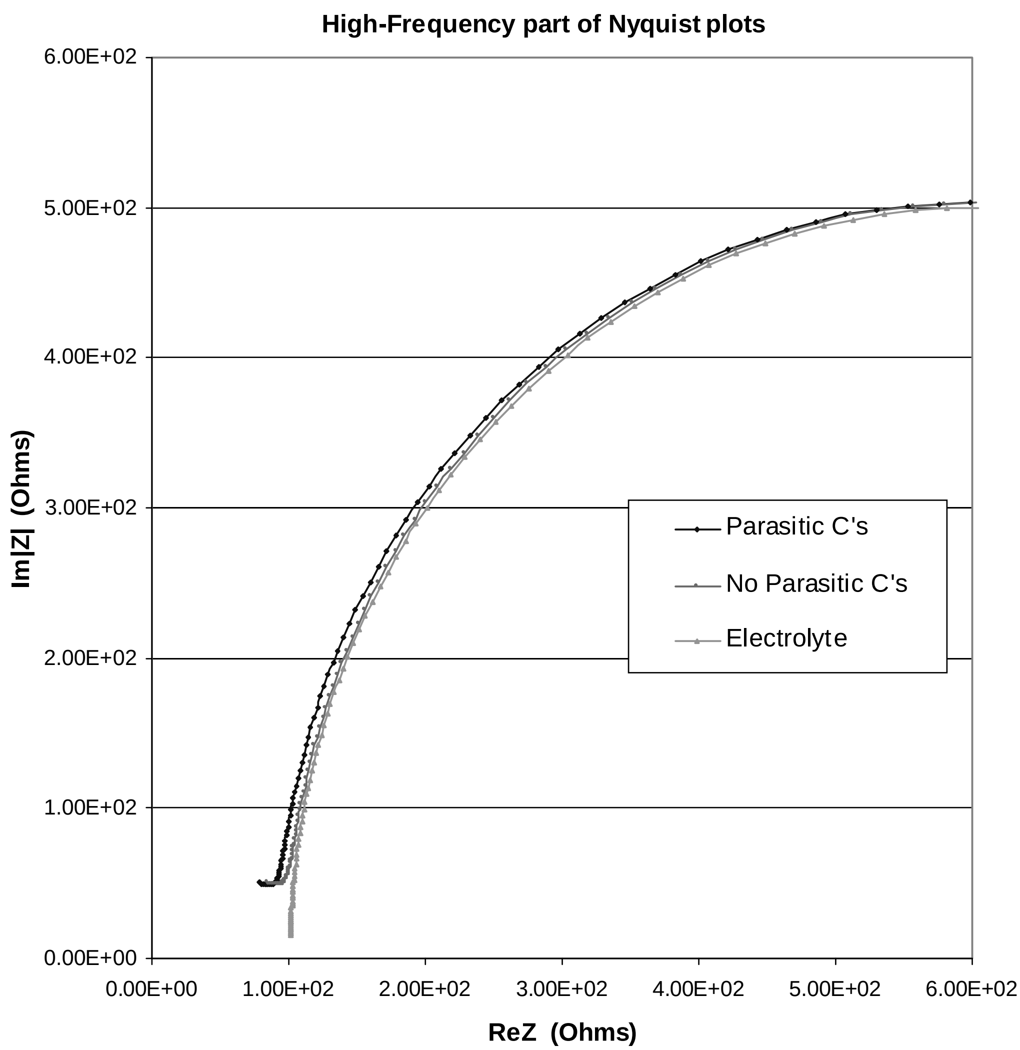

Fig. 5. High-frequency portion of the Nyquist plot. Label of the curves refer as follows: parasitic C to the computer simulation with parasitic capacitances included in the equivalent circuit. No-parasitic C, as it is usually simulated in the literature and electrolyte, impedance simulation of the electrolyte-alone equivalent circuit.

by Hsieh [6]. In the high-frequency portion of the plot, the influence of this capacitance is apparent. A slight deviation from the actual electrolyte impedance is observed, that is higher than the distortion shown when these capacitances are not taken into account. The latter distortion has been attributed [6] to the voltage divider effect introduced by the reference electrode. The influence of the reference electrode observed from the simulations with SPICE is in accordance with the findings reported by Hsieh. It is clearly seen in the low-frequency part which corresponds to the working electrode impedance, the semicircle showing that the three-point simulated measurement configuration has the input at the instrument side between the reference electrode and the WE. This measurement configuration is referred as three-point LO-pin [6].

Fig. 5 shows a close-up of the high-frequency portion of the Nyquist plot of Fig. 4. Here, the distortion introduced by these parasitic capacitances is clearer. The beginning of a new semicircle in this part of the Nyquist plot is related to the input impedance of the instrument that was simulated as a parallel *RC* circuit ($R = 1\,\mathrm{M\Omega}$ and $C = 35\,\mathrm{pF}$). The parasitic capacitance effect is certainly small when considering devices of the sizes reported by Hsieh et al., and addressed in this work. However, when device dimensions are scaled down, the inter-electrode capacitance increases with the smaller electrode separation, which could become an important issue when these micro-devices are electrically characterized.

A positive feature of using an electronic circuit simulator comes from the fact that voltage nodes, and branch currents, are easily listed or plotted as a function of frequency. This is particularly useful, when the frequency range where electrodes have influence on the solid cell impedance is important. By examining the frequency dependence of the voltage nodes connected to the electrolyte equivalent circuit, the frequency interval where electrodes affect the overall structure impedance it is immediately determined.

4. Conclusions

The problem of inter-electrode parasitic capacitances addressed in this paper show that they affect impedance measurement as long as the device dimensions are small. They introduce distortion at the high-frequency portion of Nyquist plots that are normally used to electrically characterize electrolyte impedance in electrochemical solid cells used for gas detection.

Solid-state electrochemical cells simulation using SPICE, a well-known electronic package simulator, prove to be quite useful to monitor the behavior of the different cell branches equivalent circuit. Analyzing the node voltages and branches current, the electrolyte and the electrode behavior is easily determined, even before obtaining the Nyquist plot.

Acknowledgements

Fondecyt funded this work under contract 1990190. The assistance of Professor Patricio Cordero of the Physics Department of the Faculty of Mathematical and Physical Science of the University of Chile, in solving the potential of circular electrode structure is gratefully acknowledged.

References

[1] J. Shappir, A. Anis, I. Pinsky, Investigation of MOS capacitors with thin ZrO_2 layers and various gate materials for advanced DRAM applications, IEEE Trans. Electron Dev. ED-33 (4) (1986) 442–449.

[2] T. Hata, K. Sasaki, Y. Ichikawa, K. Sasaki, Yttria-stabilized zirconia (YSZ) heteroepitaxially grown on Si substrates by reactive sputtering, Vacuum 59 (2000) 381–389.

[3] I. Kosacki, T. Susuki, V. Petrovsky, H.U. Anderson, Electrical conductivity of nanocrystalline ceria and zirconia thin films, Solid State Ionics 136–137 (2000) 1225–1233.

[4] P. Gao, L.J. Meng, M.P. dos Santos, V. Teixeira, M. Andritschky, Study of ZrO_2–Y_2O_3 films prepared by rf magnetron reactive sputtering, Thin Solid Films 377–378 (2000) 32–36.

[5] N. Beltrán, C. Balocchi, X. Errazu, R. Avila, G. Piderit, Rapid thermal annealing of zirconia films deposited by spray pyrolysis, J. Electron. Mater. 27 (2) (1998) L9–L11.

[6] G. Hsieh, T.O. Mason, E.J. Garboczi, L.R. Pederson, Experimental limitations in impedance spectroscopy. Part III. Effect of reference electrode geometry/position, Solid State Ionics 96 (1997) 153–172.

[7] P. Xie, P. Gu, J.J. Beaudoin, Electrical percolation phenomena in cement composites containing conductive fibres, J. Mater. Sci. 31 (1996) 4093–4097.

[8] S.J. Ford, T.O. Mason, B.J. Christensen, R.T. Coverdale, H.M. Jennings, E.J. Garboczi, Electrode configurations and impedance spectra of cement pastes, J. Mater. Sci. 30 (1995) 1217–1224.

[9] J.E. Bauerle, Study of solid electrolyte polarisation by a complex admittance method, J. Phys. Chem. Solids 30 (1969) 2657–2670.