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Dependence of an electrochemical cell performance upon the thickness of the ionic conductor

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ABSTRACT

The thickness of the ionic conductor in an electrochemical cell is shown to be among the governing parameters of the cell's performance. Internal field, *I–V* characteristics and p–n 'junctions' formed upon voltage application are investigated through a computer model based on fundamental charge transport equations including also Poisson's equation.

1. Introduction

The application of voltages on ionic materials and mixed conductors situated between two electrodes results to a shift of charged mobile species, ionic and electronic, from one electrode to the other. This shift can cause the formation of local inhomogeneities in the material leading to changes in the electrical and optical properties of the devices. Changes in the material composition, which can also lead to the formation of p–n 'junctions' after the application of biases have been reported. These reports are based either on experiment [1–5], simulation [6–8] or theory [9–11]. Furthermore, the shift of ionic species can result to the generation of an internal field, a subject which has raised debates between researchers going on even up to now [12–14]. Internal field is reported to be dependent upon the material partial conductivities, the applied voltage and the type of electrodes [7,8,12]. The type of electrodes has been long investigated, playing a major role for the device performance. Especially, the case of one or both of them being blocking has been extensively studied.

The subject of the effect of the size of devices based on ionic materials or mixed conductors on the device response has been raised long before the 'revolution' of nanotechnology. Simulation results by Franceschetti and Macdonald [15] have proved the thickness of a material with mobile charge carriers situated between two blocking electrodes to be among the determining factors for the system response. In publications that have appeared much later [16] it has been extensively discussed that whilst for larger systems the field in the bulk is substantially reduced by the formation of space charge layers, for thin films the applied field is weakly screened by the mobile charge. This leads to the conclusion that with size reduction down to approaching Debye lengths usual approximations like electroneutrality and thermal equilibrium are not expected to be valid. Space charge layers that play a minor role in devices of conventional dimensions prove to be of major importance for devices in the nanoscale. As dimensions are decreasing, space charge regions are dominating the whole device and an enhanced ionic conductivity is both theoretically predicted [16] and experimentally proved [17]. In more recent studies the validity of local neutrality approximation is extensively investigated in connection to the dimensions of a device [18,19] proving to be a valid assumption for thick samples only.

This paper is a follow up of a previous work [20], focused on the electrochemical potential gradient being the governing parameter of the response of an yttria-stabilized zirconia (YSZ) galvanic cell with one electrode ionically blocking and the other reversible. YSZ is a material of extensive and up to date research interest [21–28] due to its pronounced technological importance in a vast area of applications extending from gas sensors [29], mesoporous fibres [30], thermal barrier coatings [31] to biomaterials [32].

In the present work the zirconia thickness is shown to be also an important parameter for the appearance of local inhomogeneities, the characteristics of the 'junctions' formed and most importantly the response of the galvanic cell.

2. The numerical model

The numerical model used to derive the results is based on the system of the fundamental equations governing charge transport

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and Maxwell's equation, which connects the electric displacement vector with electric charge density and is reduced to Eq. (8), known as Poisson's equation. This system of equations formulated by van Roosbroeck [33] back in the early 1950s forms the so-called semiconductor device equations, which describes potential distribution, carrier concentrations and current flow in arbitrary semiconductor devices. This set of equations is the basis of any physical device model up to now [34–39].

In this work the governing Eqs. (1)–(8) are considered as one dimensional and under steady state conditions.

$$J_h(x) = -qu_h C_h(x)\frac{\partial \Psi(x)}{\partial x} - qD_h\frac{\partial C_h(x)}{\partial x} \tag{1}$$

$$J_e(x) = -qu_e C_e(x)\frac{\partial \Psi(x)}{\partial x} + qD_e\frac{\partial C_e(x)}{\partial x} \tag{2}$$

$$J_v(x) = -qu_v C_v(x)\frac{\partial \Psi(x)}{\partial x} + qD_v\frac{\partial C_v(x)}{\partial x} \tag{3}$$

$$\frac{\partial J_e(x)}{\partial x} = 0 \tag{4}$$

$$\frac{\partial J_h(x)}{\partial x} = 0 \tag{5}$$

$$\frac{\partial J_v(x)}{\partial x} = 0 \tag{6}$$

$$J(x) = J_e(x) + J_h(x) \tag{7}$$

$$-\varepsilon_s\frac{\partial^2 \Psi(x)}{\partial x^2} = C_h(x) + C_V(x) - C_e(x) - C_D \tag{8}$$

In order to solve the system of Eqs. (1)–(8), the equations are written in a normalized form according to de Mari [40] with concentrations of the mobile charged species (electrons, holes and oxygen vacancies) at each point x in the material written as functions of the potential at each point and the respective electrochemical potentials as

$$C_e(x) = \exp[-(+\eta_e(x) + \Psi(x))] \tag{9}$$

$$C_h(x) = \exp(\eta_h(x) + \Psi(x)) \tag{10}$$

$$C_v(x) = \exp[-(+\eta_v(x) + \Psi(x))] \tag{11}$$

The normalized set of equations is solved numerically by applying a finite difference method, following a well established iterative technique [41], with a second order accuracy.

Evaluations are performed for $T = 800\,^{\circ}\mathrm{C}$, a temperature for which various quantities of interest have been measured and reported in the literature. Thus, mobility values for electrons and holes are taken as $u_e = 2\times10^{-6}\,\mathrm{m^2/V\,s}$ and $u_h = 6.3\times10^{-9}\,\mathrm{m^2/V\,s}$ and values for electron and hole densities as $C_e = 1.2\times10^{16}\,\mathrm{m^{-3}}$ and $C_h = 4\times10^{23}\,\mathrm{m^{-3}}$ with $C_V = 2.7\times10^{27}\,\mathrm{m^{-3}}$, as quoted in the literature [42–44]. The fraction of the oxygen sublattice x_V available for oxygen vacancy distribution for the temperature under consideration is taken as 0.15 according to [44]. Applied voltage at the ionically blocking electrode ($x = L$) is always taken negative in respect to the reversible one ($V(L)<0$). Oxygen vacancy concentration at this electrode is given through the analytical expression:

$$C_V(L) = C_V x_V \exp(-V(L)) \tag{12}$$

As a wide range of values for zirconia thickness is considered in this work, the dielectric constant of zirconia has been taken thickness dependent according to Natori et al. [45], with a bulk value equal to 40. The strong decrease with thickness of an effective dielectric constant has been proved by the above researchers to be an intrinsic effect rather than attributed to a degradation of film quality. A list of the physical significance of the symbols used is given in Appendix A.

3. Results and discussion

Results are derived for all quantities of interest for different values of YSZ thickness ranging from 10^{-6} to 10^{-9} m and different values of applied voltage ranging from 0.4 to 1.5 V.

Results for field distribution throughout the cell and for different values of the zirconia thickness are shown in Fig. 1. As expected, there is no screening for the field in the bulk when the oxide thickness becomes very small, while the field is minimized for larger thickness values.

In Fig. 2 the characteristics of the p–n 'junctions' formed upon voltage application and in particular the points at which the 'junctions' appear are shown to be thickness dependent. The formed p–n 'junctions' are shifted towards the blocking electrode with increasing thickness. The same shift results also by decreasing the applied voltage as shown in Fig. 3. Both thickness

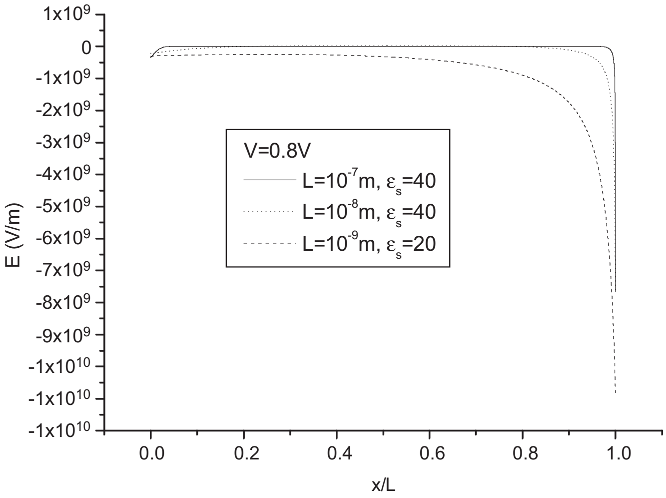

Fig. 1. Electric field in the bulk versus applied voltage for three values of YSZ thickness.

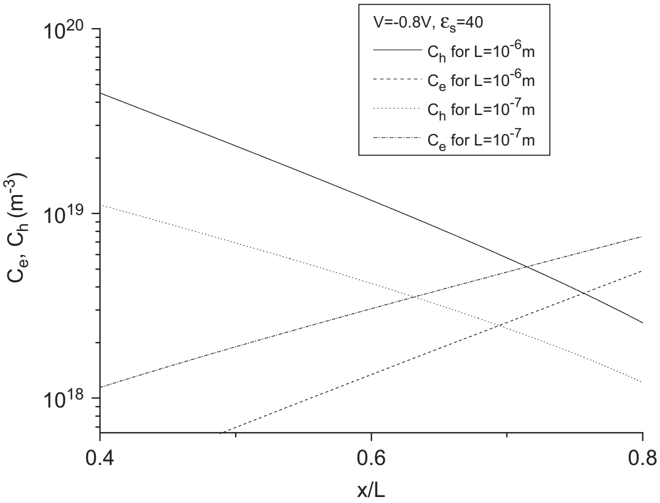

Fig. 2. Electron and hole distributions throughout the device for two distinctive values of YSZ thickness.