



Logic gates with ion transistors

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ABSTRACT

Electronic logic gates are the basic building blocks of every computing and micro-controlling system and typically require the integration of several switching elements. Ion circuits are much slower than their electronic counterpart; yet combining chemistry or bio chemistry with digital aspects is an intriguing concept. Here we demonstrate ion-XOR and ion-OR gates with two electrochemical cells without pre-ion separation. The cells were modified to include a third, permeable and conductive mid electrode (the gate), which was placed between the anode and cathode. Key to our demonstration is the use of small biasing gate power with respect to the circuit's power output. The effect is reversible and a demonstration of self-powered ion circuitry.

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1. Introduction

Logic gates are made of switches, such as diodes and transistors and attempts were made to emulate them with ion channels by using ion-selective membranes [1–8]. We want to circumvent the stage of charge separation and use electrochemical cells as power sources, instead. In order to make the switch efficient we want to control the cells with little power much smaller than the cell's power output. The two half-cells that make an electrochemical cells are typically connected via an insulated permeable membrane, which enables the passage of ions, yet, limits the flow of the bulk electrolyte molecules [9–10]. We replaced the bridge with a conductive, nano-pore membrane.

We wish to control the ion flow inside electrochemical cells, electrically. Control of the reaction near the anode or the cathode could be made with an auxiliary electrode and a saturated reference electrode using potentiostats or galvanostats. This approach may affect the surface potential of either electrode and the control process could become nonlinear. Our approach is different: here, a third permeable electrode (the gate electrode) is placed between the anode and the cathode. Upon biasing of this mid-electrode we form an electrolyte barrier to the flowing ions. Consequently, the external current and voltage of the cell are controlled [11–13]. Since the Debye's screening length in electrolytes is rather small, the pores of the metallic gate membrane ought to be on nanometer scale, smaller than the double-layer thickness [5].

Our approach is also different than what is accustomed to in the literature. The latter are typically conducted with functionalized membranes [14–15] for the purpose of ion separation. A Bipolar Ion Transistor reported in Ref. 1 is a good example – the design was based

on ion-selective membranes, and hence was ion specific. In contrast, we aim at controlling both anions and cations by the same electrolyte barrier potential.

2. Simulations

Simulations employed a commercial tool, based on finite elements (COMSOL v5.0). We used a very simple Zn–Pt cell: a Zn electrode as the anode and a Pt electrode as the cathode. The model allowed us to deal with a single ion component (Zn^{2+}) and took into account the reactions at the anode (oxidation of Zn) and on the cathode (formation of hydrogen), yet assumed no reaction at the gate. The diffusion of ions in the cell has considered only excess Zn^{2+} ions in the electrolyte. The local ion current density was assessed as the negative spatial derivative of the local electrolyte potential multiplied by the electrolyte conductivity. The ion current density is also proportional to the local electric field multiplied by the cell's ion conductivity. The effective electrolyte-to-metallic volume ratio in the porous electrode was 1:1. Other simulation parameters were: electrical conductivity of Pt, Zn, porous electrode and Zn^{2+} concentration in the electrolyte, respectively: 10^8 , 10^7 , 3×10^5 , 0.01 S/m. The upper tip of the Pt cathode was grounded and the upper tip of the Zn anode was kept at (–0.8) V, slightly lower than the standard potential of the Zn anode ($E_0^{\text{Zn}} = -0.82$ V). This means that the cell's voltage (between Pt cathode and the Zn anode) was +0.8 V.

Results are shown in Figs. 1, 2. In the absence of gate reaction, the gate voltage that stops the battery from functioning (the stopping potential) is 0 V when the gate is biased with respect to the grounded cathode. This values depends on the cell voltage though. The cell's current increases for negatively biased gate potential. The cell's current is dropping after a while due to a diminishing supply of Zn^{2+} ; yet, the stopping voltage remains the same. When the anode is chosen as

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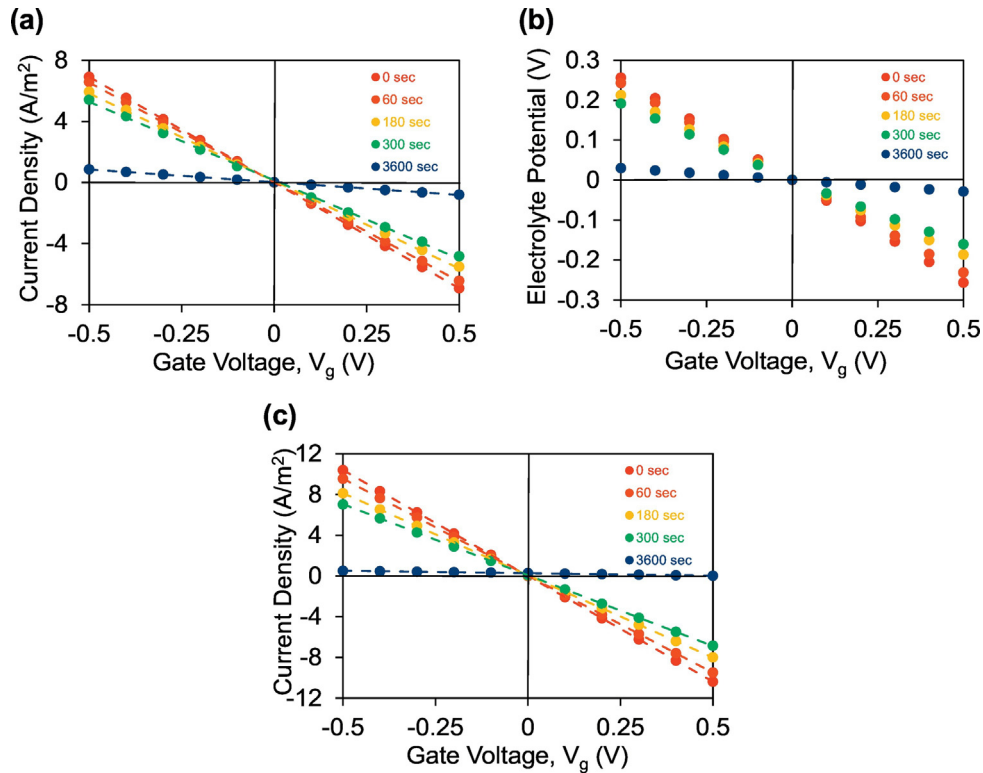


Fig. 1. (a) External cell's current density as a function of gate voltage. The current density is presented at various times. (b) Electrolyte potential at the mid-gate position as a function the gate voltage. The electrolyte potential is presented at various times. (c) The same with (a) yet, allowing a small reaction at the gate. One may notice a small but consistent temporal shift for $i_{cell} = 0$ as a function of V_g until V_g can no longer stop the cell from functioning.

ground, the trend of the curves is similar to the trend exhibited in Fig. 1 but the electrolyte potential is converging to a larger value after a long time; for example, 0.55 V at a cell voltage of 0.5 V. The reason is that the model implicitly assumes that the overpotential of the gate electrode is zero.

Adding a small reaction component to the gate (Butler-Volmer equation with an exchange current density of 1 mA/m² and anodic and cathodic transfer coefficient of 0.5), makes the stopping voltage larger and larger over time until one may no longer be able to stop the cell from functioning (Fig. 1c).

We may conclude that: (1) changing the electrolyte potential barrier at the gate affects the external cell's current; and (2) we can bias the gate such that the external cell's current is stopped from flowing if the reaction at the gate remains small.

A more detailed view of the electrolyte potential is given in Fig. 2. Shown are cross-sectional slices of the cell (the entire cell is 100 mm × 100 mm). For a gate potential of $V_g = -0.1$ V the electrolyte potential in the cell is positive, whereas when the gate potential is

$V_g = +0.1$ V, the electrolyte potential is negative. The rim of the gate electrode is outside the electrochemical cell and its potential is the biasing gate potential. We also note that the distribution of the electrolyte potential is not uniform and it is concentrated along the center of the gate electrode. This is due to the shape of the anode and cathode and their distance from the gate electrode. The curves of Fig. 1b,c were produced by selecting a mid-gate electrode point, yet similar results may be obtained for an averaged value throughout the gate electrode.

The model is adequate only up to a point. While it includes the effect of a double-layer capacitance at the porous gate electrode ($C = 0.2$ F/m²) it does not include ion trapping that may lead to membrane selectivity similarly to ion channels [4,5]. The model includes only one ion species (the Zn^{2+} ions and not the SO_4^{2-} ions) and it does not account for actual electrical circuitry which may lead to unintentional formation of hydrogen at the gate electrode [13]. When the actual circuit is assembled, the placement of ground is important. In the model, the ground was placed on the cathode. In the experiment, the ground was placed on the anode. In that case, the current trend is reversed because

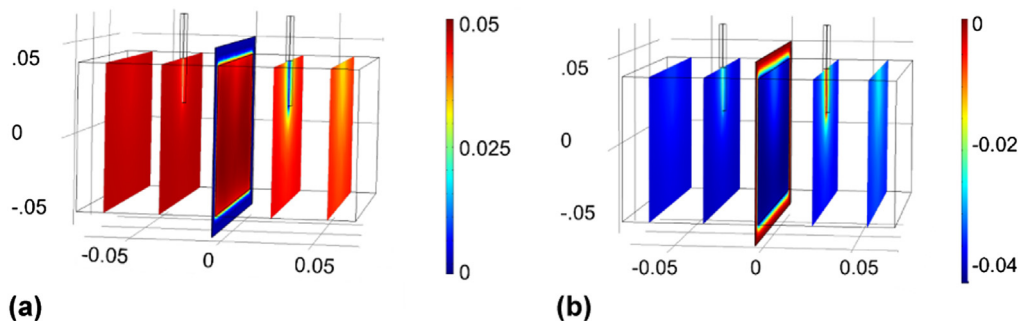


Fig. 2. Slices of the Electrolyte Potential at (a) $V_g = -0.1$ V (a) and at (b) $V_g = +0.1$ V after 60 s. The rim of the gate electrode is outside the electrolyte and its potential is the biasing potential, V_g .

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