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Electrochemical cells with intermediate capacitor elements

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ABSTRACT

Our goal is to electronically regulate electrochemical cells. For this, we introduced a third element, called the gate, which was placed between the cathode and the anode electrodes of the cell. Voltage applied to this element controlled the electronic current in the external circuit. The change in the cell's current was attributed to local change in the electrolyte potential, which impacted the flow of ions within the cell. We provide simulations and experimental data as a proof of concept. This is but the first step toward a demonstration of a two-dimensional, bi-carrier ion transistors.

1. Introduction

Electrochemical cells have been studied since the early eighteenth century [1,2]. Two half-cell reactions may be identified: one is the oxidation at the anode, dissolving positive metal ions into an electrolyte. The generated electrons flow from the anode through an external load to the second half-cell, containing the cathode, where a reduction is taking place; in our case, it is the generation of hydrogen. The circuit is completed by drift and diffusion of ions within the electrolyte(s) in both half-cells. The two-half cells are typically connected by a salt-bridge, which enables passage of ions, yet, limits the flow of the bulk electrolyte molecules. We replaced the salt bridge by an electronic element, which we call the gate. In the past we have used graphene – monolayer of graphite – as a single gate electrode [3,4]. Here we studied a capacitor-like gate element, instead.

2. Experiment

Simulations employed a commercial tool, which is based on finite elements (COMSOL). A wet-cell, rectangular-shape battery, with Zn electrode as the anode and Pt electrode as the cathode was used. The model took into account the reactions on the anode (oxidation) and on the cathode (formation of hydrogen), yet assumed that no reaction occurred at the gate. The diffusion of ions in the cell considered only excess Zn^{2+} ions in the electrolyte. The local current density was assessed as the negative spatial derivative of the local electrolyte potential (which is proportional to the local electric field) multiplied by the electrolyte conductivity. The permeable gate capacitor was modeled by two porous electrodes without (and sometimes with) a mid-porous insulating film. The effective electrolyte-to-metallic volume ratio in the porous electrode was 1:9. In this ideal case, we did not consider a reaction between the metallic capacitor and the electrolyte, hence, the potential of the solid portion of the porous electrode was kept at the gate potential, V_g. Other simulation parameters were: electrical conductivity of Pt, Zn, porous capacitor electrodes and Zn^{2+} in the electrolyte, respectively, 10^7, 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 −0.78 V, slightly lower than the standard potential of the Zn anode ($E_0^{(Zn)} = -0.82$ V). This means that the cell's voltage was 0.78 V. While the model is simple, it was able to capture the essence of effect.

In the experiments we used either 5% acetic acid, or 5% H_2SO_4 as electrolytes in both half-cells. The Zn^{2+} ions ended up in the electrolyte whereas protons turned into hydrogen gas at the Pt electrode. The gate electrode was constructed as a permeable capacitor: an Au/Pd film was first sputtered on one side of a 10-μm Teflon filter and two such filters were later pressed together to form a capacitor. The resistance of each metal film, while dry was ca 2×10^4 Ω/cm. The gate element was placed on a plastic plate at the cell's center. A 0.375 cm^2 hole in this mid-plate allowed ions to flow through [3,4]. The gate element was, thus, conductive and permeable to the passing ions. One plate of the gate capacitor, facing the anode was grounded; the gate bias V_g was applied to the other capacitor plate, facing the cathode (Figure 1a). The Pt cathode was grounded to prevent the biasing potential from floating. An Ag/AgCl reference electrode was attached to the biased capacitor plate with some potential drop at the contact. Calibration curve of the gate potential with respect to the reference electrode was obtained (Figure 1b).

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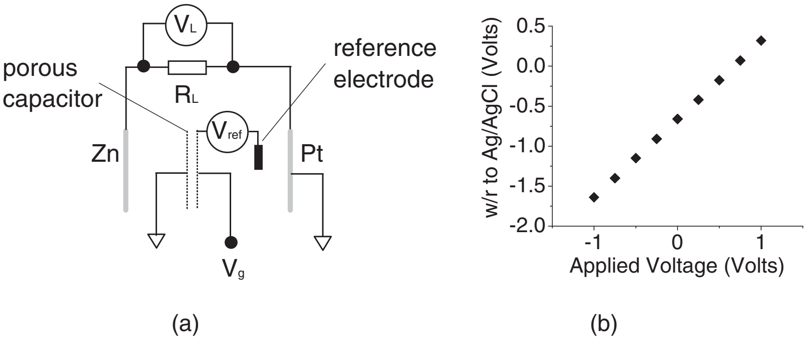


(a) (b)

Figure 1. (a) The cell's configuration. (b) Calibration in up and down ramp: capacitor voltage with respect to the reference electrode as a function of applied gate bias, V_g.

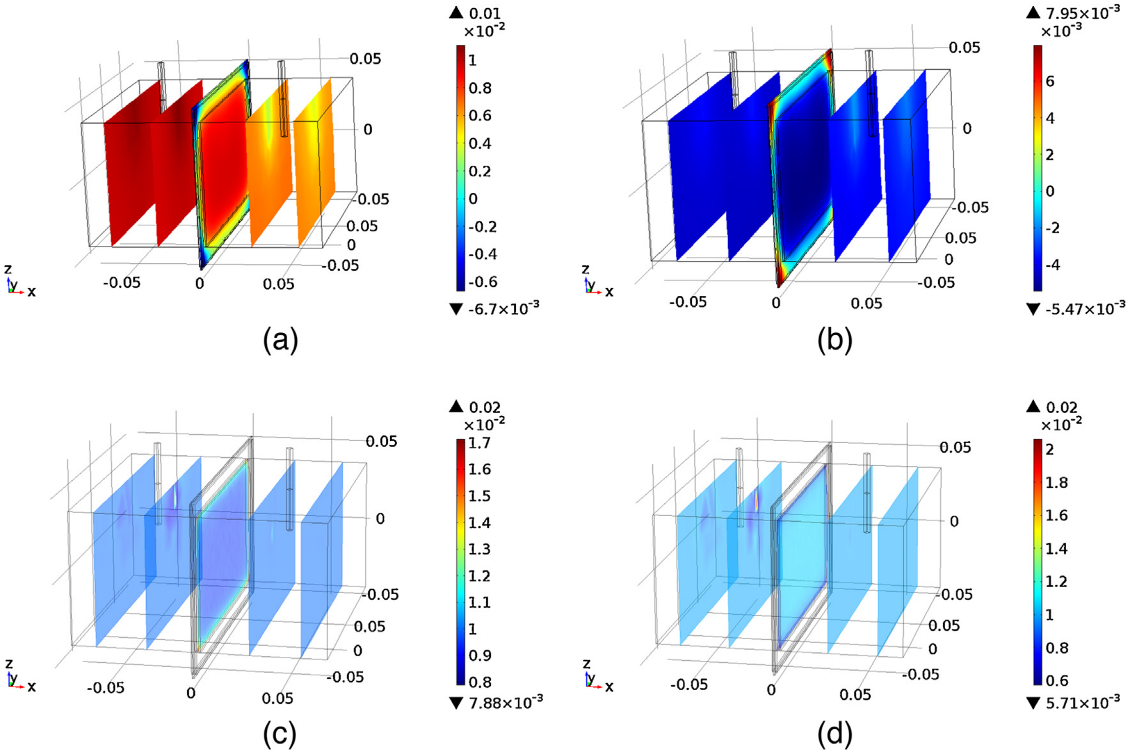
3. Results

In Figure 2a and b we show distribution of the electrolyte potential at various cell's cross sections for $V_g = \pm 0.1$. In Figure 2c and d we show the electrolytic concentration distribution (mol/m^3) at the capacitor for $V_g = \pm 0.1$ V. In Figure 3a we show simulations for the average electrolyte potential at the gate element as a function of the gate bias. The decrease in the electrolyte potential resulted in an electronic current decrease, which was assessed at the Pt electrode upper tip (Figure 3b).

For the experiments we considered two cases: one with load resistance much smaller than the internal cell resistance and one with load resistance larger than internal cell resistance. In Figure 4a and b we show experimental data for the first case. Here, the cell's current, flowing in the outer circuit through a load of 100 Ω, is plotted as a function of the gate bias (Figure 4a). In Figure 4b we plot the cell's current as a function of the voltage developed between the capacitor and the reference electrode. The curve is shifted due to the standard potential of the Au/Pd film in addition to the voltage drop at the contacts. When the cell's load was 50 kΩ, the I_{cell}–V_g curve became non-linear, saturating at $V_g \sim 0$ V with respect to the reference electrode. This may be expected if hydrogen was generated at the grounded capacitor plate and less hydrogen was formed at the Pt wire. We minimized the current to the grounded capacitor plate by interfacing it with a large resistor; in that case the I_{cell}–V_g curve remained linear (for both $R_L = 100\ \Omega$ and $50\ \mathrm{k}\Omega$) and the cell's current approached zero (Figure 5). We will return to this latter point later on.

4. Discussion and conclusions

Considering the simulation, the difference between the potentials on the solid electrode ϕ_S, the liquid electrolyte ϕ_L and the standard potential of the electrode E_0 is known as the overpotential: $\eta = \phi_S - \phi_L - E_0$. Initially, at the cathode, $\eta \sim 0$ and the electrolyte potential near the grounded cathode ($\phi_S = 0$, $E_0^{(\mathrm{cathode})} = 0$) is small; $E_0^{(\mathrm{cathode})} = 0$ because hydrogen is formed at the cathode. At the Zn anode, $\phi_S \equiv -0{\cdot}78$ V and $E_0^{(\mathrm{Zn})} \equiv -0.82$ V. Thus, the initial electrolyte potential is small, as well. If we assume that the porous gate electrode is screened by the slow flowing ions, then the electrolyte potential at its vicinity will be proportional to $-V_g$ and will decrease upon increasing the gate bias. We interpret



(a) (b) (c) (d)

Figure 2. Simulations: time dependent solution obtained after 60 min: local electrolyte potential (in Volts) when the applied gate voltage was (a) $V_g = -0.1$ V and (b) $V_g = +0.1$ V. The cell's voltage was 0.78 V. The electrolyte potential at the rim of the gate element is of no consequence since this portion of the gate electrode is outside the cell. The Zn^{2+} ion concentration distribution (in mol/m^3) for (c) $V_g = -0.1$ V and for (d) $V_g = +0.1$ V.