AN ACTUATION PRINCIPLE: THE ELECTROLYSIS OF WATER

Cristina Neagu, Henri Jansen, J.G.E. Gardeniers and Miko Elwenspoek

MESA Research Institute, University of Twente, P.O.Box 217, 7500AE Enschede
Phone: 053-4892805/2751; Fax: 053-4894434; E-mail: C.Neagu@el.utwente.nl

0. Abstract

In this paper the theory of water electrolysis in a closed electrochemical cell, that contains two electrodes, an electrolyte and a pressure sensor is described. From the leakage and electrochemical experiments done with this cell it is possible to obtain information about the applicability of the electrochemical principle in a closed cavity, the choice of the electrodes and electrolyte, and different types of leakages. Further, tests done with a control system, that consists of an electronic feedback system together with the electrochemical macro cell and the pressure sensor are presented. A value of the pressure is set and the regulator will actuate the electrochemical cell in such a way to get the desired pressure.

Keywords: electrolysis

1. Introduction

In the field of MEMS there is an ever increasing need for actuators able to deliver a relatively large amount of mechanical power, i.e. they should create sufficient displacement together with a big force or pressure. When a big force is needed, generally piezoactuators are used, however, this type of actuators suffer (except for piezoelectric bimorphs) from a small displacement. In contrast, electrostatically driven comb actuators are found when the displacement should be high, but, now the force is relatively small.

To overcome this limitation, in 1996 the authors introduced a new actuation principle in the field of MEMS characterised by a large displacement while maintaining a high pressure: the electrochemical (EC) actuator [1, 2]. In such an actuator, a miniaturised gas sealed cavity filled with an electrolyte and two electrodes is connected to an external power supply to generate gas from the electrolyte by way of electrolysis. The produced gas is used to deflect a membrane, which in turn can be used to perform mechanical work.

The paper will start with a short description of the reaction kinetics underlying the electrolysis and vaporisation of water. After this, the design of an EC cell and experiments will be discussed. To stabilise generated gas pressure at a desired value, as well as the deflection of the membrane, a feedback control system has been incorporated as discussed in the last section.

2. Theory
2.1 Electrolysis of water

The electrolysis of water is a well-known principle to produce oxygen and hydrogen gas from water. In figure 1a, a schematic of a sealed electrochemical cell is shown. The cell is partly filled with pure water and has two electrodes which are connected with an external power supply. At a certain critical voltage between both electrodes, the electrodes start to produce hydrogen gas at the negatively biased electrode and oxygen gas at the other one. The amount of gas evolved per unit time is directly related to the current passing the water.

In water, there is always a certain percentage found as ionic species; H^+ and OH^- represented by the equilibrium equation:

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq) \tag{1}$$

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At the negative electrode, the H^+ ions will gain an electron thereby forming hydrogen. At the positive electrode, the OH^- ions will deliver an electron and finally creates oxygen gas:

positive electrode: $4OH^- - 4e^- \rightarrow 2H_2O + O_2$ (2a)

negative electrode: $4H^+ + 4e^- \rightarrow 2H_2$ (2b)
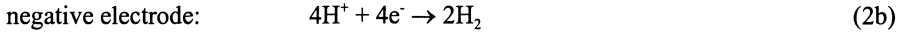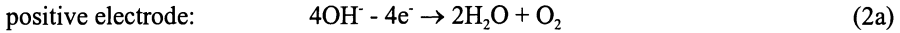
In case of acidic or basic water, the reactions which occur at the electrode interface are slightly different. Anyhow, the overall reaction kinetics, i.e., presuming no additional side reactions is:

$$2H_2O \Rightarrow (4e^-) \Rightarrow O_2 + 2H_2 \qquad (3)$$

So, the production of 3 gas molecules out of two water molecules needs 4 electrons. The complete electrolysis of 1 mole of water molecules is, therefore, accompanied by 2 moles of electrons. The charge of 1 mole of electrons is known as Faraday's constant, $F = 96400$ [C]. For the electrolysis of water, the standard reaction enthalpy ΔH^0 is, $\Delta H^0 = 285830$ [J/mol] and the free energy can be calculated as:

$$\Delta A^\circ = \Delta H^\circ - TR\Delta n - T\Delta S^\circ = 233147 \text{ [J/mol]} \qquad (4)$$

In our case of a closed cell we use ΔA instead of ΔG, that is used for an open cell. The voltage necessary for an electron to overcome the Helmholtz energy barrier is, thus: $\Delta V_a^\circ = \Delta A^\circ / n \cdot F = 1.21$ volt, defined as the standard free voltage.

To start a reaction, it is normally necessary to overcome an (extra) energy barrier; the activation energy E_{act}. The number of molecules able to overcome this barrier is controlling the reaction rate, ρ, and it is given by the statistical Maxwell-Boltzman relation which has an exponential behaviour: $\rho \sim \rho_0 \cdot \exp(-E_{act}/RT)$. So, the activation energy is depicting the speed with which a reaction occurs.

We are now able to write down the energy balance during the electrolysis of water. Assume that 5 V is applied to the sealed EC cell, fig. 1a. The energy, ΔE_{elec}, supplied by the voltage source, ΔU, per mole of water is $\Delta E_{elec} = \Delta U \cdot nF = 5 \cdot 2 \cdot 96400 = 964$ kJ/mol. This energy equals the reaction free energy plus the IR drop ($E_{IR} = IR \cdot nF$; i.e. losses causing Joule heating) plus the overpotential, η, per electron ($E_\eta = \eta \cdot nF$), fig. 1b. The IR-drop is caused by the low electrical conductance of the water. It can be improved by making the electrolyte acid or alkaline, or by adding a support electrolyte which delivers extra charge carriers. The overpotential is responsible for the typical exponential behaviour of the current flowing through the solution as given by the so-called Bultler-Volmer equation. The activation energy can be lowered by using electrodes with a catalytic action such as platinum. This action can be described as [3]:

$$H_2 + 2Pt \Rightarrow 2Pt\text{-}H \qquad (5a)$$
$$O_2 + 2Pt \Rightarrow 2Pt\text{-}O \qquad (5b)$$
$$2Pt\text{-}H + Pt\text{-}O \Rightarrow 3Pt + H_2O \qquad (5c)$$

As can be observed in fig. 1b; the balance of energy per mole of reaction events is:

$$\Delta E_{elec} = \Delta A + E_{IR} + E_\eta \qquad (6)$$

All the energies involved in this equation of balance, except for ΔA, will leave the reaction as heat: $T\Delta S$. In first instance, this heat will be used for the vaporisation of the water
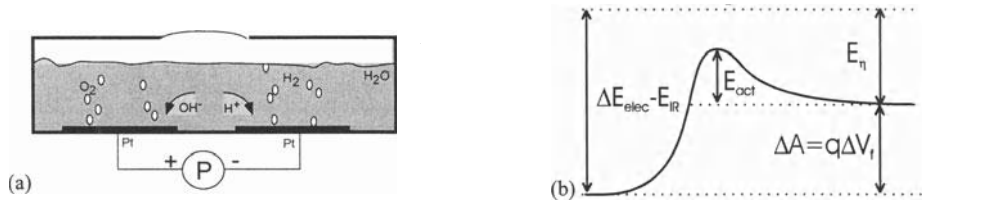

Figure 1. (a) Simplified schematic of a sealed electrochemical cell. (b) Schematic representation of energies involved in a reaction.

and, thus, increasing the pressure inside the cell. However, after a while all this heat will be lost due to heat transport to the surroundings and the pressure will decrease again. Of course, heat will be exchanged with the surroundings. So, in fact we have to take the enthalpy instead of Helmholtz as the energy involved in the electrolysis process. The efficiency, ε, of an electrolysis cell is thus:

$$\varepsilon = \Delta H/\Delta E_{elec} = \Delta H/(\Delta A + E_{IR} + E_\eta) \tag{7}$$

For water electrolysis, the value of $\Delta H = 285.830$ J/mol and $\Delta A = 233.147$ J/mol. Hence, under ideal reversible conditions, $\varepsilon = 120\%$. This means that the electrolysis would take place with 120% efficiency in respect to the electrical energy source. Thus, heat would have to flow into the cell from the surroundings. When the value of the denominator in eq. 7 is 1.48 nF, i.e. electrolysis is performed at an over-potential of 0.25 Volt, the electrolyser would perform at 100% efficiency. Under these conditions, the cell neither heats nor cools. $V_{th} = \Delta H/nF$ is denoted as the thermoneutral potential. In practice, the IR drop may itself be around 0.25 V. Anyway, the overpotential η should be kept low in order to maximise the efficiency and to minimise the production of heat. Of course, the lower the overpotential the slower the reaction will proceed and we would be forced to make a compromise. A way to increase the current without increasing the overpotential is to increase the contact area between the electrodes and the liquid.

2.2 Vaporisation of water

Another way to increase the pressure inside a closed volume is by increasing the temperature. In case of liquids, the temperature dependency of the pressure is normally much higher due to the production of vapour gas. In case of water, the overall reaction is:

$$H_2O(l) \Leftrightarrow H_2O(g) \tag{8}$$

$\Delta H^0 = 44004$ J/mol, the standard enthalpy of vaporisation. The vapour pressure is increasing exponentially with the temperature as can be found in most books considering thermodynamics. In case of a constant volume the relation is:

$$P_v(T) = P^o \exp\left(\frac{-\Delta A^o}{RT}\right) = P^o \exp\left(\frac{R\Delta n + \Delta S}{R}\right) \exp\left(\frac{-\Delta H^o}{RT}\right) \tag{9}$$

The sensitivity of the vapour pressure with respect to the temperature can be found by differentiating $P_v(T)$ with respect to T. We arrive at:

$$\frac{dP_v}{P_v} = \frac{\Delta H^o}{RT} \cdot \frac{dT}{T} \tag{10}$$

3. Experimental

As a start, it is necessary to close the macro cell hermetically from the surroundings to harness the gases produced. In principle this is not difficult, however, we would like to have a cell which can be easily modified with respect to the electrode materials and electrolytes. The final version did incorporate some basic ultra high vacuum components from the vacuum technology. In figure 2, an art impression of a basic macro cell is shown. A stainless steel blank flange was machined (a hole was drilled) to be able to mount the pressure sensor. The pressure sensor was connected by way of a Viton 'O' ring and Teflon tape to ensure a leak-free montage. The electrodes were inserted inside standard K40 "window-glasses" that has a stainless steel support-ring. Holes, 1mm in diameter, were drilled into the glass through which the electrodes were inserted. The residual gaps were filled with Torrseal to prevent leakage. After filling the cell with the electrolyte, all the parts were assembled and closely tight by way of a flange clamp.

During long-term measurements (exceeding many days) pressure and temperature fluctuations in the atmosphere could alter our monitored signal and validity of the conclusions drawn drastically. When the macro cell is closed under atmospheric pressure and is placed inside a vacuum surrounding, only fluctuations of the base pressure caused by the vacuum pump will disturb the signal. The set-up of the macro cell inside the vacuum chamber is given in figure 3. The pressure sensor to measure the gas evolution due to electrolysis is a miniature vented gauge transducer of Data Instruments (MM10013). The sensor is temperature compensated in stainless steel housing and able to measure pressures up to 100PSI~ 7bar. It uses piezo-resistive elements driven by a stabilised 5 V supply from an external voltage source (Voltcraft TNG35). To minimise the ripple from this source, a voltage regulator is utilised (LM7805). The voltage monitor of the pressure sensor is a programmable unit from Hewlett Packard (HP34401a) with an IEEE488 (GPIB) port to enable data exchange. This data from the pressure sensor is recorded with the use of HP-Vee software.

Now the cell has been placed inside a vacuum chamber, the problem arises how to connect the electrical leads from the pressure sensor to the units outside the vacuum chamber. The standard electrical feed-through flange from the vacuum technology is not appropriate because temperature differences between the two leads of the sensor signal at the flange interface would cause thermo-voltages much too large to be neglected. Therefore, again a modified blank flange is used. The leads are directly led through the flange without introducing an extra electrical contact to avoid thermo-voltages. The gaps left are filled with Torrseal to prevent leakage.
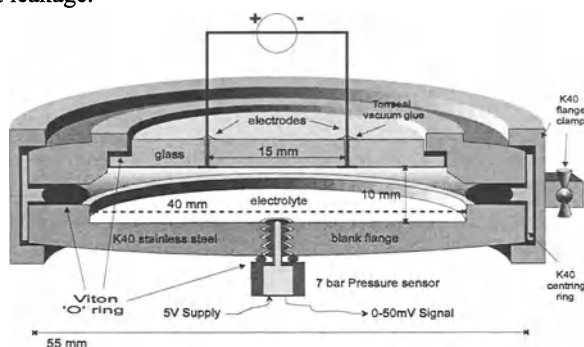

Figure 2. Basic set-up of the vacuum sealed macro cell with standard UHV components.
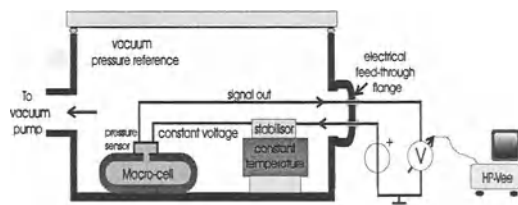

Figure 3. Basic experimental set-up of the macro-cell.

4. Results

Gold: In the first experiment, the macro cell has two gold electrodes and the result is given in figure 4. The plot shows three peaks; the first peak is caused by a current through the cell of 500µA for 200sec at 3.8V, the second one by 100µA for 1000sec at 3.0V, and the third peak is caused by 20µA for 5000sec at 2.5V. So, the total charge transported to the cell was constant for all peaks. Clearly, the increase in pressure is identical for all the three peaks, as it
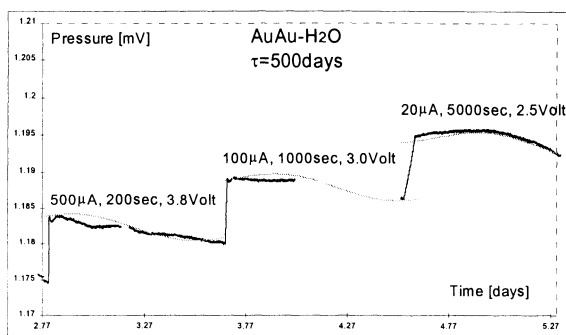
Figure 4. Behaviour of the EC cell with gold electrodes, the 'lifetime' of the open circuit state is > 500 days.

should because the current of electrons controls the flow of reaction gases out of the electrolysis process. The drop in pressure after switching the electrolysis current of is a very slow process with a response time better than 500 days. This means that the leakage of the cell or the pressure drop caused by other processes is minimal.

Platinum: The next experiment is using two platinum electrodes (figure 5a). Again three electrolysis sequences have been performed; the first peak is caused by 2mA for 50sec, the second by 1mA for 100sec, and the third is 0.5mA for 200sec. It can be seen that the signal is reaching a plateau after a sharp initial peak directly after switching of the electrolysis current. The sharp peak is thought to be caused by the relatively large over voltage necessary to sustain such a high current. This voltage will heat the liquid and vaporise some water. After switching the current off, the cell is loosing its heat quickly to the surroundings and, therefore, the water vapour will condense back to liquid water. It is found that the height of the plateau is directly related to the amount of electrons driven through the cell, i.e. the flow is proportional to the current times the time the cell is fed with this current. To show the influence of the catalytic action of the platinum, a current of 0.5mA was driven through the cell for a very long time of 90 minutes (fig. 5b). It is observed that the pressure drops quickly to its value back with a response time of 3.5 days. This drop is thought to be caused by the catalytic action of the platinum.
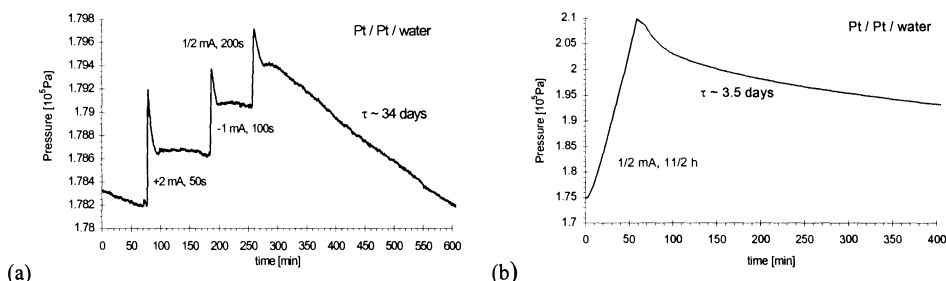

(a)

(b)

Figure 5. The EC cell with platinum electrodes. The lifetime of open circuit state is very short (~3.5 days). a) The behaviour for short current pulses and b) for a long pulse.

Silver: The last material which has been tested for the electrolysis of water is silver. In fig. 6 the result is shown. As can be observed in fig. 6a, the increase of pressure is again directly related to the charge which has been driven through the cell. A remarkable difference, however, is that there is no sharp peak is observed directly after the current is switched off. This difference is probably caused by a leakage of the cell: This leakage will cool the water inside the cell very quickly due to the heat needed for the vaporisation (ΔH). After the cell

was cleaned and assembled again, the characteristic sharp peak appeared. The decay time was approximately 34 days. Moreover, after disassembling the cell, it was found that the electrodes were completely eroded and a black substance, probably silver oxide, was found as an emulsion in the water.

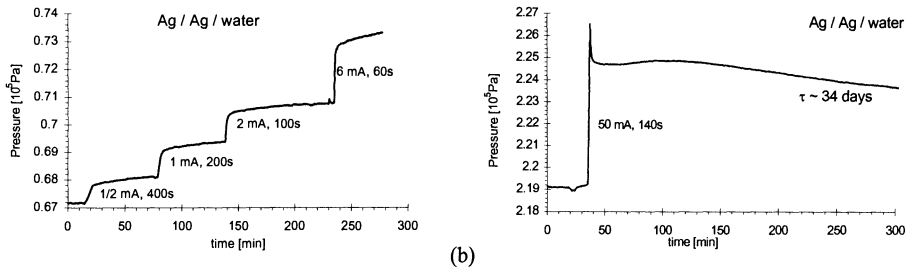(a)   (b)

Figure 6. The EC cell with silver electrodes. The lifetime of the open circuit state is intermediate (34 days). (a) The behaviour for short current pulses and (b) for a long pulse.

5. The feedback control system

A constant cell pressure can be achieved by incorporating a feedback controller, together with the sensor and actuator forming a regulating system. In fig. 7a, such a total regulated system is shown and in fig. 7b the electronic circuit of feedback controller is given in detail. It consists of three sections; a 100 times amplifier for the sensor signal (OP27), an integrator build around a comparator to pre-set the cell pressure (CA3140), and a current amplifier to feed the electrolysis sequence (BD139). After amplification, the signal is fed to the CA3140 where it is compared to the requested pressure. This is achieved by a trim-potentiometer "Pressure Set" which is able to maintain a pressure inside the cell up to 7bar. The signal is integrated to filter out any noise. The integration time is controlled by a replaceable capacitor, in this case 10nF. The capacitor across the base emittor of the current amplifier BD139 is meant to prevent parasitic oscillations.

The result of the feedback controller upon the pressure inside the cell is shown in fig. 8. Clearly, the circuit is stabilising the cell pressure much better as would be possible without the controller.

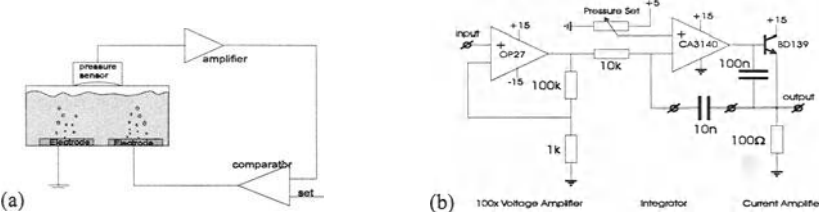(a)   (b)

Figure 7. (a) Schematic of the feedback controller to stabilise the cell pressure. (b) Electronic circuit of the feedback controller to settle the cell pressure.
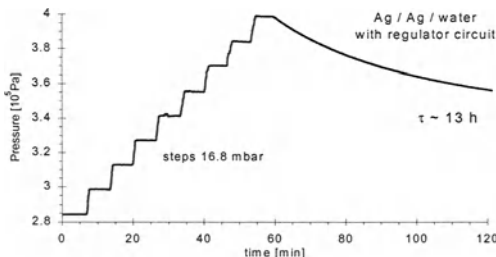

Figure 8. Output of the cell pressure with feedback controller

6. Conclusions

In this paper the results of an electrochemical cell have been presented. It is found that the pressure drops relatively fast (a few days) back to its initial value when platinum is used. The reason would be that platinum has a low so-called activation level to make the transition of hydrogen with oxygen gas into water possible. Due this characteristic, the non-equilibrium state, i.e. hydrogen and oxygen gas, is difficult to sustain. It is proven experimentally that the decay of the pressure after switching the cell off (the so-called passive state of the cell) is indeed improving by the use of gold electrodes. However, a disadvantage of this higher activation energy level is the higher so-called over-potential necessary to drive the cell from one passive state (e.g. low cell pressure) into another passive state (e.g. high cell pressure). This higher overpotential will give rise to the production of heat which will be used to convert water into water vapour. After the current to the cell is switched off, this vapour will condense until thermal equilibrium is reached again. This thermal decay effect is a relatively fast process with respect to the electrolyse back reaction and, therefore, an extra and sharp peak on top of the step caused by the electrolysis is found.

With respect to the usability of an electrolysis process as an actuator, it can be stated that the effect of vaporisation of water is the main bottleneck. Rapid changes in temperature will cause large water vapour pressure changes. These changes are compensated for by the electrolysis process with the help of a feedback control circuit. This circuit has been tested in this paper with very good results. However, the circuit was in fact meant to regulate the cell pressure and not the vapour pressure! So, under certain circumstances it is possible that the EC cell will be more busy with controlling the vapour pressure of the cell than with regulating the cell pressure.

When the efficiency of the electrolysis process and the additional vapour pressure peak is not a problem, it can be said that the EC actuator is able to create and maintain a very high pressure inside a closed cell. Pressures beyond 7 bar have been reached without any difficulties. This maximum is only restricted by the limitation of the pressure sensor itself. Due to this characteristic, the EC cell can open possibilities far beyond the reach of other types of actuators, such as the thermal actuator, piezo actuator, or magnetic actuator.

To create a more efficiently operating cell, we may study equation 7. A first approach would be to minimise the IR drop, E_{IR}, by increasing the conductance of the solution. Secondly, E_η can be minimised by using a catalytic material like platinum or increasing the active surface of the electrode. This can be achieved by creating very rough surfaces, i.e. so-called black platinum. However, to avoid a fast recombination of the gases towards water, the activation energy should be high (i.e. gold instead of platinum electrodes).

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