



The electrolysis of water: an actuation principle for MEMS with a big opportunity

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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 macrocell 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 leakage. To control the pressure of the electrochemical actuator automatically, an electronic feedback system was connected to the cell. A value of the pressure is set and the regulator will actuate the electrochemical cell in such a way to get the desired pressure. © 2000 Elsevier Science Ltd. All rights reserved.

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.

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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 gas sealed microcavity 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 macrocell and experiments will be discussed. To stabilise generated gas pressure at a desired value, a feedback control system has been incorporated.

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 Fig. 1, a schematic of a sealed electrochemical cell is shown. The cell is 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 cell. In water, there is always a certain percentage found as ionic species; H^+ and OH^- represented by the equilibrium equation:



Oxygen and hydrogen gas can be generated at noble metal electrodes by the electrolysis of water:

‘+’ electrode:

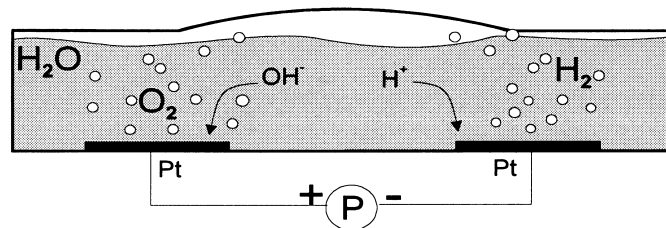


Fig. 1. Sketch of a sealed electrochemical cell.

‘-’ electrode:



In case of acidic or basic water, the reactions which occur at the electrode interface are slightly different. In water electrolysis there are no side reactions that could yield undesired products, thus the net balance:



The minimum necessary cell voltage to start electrolysis, E_{cell}^0 , is given under standard conditions (P , T constant) by:

$$E_{\text{cell}}^0 = \frac{-\Delta G^0}{nF} \quad (4)$$

where ΔG^0 is the change in the Gibbs free energy under standard conditions and n is the number of electrons transferred. In our case of a closed EC cell, the conditions change slightly from standard conditions, open cell (P , T) = constant to closed cell (V , T) = constant because the change in the cell volume is smaller compared to that of pressure. Thus, instead of ΔG we use ΔA , the free energy (Helmholtz).

The voltage necessary for an electron to overcome the Helmholtz energy barrier is thus:

$$E_{\text{cell}} = \frac{-\Delta A^0}{nF} \quad (5)$$

$$\Delta A^0 = \Delta H^0 - TR\Delta n - T\Delta S^0 \quad (6)$$

For the electrolysis of water, the standard reaction enthalpy is, $\Delta H^0 = 285.8$ [kJ/mol], $\Delta n = 1.5$, $\Delta S^0(\text{H}_2) = 130.6$, $\Delta S^0(\text{O}_2) = 205.1$, $\Delta S^0(\text{H}_2\text{O}(\text{l})) = 70$ J/mol K, $\Delta S_{\text{tot}}^0 = 130.6 + \frac{1}{2} \cdot 205.1 - 70 = 163.14$ J/mol K, and $\Delta A^0 = 233.1$ [kJ/mol]. So, the minimum necessary cell voltage is $E_{\text{cell}} = 1.21$ V. In the case of an open cell, $E_{\text{cell}}^0 = -\Delta G^0/nF = 1.23$ V, with $\Delta G^0 = \Delta H^0 - T\Delta S^0 = 237.2$ kJ/mol (standard conditions, 1 bar, 25°C). To start a reaction, it is 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, r , and it is given by the statistical Maxwell–Boltzman relation which has an exponential behaviour: $r \sim r_0 \exp(-E_{\text{act}}/RT)$ [3]. So, the activation energy is depicting the speed with which a reaction occurs.

The maximum possible efficiency of an ideal closed EC cell is defined as:

$$\epsilon_{\text{max}} = \frac{\Delta H}{\Delta A} = -\frac{\Delta H}{nFE_{\text{cell}}} \quad (7)$$

In reality, the efficiency of an EC cell is given by:

$$\varepsilon_{\text{real}} = \frac{\Delta H}{nE_{\text{elec}}} \quad (8)$$

where ΔE_{elec} is the voltage to drive the EC at I :

$$\Delta E_{\text{elec}} = \Delta A + IR + \Sigma\eta \quad (9)$$

where R is the total ohmic series resistance in the cell including external circuit resistance, electrolyte, electrodes, membrane material; $\Sigma\eta$ is the sum of the overpotentials (activation overpotential at the cathode and anode, and the concentration overpotential due to the mass transport of the gaseous products away from the electrode surfaces). The activation overpotential increases numerically by increasing the current density and can be lowered by using electrodes with a catalytic action such as platinum. The balance energy, per mole of reaction events, during the electrolysis of water is schematically shown in Fig. 2. All the energies involved in this equation of balance, except for ΔA , will leave the reaction as heat: $T\Delta S$ (Joule heating).

For water electrolysis, under ideal reversible conditions, $\varepsilon_{\text{max}} = 120\%$. 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 $1.48nF$ (overpotential of 0.25 V), the EC would perform at 100% efficiency. Under these conditions ($\Delta S = 0$, $\Sigma\eta = 0$, so $\Delta G = \Delta H$), the cell neither heats nor cools: $E_{\text{tn}} = \Delta H/nF = 1.47$ V is denoted as the thermoneutral potential [4,5]. The cell gives out heat at potentials above 1.47 V and takes it in at potentials below this value, under the condition that cell temperature is to be maintained constant. In practice, the IR drop may be ca 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 have 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.

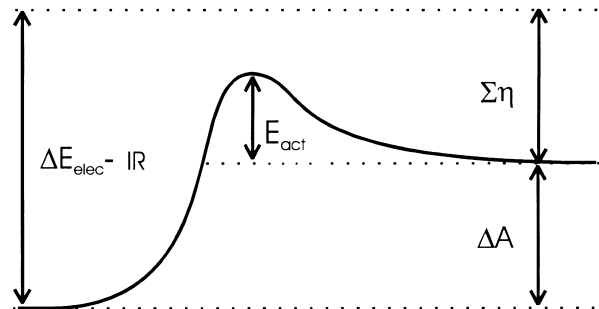


Fig. 2. Schematic representation of the energies involved in a reaction.

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 much higher due to the production of vapour gas. In case of water, the overall reaction is:



$\Delta H^0 = 44004 \text{ J/mol}$, the standard enthalpy for vaporisation. The vapour pressure is increasing exponentially with the temperature. In case of a constant volume the relation is:

$$P_v(T) = P^0 \exp\left(\frac{-\Delta A^0}{RT}\right) \quad (11)$$

The sensitivity of the vapour pressure with respect to the temperature:

$$\frac{dP_v}{P_v} = \frac{\Delta H^0}{RT} \cdot \frac{dT}{T} \quad (12)$$

The minimal energy needed for the transition of water into water vapour gas is lower than that of the transition of water into O_2 and H_2 gas by a factor $\Delta H_T / \Delta A_{EC} \sim 1/5$. So, why not use vaporisation by heating instead of the electrolysis of water? The reason is the difficulty to maintain the non-equilibrium condition, i.e. the gasses stability with respect to the back reaction. Due to the activation energy, the EC cell is, in principle, a switching device; only during changing the pressure, energy is needed. When the power is disconnected, the pressure sustains at the same level (non-equilibrium condition!). In the case of the heating, energy has to be supplied constantly to maintain the non-equilibrium.

3. Experimental

The macrocell has to be hermetically closed from the surroundings to harness the gases produced. In principle this is not difficult, but we would like to have a cell which can be easily modified with respect to the electrode materials and electrolytes. The macrocell (Fig. 3) uses basic high vacuum (HV) components from the vacuum technology.

During long-term measurements, pressure and temperature fluctuations in the atmosphere could alter the monitored signal and validity of the results drastically. When the macrocell is closed under atmospheric pressure and is placed inside a vacuum surrounding, the fluctuations of the atmospheric pressure will not influence the signal of the differential pressure sensor (only fluctuations of the base pressure caused by the vacuum pump may disturb the signal). Due to this vacuum reference we have changed the differential pressure sensor into an absolute sensor.

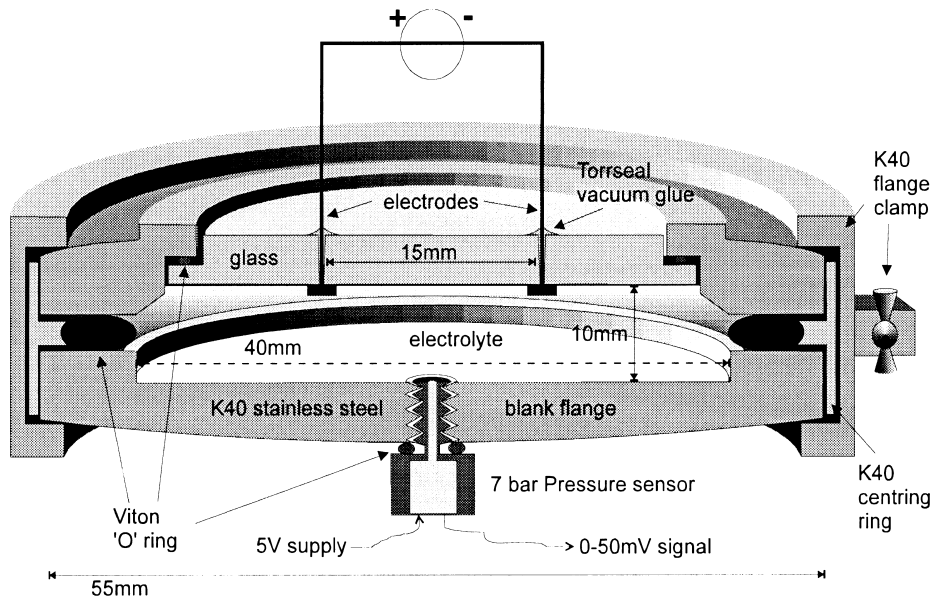


Fig. 3. Basic set-up of the vacuum sealed macro cell with standard HV components.

The pressure sensor is a vented gauge transducer of Data Instruments (MM10013), sensing at constant volume using piezoresistive elements. It is temperature compensated in stainless steel housing and measures up to 7 bar (100 PSI). The voltage monitor of the pressure sensor is a programmable unit from Hewlett Packard (HP34401a) with an IEEE488 (GPIB) port to enable data exchange, recorded with HP-VEE software.

The electrical connections from the pressure sensor, inside the vacuum chamber to the outside units are not appropriate to be done by the standard electrical feed-through flange 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. So, the leads are directly led through the flange without introducing an extra electrical contact and the gaps left are filled with Torrseal to prevent leakage. The electrodes tested for the electrolysis of water (gold, platinum, silver, and copper) were wires of 1 mm diameter, area ca 0.3 cm², purity 99.99% from Goodfellow.

4. Results

4.1. Platinum

In a macrocell with two Pt electrodes, three electrolysis series have been performed (Fig. 4); 2 mA for 50 s (5 V), 1 mA for 100 s (3.8 V), and 0.5 mA for

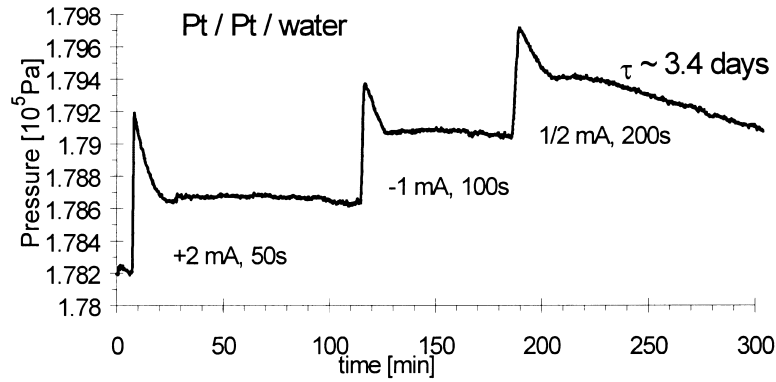


Fig. 4. The EC cell behaviour with Pt electrodes for big current pulses. The pressure decay is very short ~ 3.5 days.

200 s (3.2 V). The signal is reaching a plateau after a sharp initial peak directly after switching off 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 may heat the water creating an extra pressure due to the thermal expansion or vaporisation of the water. After switching the current off, the cell is loosing its heat quickly to the surroundings and, the water pressure will drop fast. The height of the plateau is directly related to the amount of charge driven through the cell. The decay of pressure after switching the electrolysis current is fast, ca 3.5 days.

4.2. Gold

Three electrolysis series are done (Fig. 5): 500 μA for 200 s (3.8 V), 100 μA for 1000 s (3.0 V), and 20 μA for 5000 s (2.5 V), such the total charge transported to

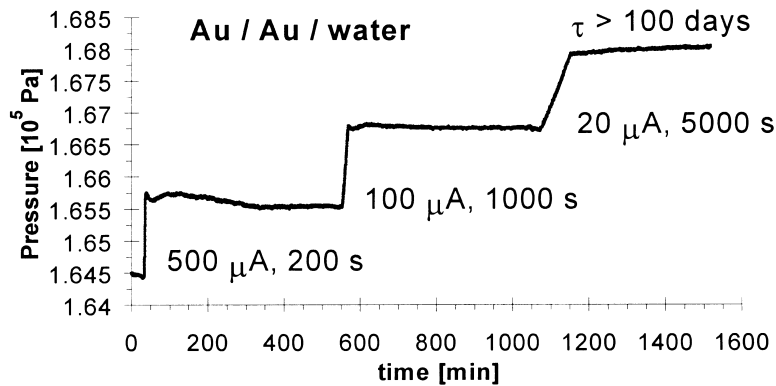


Fig. 5. Behaviour of the EC cell with Au electrodes. The open circuit decay is very long, over 100 days.

the cell was constant for all peaks. Clearly, the increase in pressure is identical for all three series. The open-circuit pressure decay is long, more than 100 days. This means that the leakage of the cell or the pressure drop caused by other processes is minimal.

The cell voltage for Au/Au electrodes is ca 0.5 V bigger than for Pt/Pt order to get the same current. This extra voltage is related to the difference in the activation energy.

The influence of the catalytic action of the platinum was also tested by using two gold electrodes and a piece of Pt inserted in the macrocell (it is fixed by glue on the glass). The open circuit decay decreases significantly from more than 100 days to ca 12 days.

4.3. Silver

The electrolysis of water is shown in Fig. 6: 0.5 mA, 400 s (0.5 V); 1 mA, 200 s (0.8 V); 2 mA, 100 s (1.1 V); and 6 mA, 60 s (2 V). These potentials across the cell are much smaller than those for Pt/Pt, and Au/Au for the same currents. This may be because another reaction occurs, e.g. silver oxide formation at low potentials. At the other one hydrogen is generated thus, the cell potential to generate gas is much smaller.

The increase of pressure is again directly related to the charge which has been driven through the cell. A difference is the absence of the sharp peaks after the current is switched off. This comes from the low potential across the cell, so no heat is created. When the current is set at a high value the characteristic sharp peak appeared. The decay time was approximately 34 days.

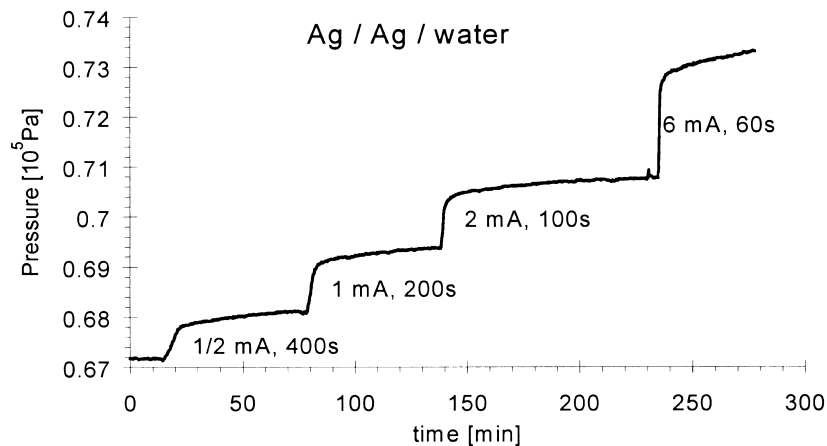


Fig. 6. The EC cell with Ag electrodes for big current pulses. The pressure decay for open-circuit is intermediate 34 days.

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. 7 such a total regulated system is shown. 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). Fig. 8 shows the result of the feedback controller upon the

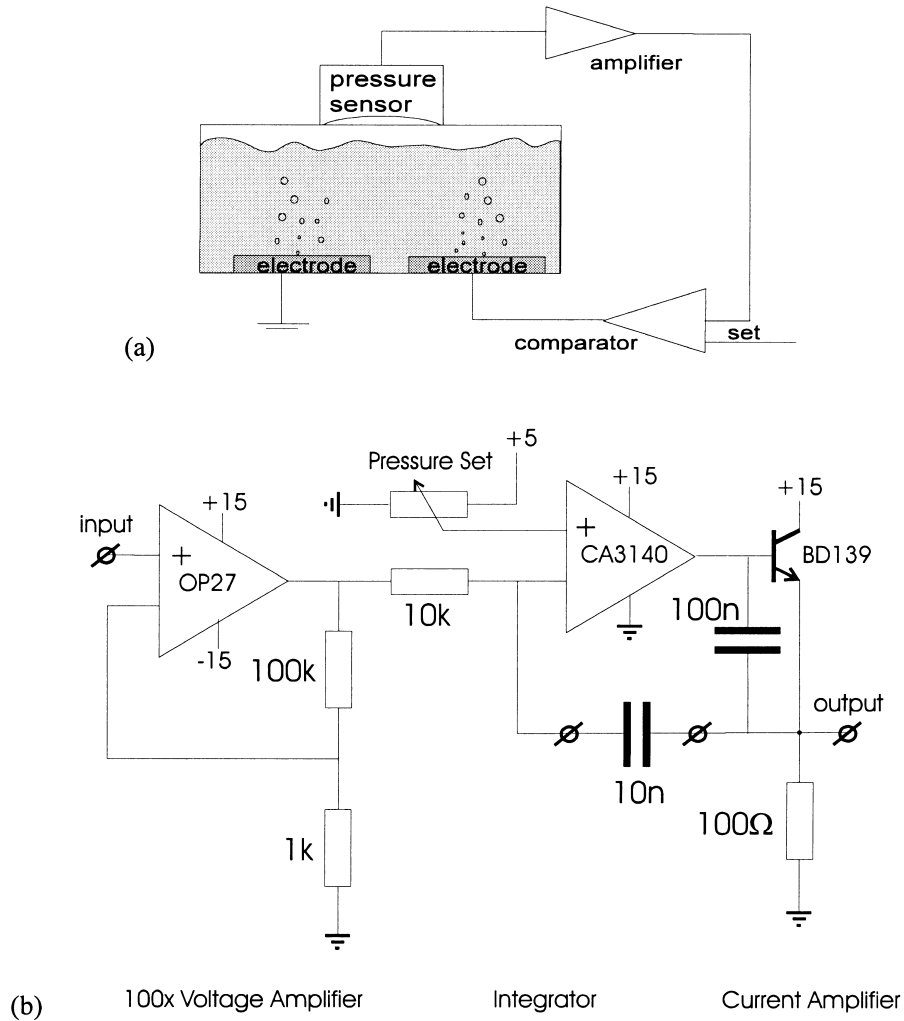


Fig. 7. (a) Schematic of the feedback controller to stabilise the cell pressure. (b) Electronic circuit of the feedback controller to settle the cell pressure.

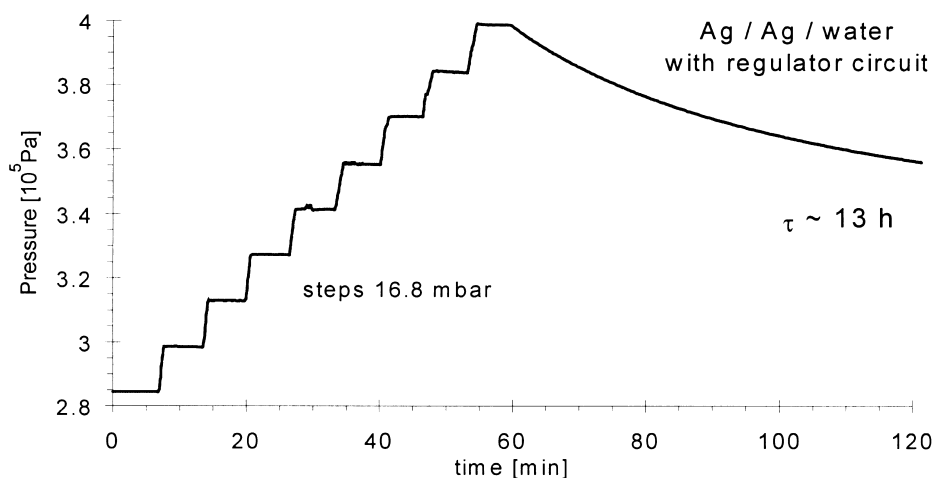


Fig. 8. Output of the cell pressure with feedback controller.

pressure inside the cell. Clearly, the circuit is stabilising the cell pressure much better as would be possible without the controller.

6. Conclusions

In this paper the results of an electrochemical macrocell have been presented. The increase of pressure is directly related to the charge driven through the cell. The pressure drops relatively fast (few days) back to its initial value when Pt is used. The reason would be that platinum has a low activation energy that facilitate the reaction of H_2 with O_2 gas to water. It is proven experimentally that the open-circuit pressure decay (EC passive state) is improved by the use of Au electrodes. However, a disadvantage of a bigger activation energy is the higher overpotential necessary to drive the cell from one passive state to another. This higher overpotential might be added to the heat production, creating an extra water pressure overlapping the electrolysis pressure. After the current to the cell is switched off, this thermal decay effect is a relatively fast process with respect to the electrolysis back reaction and an extra and sharp peak on top of the step caused by the electrolysis is found.

The feedback circuit was controlling automatically the cell pressure: by setting a value of the pressure, the regulator actuated the electrochemical cell in such a way to get the desired pressure.

When the efficiency of the electrolysis process is high (i.e. low ohmic losses, overpotentials), it can be said that the EC actuator is able to create and maintain a very high pressure inside a closed cell. 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.

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