

Theory and operation of a steady-state pH differential water electrolysis cell

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The reversible potential for conventional water electrolysis is rather high, 1.23 V at 25° C. In this paper we present a new water electrolysis process using a steady-state pH differential. Expressions for the reversible potential as a function of temperature show that the water splitting reaction does not require electrical energy for a temperature of 331° C. A cell that operates with a steady-state pH differential, maintained by a heat source and consuming considerably less electricity than the conventional method for electrolytic hydrogen production has been built and tested. The total energy consumed in the process is also discussed.

1. Introduction

Hydrogen production is essential to the chemical industry [1] for the synthesis of ammonia, methanol etc. Hydrogen is also of great importance in energy storage and transformation [2]. A method of producing hydrogen is the electrolysis of water.

Since conventional water electrolyzers have efficiencies far below the maximum theoretical value, several ways of improving the electrolytic process are under investigation. Research is primarily centered on more efficient electrocatalysts as electrode material and on hybrid schemes such as steam electrolysis and photoelectrolysis, where all or part of the energy for the decomposition of water is supplied by a form of energy other than electricity. None of these methods, however, has proved more viable commercially than conventional electrolysis.

In this paper we report a new method of decreasing the electrical energy necessary for the electrolysis of water. The method utilizes a steady-state pH differential between the anode and cathode produced by a low grade energy source such as waste heat. The main advantages of this method are: the use of low grade energy, instead of electrical energy, and improved mass transport at the cathode. This method offers higher versatility for different utilizations, since several

types of energy sources such as solar, nuclear or mechanical can be used to maintain the pH differential.

2. Theory

The minimum voltage required for water splitting at 25° C and 1 atm is 1.23 V (reversible voltage). Under these conditions hydrogen would be produced only if heat is added. If no heat exchange with the surroundings takes place, the cell cools down. The thermoneutral potential at 25° C is 1.47 V.

Figure 1 is a reversible potential versus pH diagram for hydrogen and oxygen evolution in liquid phase water; it shows the reversible potentials of the oxygen and hydrogen electrodes as a function of hydrogen ion concentration in the pH range 0 to 14. The thermodynamic voltage for the electrolysis of water is independent of pH when both the cathode and the anode are operated at identical pH values.

However, it may be noted that oxygen evolution occurs at a value 800 mV less positive at pH 14 than at pH 0. Also, hydrogen evolution has a lower voltage in acidic solution. It is then possible to build a cell where the pH in the catholyte is zero, and the anolyte is 14 and thereby obtain, theoretically, water decomposition with a minimum voltage of approximately 0.4 V. The

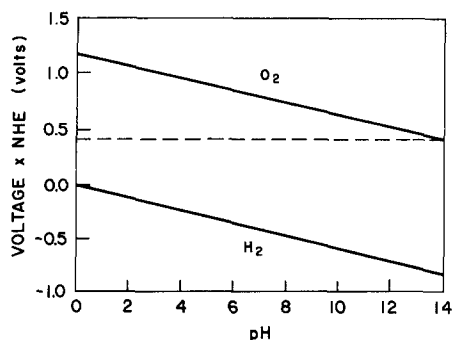
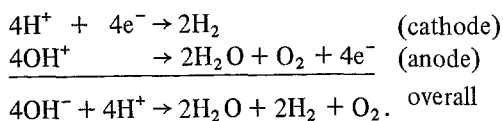


Fig. 1. Thermodynamic voltage versus pH.

above condition, obviously is not obtained under thermodynamic equilibrium. The flow rates in the cathode and the anode of the injected solutions, and the current density, determine the operating conditions.

The electrolytic evolution of hydrogen in acidic and alkaline solutions occurs differently [3]. The source of hydrogen in acid solutions is the hydronium ion which is discharged at the cathode to form hydrogen. For alkaline solutions it is assumed that electrons are directly added to water molecules which then decompose to yield hydrogen and hydroxyl ions.

For electrolysis with a pH differential, i.e. acidic solution at the cathode and basic solution at the anode, the following equations may be written,



The theoretical potential for hydrogen and oxygen evolutions vary, for a pH equal to 14 for the oxygen evolution reaction and a pH equal to 0 for the hydrogen reaction, according to [3]

$$E_{\text{OH}^-/\text{O}_2} = 0.401 + \frac{2.303}{2F} RT \log \frac{[a(\text{H}_2\text{O})] [P(\text{O}_2)]^{1/2}}{[a(\text{OH}^-)]^2} + \frac{dE}{dT} (T - 298) \text{K} \quad (1)$$

and

$$E_{\text{H}^+/\text{H}_2} = 0.00 + \frac{2.303}{2F} RT \log \frac{[a(\text{H}^+)]^2}{[P(\text{H}_2)]} + \frac{dE}{dT} (T - 298) \text{K} \quad (2)$$

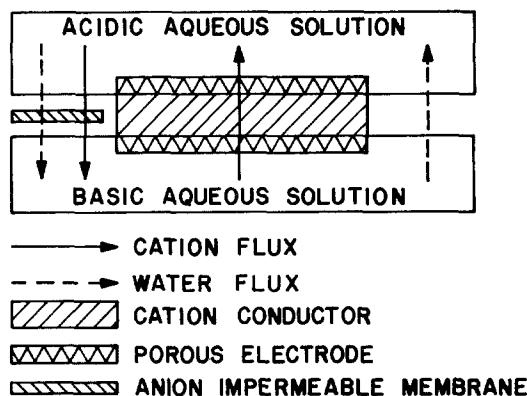


Fig. 2. Schematic representation of steady-state pH differential electrolysis.

Here F is Faraday's constant, $a(x)$ is the activity of species x and $P(y)$ is the pressure of gas y , T is the absolute temperature.

Figure 2 shows a scheme that generated a steady-state pH gradient of concentration between anode and cathode. Schematically, the steady-state pH differential electrolysis cell operates as follows: electrolysis is performed in a concentration cell with the anode and the cathode in contact with an aqueous solution of different pH, i.e. pH_A of the anolyte and pH_C of the catholyte. From the Nernst equation, the thermodynamic voltage necessary for electrolysis (i.e. 1.23 V at 25°C, 1 atm and $\text{pH} = 0$) is reduced by

$$2.3 \frac{KT}{e} (\text{pH}_A - \text{pH}_C) \quad (3)$$

where K is the Boltzmann constant, T the absolute temperature and e the absolute value of the electron charge.

The pH differential is maintained in a steady-state as shown schematically in Fig. 2. Hydroxyl ions are removed at the anode. For charge neutrality, cations (e.g. K^+) move across the cation

conductor into the acidic section of the cell, where protons are reduced to hydrogen. The cation depletion in the anodic section takes place, simultaneously, with transfer of water from the basic water section of the cell (dashed arrow on the right hand side of the figure) to the acidic water section. This water transfer can be performed in a variety of ways. For example, by evaporating water from the basic solution and recondensing it into the acidic section.

The cycle is then completed by (double arrow on the left hand side of the figure) the return of cation-rich water from the catholyte to the anolyte. This can be performed, for example, by gravity and filtration through an anion impermeable membrane. An analogous scheme based on anions instead of cations is, of course, also possible.

Clearly the energy cost necessary to separate and transfer the neutral water from the basic solutions to the acidic solutions balances the reduction in electrical energy due to the pH differential, Equation 3.

It is also worth pointing out that the proton flux across the cation conductor must be inhibited (cation conductors that are impermeable to protons are known. An example is Na- β -alumina). In fact, proton transfer across the pH gradient in the half cells requires the voltage given by Equation 3. Thus, the total electrical energy necessary for electrolysis would be unchanged for a proton transfer cell.

The reversible potential for electrolysis of water is referred to 25°C. Its value for other temperatures can be found from the corresponding isothermal temperature coefficients of the standard potentials. If the isothermal temperature coefficients are known, the standard potential of electrodes at a temperature different from 25°C is calculated from Equations 1 and 2. For the hydrogen electrode $d\epsilon_0/dt = 0.871 \times 10^{-3} \text{ V } ^\circ\text{C}^{-1}$ and for hydroxyl electrode $d\epsilon_0/dt = 0.44 \times 10^{-3} \text{ V } ^\circ\text{C}^{-1}$ [4]. If the cell is operated with pH equal to zero at the cathode (hydrogen side) and with a pH equal to 14 at the oxygen side, the water splitting reaction takes place when applying an emf of only 0.278 V across the electrodes at a temperature of 100°C. The reversible potential is zero for a temperature of 331°C. Consequently, the steady-state pH differential electrolysis does not require any electrical energy if operated at temperatures greater than 331°C [4].

3. Experiments and results

Steady-state electrolysis for a pH difference of 7, i.e. $\text{pH}_A = 14$ and $\text{pH}_C = 7$, is performed in a concentration cell with the anode and cathode in contact with aqueous solutions of different pH. Figure 3 shows a scheme that generates such a gradient of concentration between anode and cathode. In the anode compartment a solution of KOH and water ($\text{pH} = 14$) is circulated similarly to a cation exchange membrane electrolysis cell. Since the membrane is selectively permeable to cations, K^+ will migrate to the cathode. The concentration gradient and the applied electric field will transport K^+ to the cathode compartment, but since the reduction potential of hydrogen is lower than that of potassium, hydrogen evolves at the cathode. Water vapour circulates through the cathodic section. The cathode electrode is extremely thin, porous and it is in thermal contact with the anode and the solution. If a KOH solution is present in both cathode and anode compartments, the cell operates as an alkaline electrolyser; it may also operate as an acid solid polymer electrolyte (SPE) electrolyser [5].

The water electrolysis cell operates with an ion exchange membrane Nafion (DU PONT trademark), previously treated in a KOH solution, and shown in Fig. 4. Two catalysts are employed: platinum and iridium (50–50 wt %) for the anode, and platinum black for the cathode. The catalysts, in the form of fine particles, are pressed onto the membrane. Current is fed to the cell through metal screens placed against the membrane. Extra metal meshes are necessary between the current collectors and the fluid support structure in order to keep the two electrodes in close contact with the membrane. These meshes also provide free circulation of the solution and gases.

Initially, we operated the cell at single pH 14. A solution of KOH is circulated through the anode side of the cell at a rate sufficiently high so that the heat generated at the membrane electrode interface is dissipated. The mixture of KOH solution and oxygen that leaves the cell is separated and recycled back to the cell. The KOH solution is also carried around the membrane to the cathode. The performance is characterized by the applied voltage versus current plot for the cell

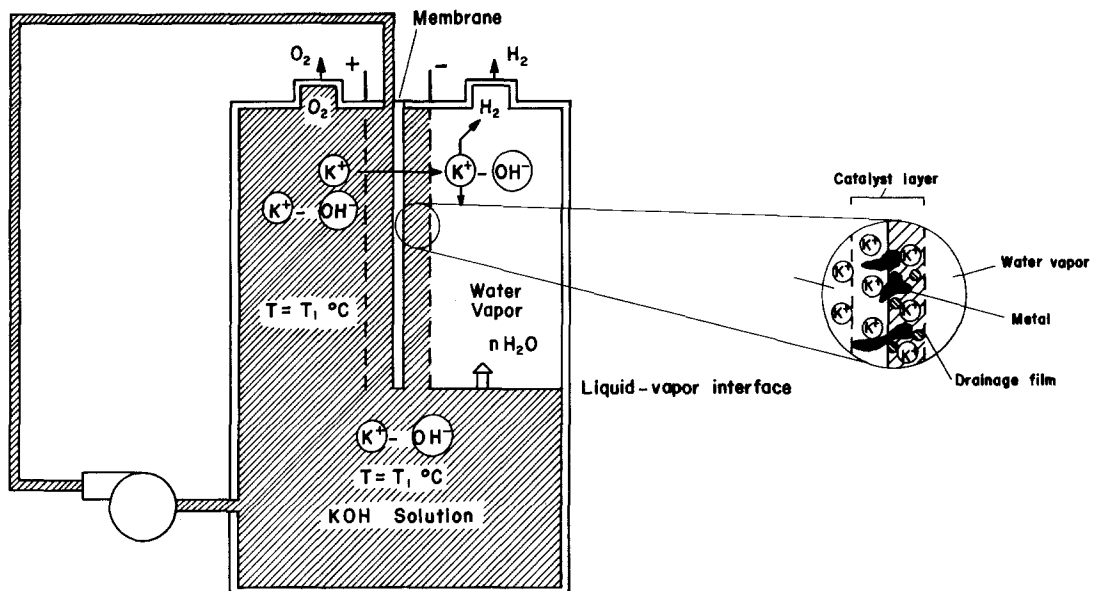


Fig. 3. Schematic diagram of the steady-state pH differential water electrolysis cell, for pH 7 at the cathode and pH 14 at the anode.

operating in this configuration in Fig. 5 (triangles), for a temperature of 103°C .

Now KOH is circulated only in the anode. A steady-state pH gradient is then established when water vapour is present at the cathode side. The K^+ ions migrate from the anode to the cathode with a subsequent increase in the pH. Water vapour circulates through the cathode compartment, and all alkaline ions are removed and injected back into the anode compartment by gravity as shown in Fig. 3.

For every K^+ ion that crosses the membrane, one molecule of water vapour is consumed. It is

worth pointing out that, in this case, for the formation of one hydrogen molecule, 1.66 eV (at 25°C) of electrical energy is needed, plus the heat of evaporation of two water molecules. Since the cell is operated under adiabatic conditions, only the heat of evaporation of these two water molecules, per hydrogen molecule formed, is consumed. The water molecules used in the solvation of the $\text{K}^+\text{-OH}^-$ ions condense on the membrane which is in thermal contact with the KOH solution. The cycle is then completed by the return of KOH-rich water from the cathode section to the anode section of the cell by gravity

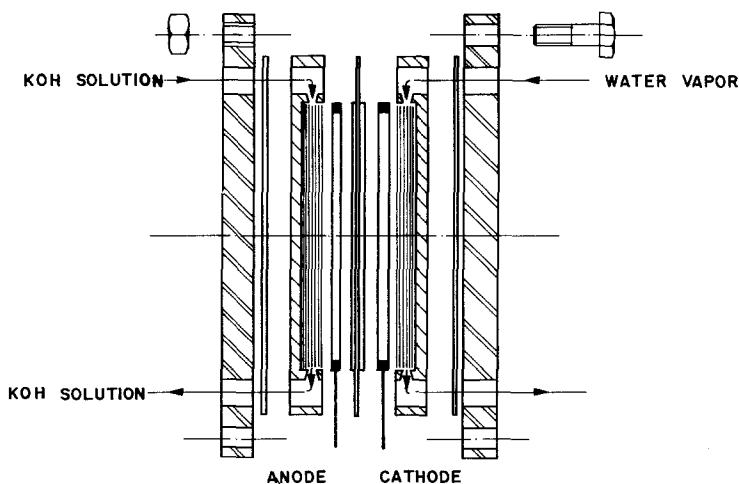


Fig. 4. Schematic diagram of the experimental set-up in which steady-state pH differential electrolysis is performed. The diagram shows the membrane, the electrode support, the anode and cathode container, the support structure and the field circuit.

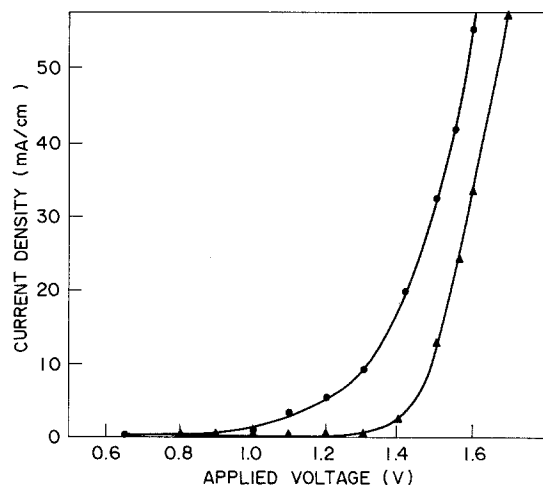


Fig. 5. Voltage versus current measurements for a cell operating at pH 14, represented by triangles and pH 7 at the cathode and pH 14 at the anode, represented by dots.

with no net heat absorption. In principle, then, this technique is as energetically efficient as the conventional water electrolysis methods.

Using this method we observed water electrolysis with steady-state H_2 evolution at 0.9 V. The performance of the cell operating in this configuration is plotted (dots) in Fig. 5. This cell was operated uninterrupted for more than 15 h with no appreciable change in behaviour. The improved performance of the cell with a pH gradient is clearly shown.

The threshold voltage at which there is water splitting, is substantially decreased, there being a difference of 0.4 V between the curves obtained with KOH solution, 25 wt %, and the steady-state pH differential scheme with the same cell.

There are various contributions to the effective pH at the membrane under dynamic conditions due, for instance, to the solution in which the membrane is soaked and to the transferred ions. At the anode the solution of KOH provides a large number of OH^- ions. At the cathode electrode a thin film of the solution is formed. There is a continuous removal of this solution film by gravity and a constant renewal of the film by the combination of the condensed water vapour and the K^+ transported ions. The concentration build up of the K^+ ions is kept low by a delicate balance imposed by the water vapour pressure, by the electrode surface, by the current density and by gravity.

The water vapour condensation and gravity are then responsible for the pH decrease even at high current density as shown in Fig. 4.

The experimental curves show that, for increasing currents, the difference in voltage between the two curves tends to decrease; this is due to the increase in pH at the cathode electrode. The KOH removal at high current densities is hindered by the catalyst layers. Experiments searching for more suitable electrodes are now under way.

This scheme has some advantages over the conventional 'pure water' solid polymer electrolyte (SPE) units besides having a dynamically created lower water splitting potential. One serious problem with conventional SPE water electrolysis units is the contact between the electrodes and the membrane, which is substantially reduced in our case due to the very high conductivity of the KOH solutions. Under dynamic conditions the pH at the cathode and anode is very acid in a conventional pure water solid polymer electrolyte cell, and noble metal coatings are necessary in order to reduce corrosion. Since the solution in this case is neutral or almost neutral at the cathode and basic at the anode, corrosion problems are minimized.

4. Conclusion

A steady-state pH differential water electrolysis cell has been operated. There is substantial lowering of the required applied voltage due to the concentration gradient between the cathode and the anode which was maintained for current densities greater than 50 mA cm^{-2} .

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