Application of Autocatalytic or Electroless Nickel for the Recuperation of Corroded Electrolytic Cells

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All wetted surfaces of electrolytic cells used in the generation of hydrogen gas, are typically nickel plated for corrosion protection. However, due to continuous use during the years, the nickel plating slowly wears off and fails to provide the proper corrosion protection. When this occurs, the corrosion process deteriorates the unprotected surfaces, particularly of the electrodes, where the dissociation of the water takes place.

In order to refurbish the electrolytic cells, a partial nickel stripping process was applied to these wetted surfaces, for the purpose of removing the nickel that was not properly adhered to the substrate. Furthermore, the corrosion was removed and then electroless nickel plated using conventional methods; since this plating process is most suitable for this specific application, due to its property to coat uniformly very complex shaped surfaces.

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Introduction

One of our clients, OXIGENOS CARABOBO, C.A. produces different gases for industrial and medical applications. In two of their lines, hydrogen gas is produced by electrolysis, which is compressed and bottled in steel cylinders.

The hydrogen gas is produced by the dissociation of water, to which a certain amount of potassium hydroxide is added, in order to attain the proper electrolyte solution.

After many years of use, the original nickel plating, present on all wetted surfaces of the electrolytic cells, wore off in some areas and consequently did not provide the proper corrosion protection. The corrosion at the strips of the grid were the dissociation of the water takes place, was to some extent affecting the efficiency of the electrodes.

Based on these circumstances, it was necessary to consider the possibility to refurbish the components of the electrolytic cells, particularly the grid of the electrodes. The basic idea was to remove the present corrosion and re-plate all wetted surfaces to assure a proper corrosion protection.

The plating technique to be implemented had to be able to coat evenly non-uniform and complex shaped surfaces. Thus autocatalytic or electroless nickel plating was applied on the components, since one of the properties of this coating, is that it covers quite uniformly those surfaces.

Basic Operation of an Electrolytic Cell[1-2]

An electrolytic cell is used to separate the constituents of a liquid, by applying direct current to the system. The process of breaking molecules to smaller components, in an electrolytic cell, is known as electrolysis.

In order for the electrolysis to take place, it is necessary that outside energy be imparted into the system thru anode and cathode electrodes and an electrolyte.

An electrolyte is a solution or fluid, which can conduct electricity. Pure water is impractical to use in electrolysis, because it is not a good electrical conductor. That problem is circumvented by the addition of a minor amount of soluble salts (such as, potassium hydroxide) that now turn the water into a good conductor. Such salts have subtle effects on the electrolytic potential of water due to their ability to change its pH. Such effects from the salts are generally so small, that they can usually be ignored.

In an electrolytic cell, where the electrolyte is water together with a minor amount of soluble salts, hydrogen gas is produced at the cathode electrode and oxygen gas is produced at the anode electrode by dissociation of this electrolyte when a direct current is applied to the electrodes, as is shown in Figure 1.

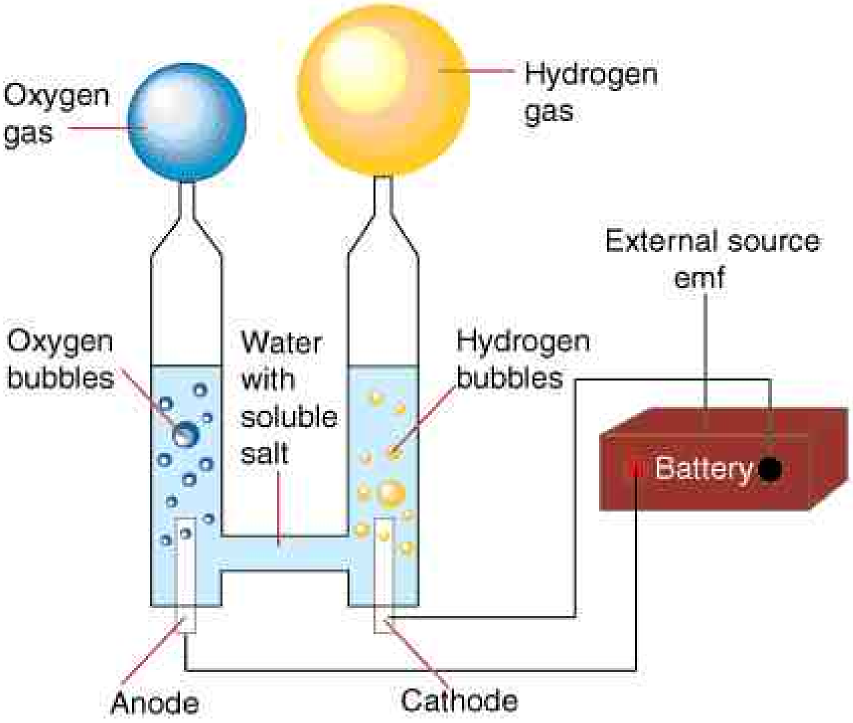


Figure 1.- Electrolysis of water.

A more detailed explanation on the energy relationships involved in the electrolysis of water is presented in Appendix A.

Electrolytic Cells to be Refurbished

Table A presents the components of the electrolytic cells to be refurbished.

Table A
Electrolytic Cells to be Refurbished

COMPONENT	QUANTITY
Cell Box (dimensions 48” x 48” x 14 ½”)	1
Anode Electrode	3
Cathode Electrode	4
Tank Cover	1

The electrolytic cell to be refurbished when assembled, has three anode electrodes and four cathode electrodes, fastened to the tank cover.

In our case, the electrolyte used for hydrogen gas production, was plain water with potassium hydroxide (KOH).

The original coating thickness, of the above mentioned components, is shown in Table B.

Table B
Original Coating Thickness of the Components
of the Electrolytic Cells to be Refurbished

COMPONENT	NICKEL COATING THICKNESS
- Cell Box - Tank Cover - Anode Electrode Structure (frame)	Typical 0.025 mm (0.001 in) Minimum 0.015 mm (0.0006 in)
- Cathode Electrode Structure (frame) - Grid and other metallic components of the grid structure	Typical 0.010 mm (0.0004 in) Minimum 0.006 mm (0.00025 in)

Original Condition of the Electrolytic Cells

Photograph 1, shows the original condition of one of the cell boxes. In this particular cell box, corrosion has taken place on the walls. Please note that there is still some original nickel plating between the corroded areas.

Photograph 1.- Inside view of a cell box.

The corrosion in the inside walls of the cell box, was quite severe. Many deep corrosion pits and grooves were present, particularly right alongside of the welding between the panels.

Photograph 2, shows the tank cover. Please note that most of the lateral area, which fits inside the cell box, is corroded. This same photograph shows the cloth bags that cover the anode and cathode electrodes.

Photograph 2.- A view of the tank cover to which the anode and cathode electrodes are fastened.

The tank cover presents a series of tubes and ducts for the continuous supply of the electrolyte, and for the extraction of the produced hydrogen and oxygen gas. It also presents a series of orifices through which the anode and cathode electrodes are supported by means of threaded copper terminals.

Photograph 3, shows a close up view of the cloth bags that cover the anode and cathode electrodes. Please note that in this particular case, the seams ripped apart and the corrosion present on the anode and cathode electrodes have stained the fabric.

Photograph 3.- Detail of the cloth bags that cover the anode and cathode electrodes.

Photograph 4, shows an anode electrode. Please note that the strips of the grid are completely corroded (they appear with a dark brownish color); while the grid support frame is partially corroded.

Photograph 4.- View of a completely corroded anode electrode.

The corrosion damage in both anode and cathode electrodes, was quite similar.

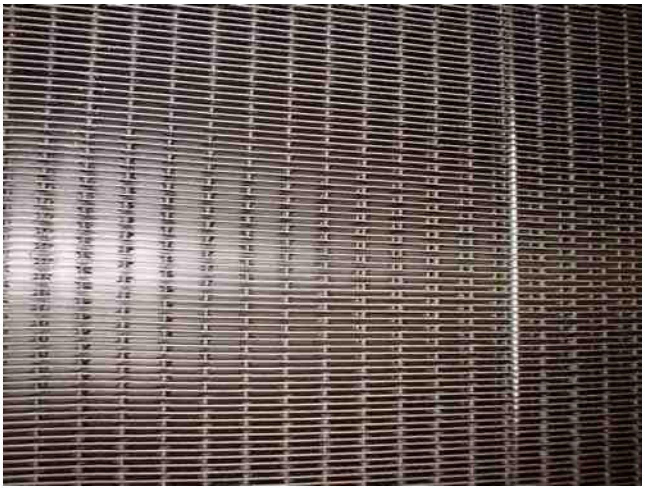
Corrosion conditions similar to what was shown in the above photographs, were present in 13 other electrolytic cells, with their corresponding cell boxes, anode and cathode electrodes and tank covers.

Analysis of the Problem

The original nickel that was still present on the different components (cell box, tank cover, anode and cathode electrodes) was basically porous, and in most of the areas presenting flakes, resembling fish scale; that is, part of the nickel was attached to the substrate, while the other part could be lifted with a sharp object.

The expensive components of this electrolytic cell are the anode and cathode electrodes. Each of these components, in our case, have a grid comprised by 292 strips made of steel that are about one inch wide and about 1/32” thick, at approximately 1/8” distance between each other, as can be observed in Photograph 5 (corresponding to an already re-plated anode electrode).

At the areas were corrosion has taken place, the thickness of the above mentioned steel strips of the grid was in some cases, paper thin; and sometimes, it was corroded right thru.



Photograph 5.- A close up view of the grid where the electrolysis actually takes place.

The cell boxes and the tank covers, presented in general, severe corrosion pitting. Additionally, the cell boxes showed corrosion right alongside the welding between the steel panels. However, in both components there was still sufficient wall thickness so that they could be salvaged, if the corrosion was stopped.

The components of the electrolytic cell, that could actually affect its efficiency in the electrolysis process, are the anode and cathode electrodes. If corrosion changes the dimensional characteristics of the steel strips of the grid of the electrodes, then their efficiency would be affected, particularly if some strips were perforated right thru.

The above mentioned situation posed an interesting problem, since it was necessary to do something about the nickel that was not properly adhered to the substrate, and it was convenient to maintain some of the original nickel that was still providing protection against corrosion and slightly some structure to the corroded strips. Furthermore, an electroless nickel plating process had to be applied, since with this process the internal walls of the corrosion pits and the totally uneven surfaces, could be protected.

Procedure Applied for the Refurbishment of the Electrolytic Cells

A slow acting alkaline stripping solution was developed to partially dissolve the original nickel. The basic idea was to allow the stripping solution to work on both sides of the original nickel plating that was not adhered to the substrate, and only on one side on the portion of the plating that was properly adhered to the substrate, as is illustrated in Figure 2.

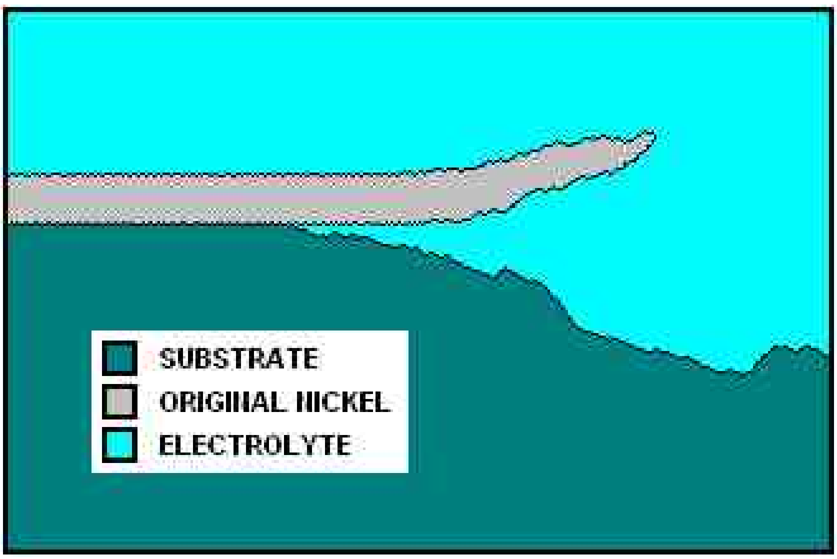


Figure 2.- Typical flake, that resembles a fish scale, on an original nickel plated steel strip.

In order to assure that the stripping process would not dissolve more than the necessary amount of nickel, the parts were lifted and washed frequently, until the flakes were no longer present, as is illustrated in Figure 3.

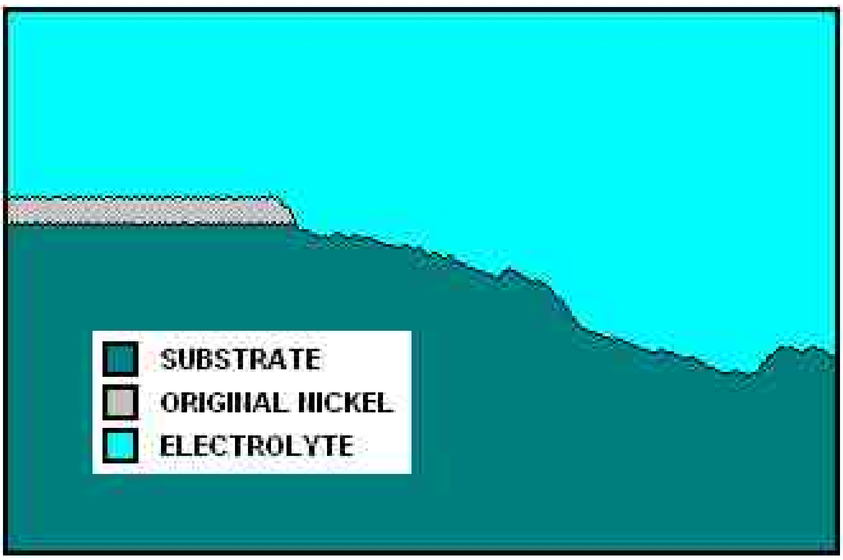


Figure 3.- Properly adhered nickel plating and exposed substrate.

Once dissolved the original nickel plating which was not properly adhered to the substrate, the components were ready for a subsequent electroless nickel plating process; since this is the most appropriate plating process for this type of application, due its property of uniformly coating uneven or very complex shaped surfaces, as is illustrated in Figure 4.

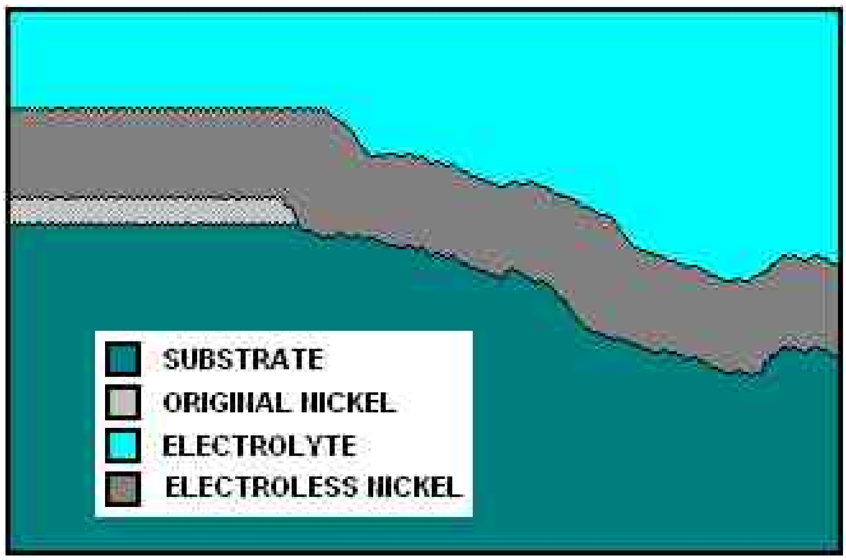


Figure 4.- Electroless nickel plating applied on the substrate and what remained from the original nickel plating.

The electroless nickel plating was performed according to conventional processes. The new deposit thickness for the different components, is shown in Table C.

Table C
Coating Thickness of the Components of the Refurbished Electrolytic Cell

COMPONENT	EN COATING THICKNESS
- Cell Box	Minimum 0.075 mm (0.003 in) Maximum 0.150 mm (0.006 in)
- Tank Cover	Typical 0.075 mm (0.003 in)
- Anode Electrode Structure (frame) - Cathode Electrode Structure (frame) - Grids and other metallic components of the grid structure	Typical 0.050 mm (0.002 in)
- Nut (threads only)	Typical 0.013 mm (0.0005 in)
- Nuts - Washers	Typical 0.050 mm(0.002 in)

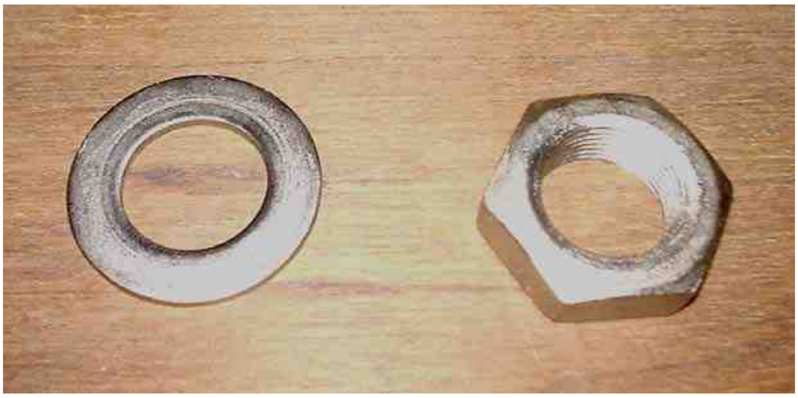
Results

Applying the above mentioned procedure, we managed to salvage all the components of the electrolytic cell, as can be observed in the following photographs.

In Photograph 6, a tank cover is presented. Please note the electroless nickel plating at the inside diameter of the protruding tubes (which were not protected with the original nickel plating).

Photograph 6.- Electroless nickel plated tank cover.

In Photograph 7, a set of protected nut and washer is presented. These components are used to fasten the anode and cathode electrode terminals to the tank cover, and were originally zinc plated. However, these components also presented corrosion, which made the assembly and disassembly of the electrolytic cells, a real chore. Now with the anti-galling property of the electroless nickel, these fasteners can easily be threaded on the copper terminals of the anode and cathode electrodes. For a proper corrosion protection, the nuts were coated in two separate processes: (a) a first coating of about 0.013 mm (0.0005 in) thickness was applied to all surfaces of the nut, including the threads; and (b) the threads were masked and a second coating was applied to the rest of the nut with thickness of about 0.037 mm (0.0015 in). The washers were coated to a thickness of about 0.050 mm (0.002 in).



Photograph 7.- Electroless nickel plated Fasteners.

In Photograph 8, the inside surface of a cell box is shown. Please observe the large quantity of protected corrosion pits present on the walls. Some cell boxes required to be re-plated up to three times, until no corrosion could be observed at the pits.

Photograph 8.- Electroless nickel plated cell box.

Not shown in Photograph 8, is a heat exchanger that is located on one of the sides of the cell box, which has the function of cooling the electrolyte solution, as the electrolysis takes place. The wetted areas of this heat exchanger, also presented quite a bit of corrosion. The shape of the box together with the heat exchanger, made it somewhat difficult to plate in a single process.

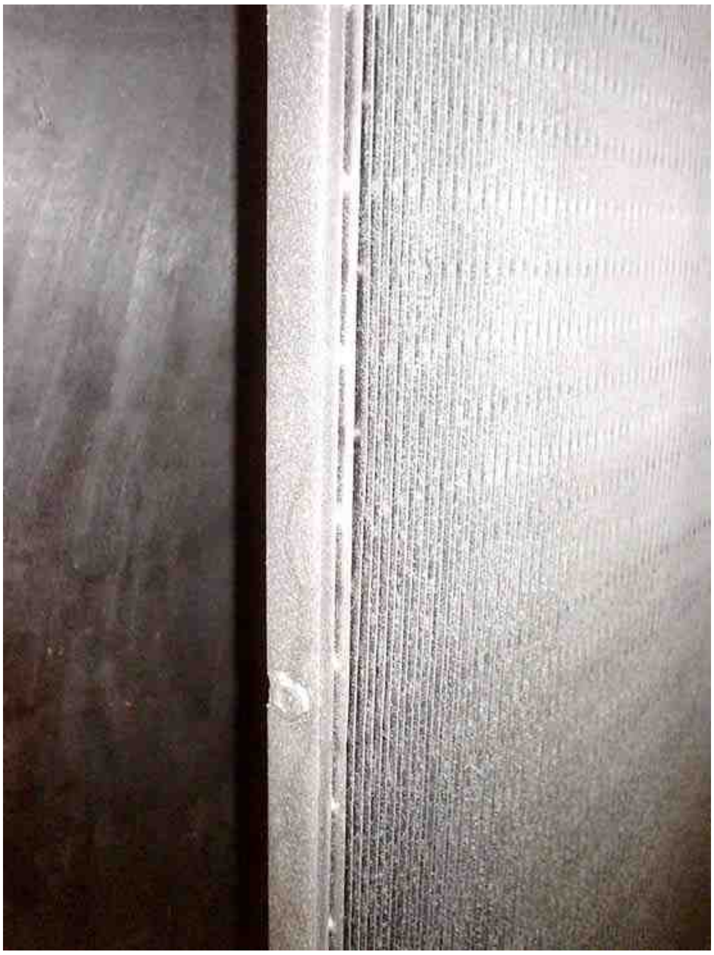
In the same photograph, deep corrosion grooves can be observed at the welding between the front and side panels. Those areas turned out to be the most difficult ones to coat, since corrosion would show up within a few days, requiring further plating processes.

In Photograph 9, a protected anode electrode is presented; while in Photograph 10, a protected cathode electrode is shown. The copper terminals at the top of the anode and cathode electrodes are threaded, and permit these components to be fastened to the tank cover by means of nuts and washers, similar to the ones shown above in Photograph 7.

Photograph 9.- Electroless nickel plated anode electrode.

Photograph 10.- Electroless nickel plated cathode electrode.

Photograph 11 is presented, just to show how the large quantity of corrosion pits were protected at the steel strips of the grid and frame of an anode electrode. This photograph is interesting, because each of the surface marks at the grid correspond to a partially stripped flake, resembling fish scale.



Photograph 11.- Corrosion pits protected against corrosion with electroless nickel.

These components have been in use for over ten years, and it is expected that by refurbishing them, they will last at least the same amount of time.

Conclusions

In this particular case, an expensive piece of equipment was salvaged with the application of autocatalytic or electroless nickel plating; therefore, our client OXIGENOS CARABOBO, C.A. was able to save on a considerable investment in the purchase of new equipment.

The refurbished electrolytic cells, operate as efficiently as the original new equipment, and are expected to last perhaps an even larger number of years than the original equipment.

Acknowledgements

I wish to thank our client OXIGENOS CARABOBO, C.A. for the trust they conferred to us in our proposed solutions, and for allowing us to perform this job, which opens the door for other similar applications.

References

1.- www.sparknotes.com/chemistry/electrochemistry/electrolytic/section1.html

2.- www.miniscience.com/projects/WaterElectrolise.htm

3.- hyperphysics.phy-astr.gsu.edu/Hbase/thermo/electrol.html

Appendix A: Electrolysis of Water[3]

By providing energy from a battery or any other direct current source, water (H_2O) can be dissociated into the diatomic molecules of hydrogen (H_2) and oxygen (O_2)., as is shown in Figure 5.

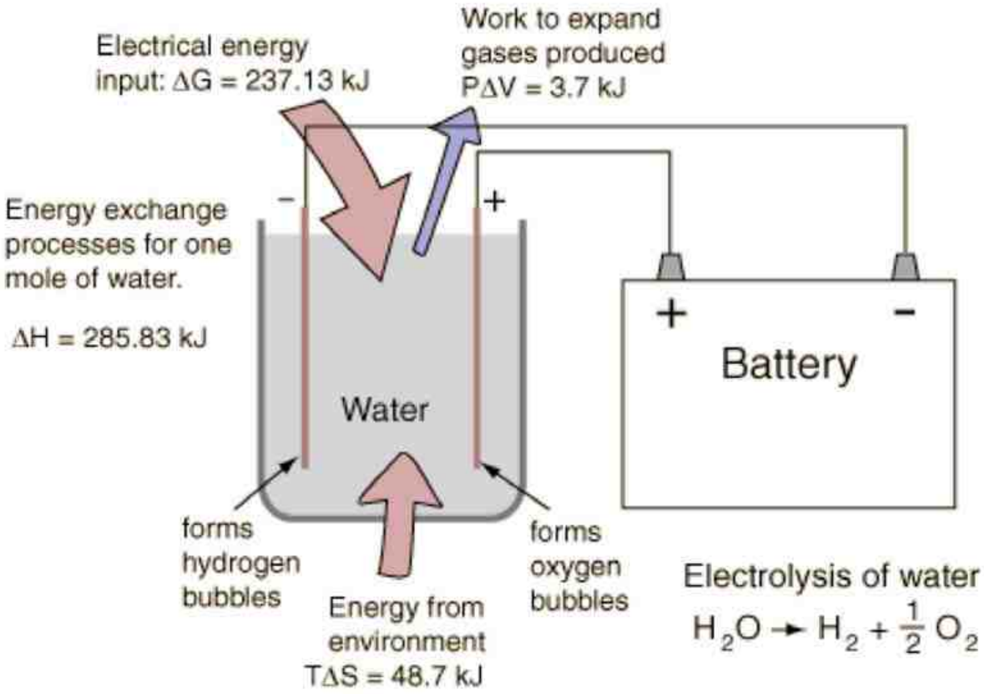


Figure 5.- Energy relationships in the electrolysis of water.

The electrolysis of one mole of water produces a mole of hydrogen gas and a half-mole of oxygen gas in their normal diatomic forms. This process is presumed to be at 298K and one atmosphere pressure, and the relevant values are shown in Table D.

Table D
Energy Values
(at 298K and 1 Atm)

Quantity	H_2O	H_2	0.5 O_2	Change
Enthalpy	-285.83 kJ	0	0	$\Delta H = 285.83$ kJ
Entropy	69.91 J/K	130.68 J/K	0.5 x 205.14 J/K	$T\Delta S = 48.7$ kJ

The process must provide the energy for the dissociation plus the energy to expand the produced gases. Both of those are included in the change in enthalpy included in the table above. At temperature 298K and one atmosphere pressure, the system work is

$$W = P\Delta V = (101.3 \text{ x } 10^{3} \text{ Pa})(1.5 \text{ moles})(22.4 \text{ x } 10^{-3} \text{ m}^{3}/\text{mol})(298\text{K}/273\text{K}) = 3715{,}37 \text{ J}$$

Since the enthalpy H= U + PV, the change in internal energy U is then

$$\Delta U = \Delta H - P\Delta V = 285.83 \text{ kJ} - 3.72 \text{ kJ} = 282.11 \text{ kJ}$$

This change in internal energy must be accompanied by the expansion of the gases produced, so the change in enthalpy represents the necessary energy to accomplish the electrolysis. However, it is not necessary to put in this whole amount in the form of electrical energy. Since the entropy increases in the process of dissociation, the amount $T\Delta S$ can be provided from the environment at temperature T. The amount which must be supplied by the battery or any other direct current source is actually the change in the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S = 285.83 \text{ kJ} - 48.7 \text{ kJ} = 237.13 \text{ kJ}$$

Since the electrolysis process results in an increase in entropy, the environment assists the process by contributing the amount $T\Delta S$.