Technical Article

pH, Hydrogen Evolution & Their Significance In Electroplating Operations

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The concept of pH is detailed. Its significance for successful operation of electroplating baths is explained. The influence of hydrogen evolution and codeposition on the deposition of single metals and alloys is analyzed from theoretical and practical points of view.

A+ an electroplating course, or even a graduate course in analytical electrochemistry, one question is frequently asked: "If pH is a measure of acidity, how is it that pH goes up when the acidity goes down?"

Many students, as well as electroplating practitioners, find the inverse relation between pH and acidity confusing. Not only is the relationship between pH and acidity inverse, but it is also logarithmic. A *decrease* of a single pH unit corresponds to a *ten-fold increase* in acidity, and when pH goes down by two units, acidity increases by a factor of 100. It sometimes takes a while for those involved to appreciate the simplicity of the pH concept, and to realize how useful it is to keep electroplating operations trouble-free.

Concept of pH

Acidity in water solutions results from the presence of hydrogen ions (H^+). This fact was first recognized by Svante Arrhenius, in 1884, and is an important feature of his acid-base theory, for which he received a Nobel Prize in chemistry in 1904. The degree of acidity is expressed in terms of H^+ concentration. With brackets to symbolize "moles per liter," $[H^+]$ represents the molar concentration of H^+ ions in a solution and is therefore a quantitative description of its acidity.

The hydrogen ions in a solution are not free-floating protons. They are actually attached to molecules of the solvent. For this reason, H^+ ions in water are often written as hydronium ions, H_3O^+, with acidity expressed as $[H_3O^+]$. This is a simplification, however, since the aqueous H^+ ion is most likely bonded to a cluster of water molecules. For purposes of this discussion, hydrogen ions are written simply as H^+ and acidity as $[H^+]$, with the understanding that H^+ ions in solution are always solvated.

The pH concept originated in 1909 with the Danish biochemist S.P.L. Sorensen. He had been working on some problems connected with the brewing of beer (in which control of acidity is important), and it occurred to him that it was needlessly cumbersome to have to say, "The concentration of hydrogen ion in this solution is one hundred-thousandth of a mole per liter," when $[H^+] = 0.00001$ (or 1×10^{-5}). Why not simply refer to the solution as having "pH 5"? Sorensen called the pH of a solution its "hydrogen ion exponent." The H stood for "hydrogen ion" and the p for "puissance" (French), "potenz" (German), or "power."

As Sorensen defined it, pH was the logarithm of the molar concentration of hydrogen ion with its sign changed so that pH values would normally be positive.

$$pH = \log_{10} \frac{1}{[H^+]} = -\log_{10} [H^+] \qquad (1)$$

An alternative and equally valid statement is that pH is more clearly identified as the "negative exponent of the hydrogen ion concentration."

$$[H^+] = 10^{-\mathbf{pH}} \qquad (2)$$

When $[H^+]$ is 0.01, which is 10^{-2}, then the pH is 2; and when $[H^+]$ is 0.0001, or 10^{-4}, the pH is 4.

Sorensen's original definition of pH is still the one most widely used, but it is not completely satisfactory in all cases. As $[H^+]$ increases, the effective concentration of H^+ ions becomes progressively less than might be expected, because of increased interionic attraction at the higher concentrations. A more specific definition of pH is:

$$\mathrm{pH} = -\log_{10\alpha_{H+}} \qquad (3)$$

where α_{H+} is the hydrogen ion *activity* (or the *effective* H^+ concentration). The H^+ activity is obtained by multiplying H^+ concentration by an appropriate *activity coefficient,* (γ), $\alpha_{H+} = \gamma\,[H^+]$. Activity coefficients are correction factors originating from thermodynamic calculations. They approach 1.00 for very dilute solutions, but become smaller as the concentration increases. Highly precise pH calculations require the use of activity coefficients, but ordinary pH is calculated from the simple relationship, $\mathrm{pH} = -\log [H^+]$, even though it tends to become less valid at higher concentrations.

For most practical purposes, the pH scale extends from 0 to 14. The midpoint of the scale at pH 7 represents neutrality, with values below 7 being increasingly acidic and those above 7 increasingly basic. Values greater than 14 are possible for concentrated strong bases, and negative pH values are possible for concentrated strong acids, but it is for dilute solutions that the pH scale is most useful. The numbers on the pH scale were not chosen arbitrarily but result from the natural equilibrium that exists between H^+ and OH^- ions in aqueous solution. Even in pure water, which is a non-conductor, there is a very small percentage of ionized molecules, about two parts-per-billion. For every 500 million H_2O molecules in a sample of pure water, one molecule is split into ions:

$$H_2O \leftrightarrow H^+ + OH^- \qquad (4)$$

The ions and undissociated water molecules are in equilibrium and, according to the law of chemical equilibrium, the following relationship must be satisfied:

$$K = \frac{[H^+][OH^-]}{[H_2O]} \tag{5}$$

where K is the equilibrium constant. A liter of water at 25ºC weighs 997 g, and the molar concentration of water in a pure sample is 997 g/18 g, or 55.3 M. This is a very large molar concentration, and it changes only slightly when soluble substances (solutes) are added to the water. $[H_2O]$ can therefore be considered a constant and incorporated into the equilibrium constant:

$$K\,[H_2O] = [H^+][OH^-] \tag{6}$$

or,

$$K_w = [H^+][OH^-] \tag{7}$$

where K_w is the *ion product* constant for water. In a sample of pure water at 25ºC, the concentration of H^+ as well as OH^-, (because the two must be identical) is 0.0000001 mol/L, or 1×10^{-7} M. Substituting this value in Eq. (7) permits calculation of K_w:

$$K_w = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14} \tag{8}$$

This implies that in any water solution at 25ºC it must be true that

$$[H^+][OH^-] = 10^{-14} \tag{9}$$

Regardless of how acidic or basic a solution may be, it must always contain both H^+ and OH^- ions, and the product of their effective molar concentrations must equal K_w. The small p in pH can be translated as "negative logarithm of" and it applies to quantities other than H^+ concentration. The term "pOH," for example, represents the negative log of the OH^- ion concentration, and pK_w is the negative log of the ion product constant for water. Starting with the equilibrium expression for water:

$$[H^+][OH^-] = K_w = 10^{-14} \tag{10}$$

then, taking the negative logarithm of each term, another useful relationship is obtained:

$$pH + pOH = pK_w = 14 \tag{11}$$

This explains the 0-14 range of the pH scale.

Significance of pH in Electroplating Operations

All aqueous electroplating solutions contain hydrogen ions, in addition to those metal ions from which deposition takes place. The pH is an important tool for proper quality control in electroplating and metal finishing operations. The pH must be held within well-defined limits to maintain optimum deposition speed, mainly governed by cathode current efficiency (CE). The cathode current efficiency depends primarily upon the ratio in which metal and hydrogen are deposited. The extent of hydrogen evolution in any given electroplating bath is contingent on the pH and the hydrogen overvoltage on the cathode. The primary purpose of pH measurements in electroplating is to define and control the acidity (or alkalinity) of a given bath within certain limits that produce the desired performance of the bath and optimum quality of deposits. pH measurements also indicate the relative anode and cathode current efficiencies. If the anode CE is higher than that of the cathode, pH increases, and vice versa.

Because many other factors influence plating solution behavior, high precision in pH measurements is usually unwarranted. In general, a precision of 0.1 pH unit is sufficient. In normal operation of electroplating baths, the pH changes very slowly, and measurements once a day are usually sufficient even in large, continuously operated baths. In many cases, weekly checks are adequate. Continuous recording of pH is not imposed on most common electroplating baths, except possibly when insoluble anodes are used, and regular neutralization is necessary to preserve a specific pH. Continuous increase in pH is also indicative of passive anodes, as well as an incorrect anode/cathode surface ratio.

In highly acid baths (*e.g.*, acid copper), the metal is deposited much more readily than hydrogen. Over a wide pH range, the cathode CE is virtually 100 percent. Because the acidity is so high (zero to 1.0), pH measurements here have little practical value. However, for chromic acid baths to anodize aluminum, where such pH values are involved, pH measurements with a glass electrode are useful for controlling the uniformity of anodic oxide films and prolonging the life of the anodizing bath.

One rationale for the importance of pH in electroplating is that most metal hydroxides are insoluble and, depending on their solubility products, will precipitate at various values of pH. The pH in the cathode film is usually higher than that in the bulk of the solution, if the cathode CE is less than 100 percent, but it is the bulk value that is usually measured.

All cyanide baths are alkaline, with pH values ranging from 9 for cyanide silver baths, to about 13 for copper, bronze, zinc and cadmium, which contain both free cyanide and free alkali. All contain carbonates, either added as a portion of the bath formulation, or formed as a result of cyanide decomposition and CO_2 adsorption (carbonation) by any hydroxides present. Measurement of pH in cyanide baths indicates the concentration of hydroxyl ions. Because cyanides and carbonates do not yield pH values much higher than 11, any higher values are indicative of actual non-complexed ("free") alkalinity (*e.g.* NaOH or KOH).

Exact calculation of the pH where precipitation will occur is usually not practical. Because the metal ion concentration in electroplating baths is so high, equating concentration to activity would be inaccurate.

Clearly, the pH of a solution is important for quality control in metal finishing. For example, the pH of a Watts nickel bath must be closely controlled between 4.2 and 4.5 to maintain optimum current efficiency, brightness, and leveling properties. Similarly, many pre- and post-treatment processes require accurate pH control. pH measurements may also be used to monitor the quality of rinsewaters and control the proper operation of effluent treatment plants.

Effect of pH on the Composition of Alloys

When metal electrodeposition is accompanied by hydrogen evolution, it may be viewed electrochemically as alloy electroplating, with hydrogen as one alloying element. The same holds true when hydrogen is discharged as a gas, because conditions for alloy deposition are met.[1] The effects of pH on the composition of an electrodeposited alloy are specific and usually unpredictable. In some baths, the pH has a large effect, and in others, a small effect on the composition. The determining factor is the chemical nature of the alloying metals, because pH does not exert its effect *per se*, but rather by altering the chemical form of the metals in solution.[2] The ions of simple metals are only slightly sensitive to variations in pH. On the other hand, the composition and stability of many metals in complex form—in both alkaline and acid solution—are a function of pH. For example, complexes such as stannates, zincates, cyanides and amines, which are stable in alkaline solution, decompose when acidified. In brass electroplating, pH effects the Cu/Zn ratio in the deposit and must be maintained by ammonia additions. As a general rule, variations of pH should have little effect on the composition of alloys deposited from baths containing the metals as simple ions, but should have a greater effect on the composition of alloys deposited from baths in which the parent metals were present as complexes with large instability constants.

Codeposition of Hydrogen with Metals

Hydrogen within the functional metals is like dust in the house. It is extremely difficult to eliminate completely, and everything that is done seems to produce some. Moreover, a little hydrogen is often all that is needed to produce a serious metal failure. Even if the bath in question plates with 98-percent efficiency, the remaining two percent of the current is evolving hydrogen instead of metal, and the amount of hydrogen plated at 5.4 A/dm^2 (50 A/ft^2) is about 6 x 10^{17} hydrogen atoms per ft^2/sec.

During electrodeposition, hydrogen is deposited and/or liberated, together with the atoms of the depositing metals. At high electrodeposition rates, the plated metal itself can be embrittled, but normally the effect is primarily that of embrittling the basis metal. The embrittlement problem is further complicated by the slow rate of diffusion through most of the metal coating. This tends to "trap" the hydrogen and makes its elimination that much more difficult.

Because of its low atomic size, hydrogen can be readily absorbed by the basis metal. Because embrittlement occurs on the atomic level, within a metal, there are no visible exterior warning signs of potential failure. The consequences are potentially more devastating than corrosion failures. Because they are unexpected, and occur within the metal, failures are much more dangerous and destructive. The liberated hydrogen gas can also adversely change the structure and properties of the deposited metal, resulting in burnt, skipped deposits, roughness or pitting.

Numerous mechanisms have been suggested for hydrogen embrittlement, but it is still open to conjecture. Hydrogen adsorbed in steel makes this metal susceptible to embrittlement. In part, it is a result of hydrogen impeding the normal slip of lattice planes under stress.[3] Build-up of molecular hydrogen in the voids present in the basis metal induces pressures greater than the tensile strength of the metal, leading to the development of blisters or cracks.

The theoretical possibility of co-deposition of metal and hydrogen depends on the shapes of the polarization curves and on the hydrogen overvoltage of the metal considered. If a significant amount of hydrogen is liberated, the metal deposition potential may be totally determined by the hydrogen overvoltage. When hydrogen overvoltage is high, currents corresponding to individual metals will be close to the limiting values. Under these conditions, an increase in the current will increase hydrogen overvoltage, with the net result being poor alloy deposition efficiency and minor changes in composition.

The deposition potential of copper from sulfate or fluoborate solutions is considerably more positive than the deposition potential of hydrogen. Thus no hydrogen, is deposited with copper during deposition from acid solutions at normal current densities. If the limiting CD is exceeded, however, hydrogen can be adsorbed on the surface.[4] On the other hand, considerable evolution of hydrogen takes place at the cathode in cyanide copper baths because of the high cathodic polarization of copper, regardless of a low concentration of hydrogen ions.

Metals such as zinc, lead and tin, which have a high hydrogen overvoltage, are deposited from highly acid electroplating baths with almost 100-percent cathode efficiency. On the other hand, metals of the iron group, which have a relatively low hydrogen overvoltage, are very sensitive to the concentration of hydrogen ions in the electroplating bath. A one-unit change of pH can noticeably affect both the cathode efficiency and deposit structure.

The pH of the cathodic film is not always the same as that of the bulk of the plating bath. The hydrogen ions take part in the current transfer and also effect the reactions taking place in the cathode film. In principle, the film pH will be higher than that in the solution bulk if the number of hydrogen ions transported by the current is smaller than the number deposited. A change in the film pH causes a diffusion gradient that tends to equalize the concentration of the hydrogen ions in the bulk of the solution and in the cathodic film. The difference between the pH value in the cathodic film and in the bulk, which tends to increase with the current density, either becomes constant or continues to increase, depending on the solution composition. This increase (alkalization) of the cathodic film in acid solutions can proceed only to pH 7, because only water will remain if **all** acidity is removed from the cathodic film.

Alkalization of the cathodic film is not limited to solutions of alkalis and metal salts, which do not form slightly soluble products like hydroxides and oxy-hydroxides. If slightly soluble products are formed, however, the maximum pH value of the cathodic film will correspond to the pH value at which these products are formed.

Alkalization is reduced with increasing temperature of the electroplating bath, agitation and a high metal concentration. Part of the hydrogen produced can be included in the electrodeposits. The product of this inclusion ("hydrogen pick-up") depends on the crystallization conditions and on the metal.[5] The hydrogen content in electrodeposits usually is very small. For instance, in zinc it varies between 0.001 and 0.01 wt% and in tin between 0.0005 and 0.0002 wt%. In metals of the iron group, the hydrogen content may reach 0.1 wt% and in electrodeposited chromium, 0.45 wt%. It has been found, however, that it takes very little hydrogen to embrittle a part.[6] Parts plated in cyanide and non-cyanide zinc baths, contain 5 and 8 ppm hydrogen, respectively. Parts with 8 ppm exhibit significantly more stress when compared to those with 5 ppm.

When studying the relation of processing steps, such as electrocleaning, pickling and plating, to hydrogen embrittlement, the number of possible variables is staggering. The plater must attempt to choose a practical course that will meet production objectives without neglecting quality. The following points are critical to the inclusion of hydrogen in electrodeposits:

1. The hydrogen content of the electrodeposited metal varies inversely with the current density.

2. The higher the pH value of the solution, the less hydrogen is absorbed by the deposit.
3. The hydrogen content of the deposit varies inversely with temperature. Hydrogen embrittlement, however, happens to be most severe at room temperature.[2]
4. Agitation of an electroplating bath reduces hydrogen content of the deposit.
5. The amount of hydrogen in the basis metal differs, even under identical external conditions and depends on the properties of the deposited metal. Porous deposits may permit easy penetration of the basis metal.
6. The hydrogen overvoltage, the rate of hydrogen entry and the amount of hydrogen absorbed by a given metal depends on the anion to which the deposited metal is bound (*e.g.*, cyanide ion in cadmium plating).[7,8]
7. The rate of hydrogen evolution depends on such conditions as porosity, heat treatment or annealing, alloy composition and surface treatments such as anodic activation and electropolishing. Appreciable differences occur between different crystallographic faces given the same treatment.[9]
8. Less efficient baths, acid or alkaline, will increase the possibility of hydrogen pick-up.[10]

We must therefore take into account the material of the cathode and its hydrogen overvoltage. Lead and tin are deposited at almost 100-percent cathode efficiency, even from strongly acid solutions, because they exhibit high hydrogen overvoltage. Consequently, the pH value of such an electroplating bath will hardly influence the hydrogen content of the deposit.

The hardness of electrodeposits in some metals is related to their hydrogen content, particularly in the cases of iron, nickel and chromium, which are frequently plated for their high wear resistance. This connection is evident from the fact that heat treatment intended to remove hydrogen causes a reduction in surface hardness. On the other hand, the electroplating conditions very often cause both the surface hardness and the hydrogen content of the deposit to increase. Hydrogen can be removed or redistributed from electrodeposited iron by prolonged heating (baking) at a temperature at which the metal does not soften. This "stress relief" has a time-temperature relationship. Thus, holding iron-plated parts for 24 hr at 165ºC and thereafter for 24 hr at 240ºC completely removed the hydrogen. No trace could be found, even at 1000ºC. The hardness, however, remained unchanged. In many cases, however, the baking process has proven to be questionable and ineffective, and in some cases, aggravate embrittlement.

The brittleness of electrodeposited metals of the iron group depends on their hydrogen content, inasmuch as the latter is not uniformly distributed over the cross section of the deposit and induces high internal stresses. More ductile deposits are obtained at higher electroplating temperatures, at which point the deposition of these metals is accompanied by lower polarization.

Avoidance of hydrogen embrittlement in the first place is, of course, most desirable. Two avenues of approach are open: (a) only use processes that do not produce hydrogen embrittlement or (b) apply barrier coatings to the basis metal prior to the operations that normally produce embrittlement. Both approaches have been employed and the details are given elsewhere.[5,11] Beyond avoidance of hydrogen embrittlement, is the use of proper process control and appropriate testing to detect it.[12,13]

Finally, hydrogen can play a role with its formation *after* metal deposition. This is caused by chemical reactions between the metal and occluded remains, such as bath residues, metal hydroxides or water molecules. In the case of zinc, it can be depicted as

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^0 \qquad (13)$$

and

$$Zn + Zn(OH)_2 \rightarrow 2ZnO + 2H^0 \qquad (14)$$

Atomic hydrogen, after recombining to form H_2 gas, can exert enough pressure to break apart the metal lattice.[14]

Pitting

Other problems with hydrogen come from the hydrogen bubbles that are sometimes trapped on the cathodic surface. Further metal deposition become impossible at such points and the metal plates around these bubbles. The deposit then becomes pitted. The pits occasionally span the entire thickness of the electrodeposit. Besides their poor appearance, such deposits have poor mechanical properties and corrosion resistance.

Pitting is mainly encountered in nickel electroplating, but is also common in other processes. The probability of entrapment depends on surface tension, visible as a wetting angle on the cathode surface. If the surface is easily wetted, this angle is very small, and the bubble adheres over a small area and the perimeter of the contact surface is small. Such bubbles are easily detached from the surface and do not attain significant dimensions. The addition of surface-active agents ("anti-pitters") decreases the contact angle and reduces pitting.

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