Polarization & Hydrogen Overvoltage

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The following is the second in a series of reviews looking back on practical articles from the distant past. Many articles contain information that is as valid today as it was when it was written. In 1976-1982, the late Dr. Donald Swalheim wrote and coordinated a series of articles, entitled "AES Update." Many of today's members may not even be aware of this material, let alone have seen it. With that in mind, we are reviewing what went before, with the thought that looking back would be of value to all. After all, those who forget history are condemned to repeat it. What follows are excerpts of this material, occasionally punctuated with my own words or comments in brackets [].

Early in the series, Dr. Swalheim discussed some elementary concepts, including polarization and hydrogen overvoltage. Grasping the practicality of these concepts is daunting to some degree, even to many seasoned platers. However, in his article, he described polarization about as clearly as I have ever had the pleasure of reading.

Polarization Simplified

"Every plater knows that he can increase the current by increasing the voltage. [Looking at Fig. 1,] it would be logical to express this relationship by drawing the lower line. If we were dealing only with the electrical resistance of the plating bath, this relationship would hold true. However, the voltage or energy requirements are similar to the fuel requirements in flying an airplane. As the velocity of the headwinds increase, it requires additional fuel to maintain a certain ground speed. Instead of a wind factor, we have resistance factors at the anode and the cathode [workpiece]. The additional voltage required to overcome these resistances is called polarization. In actual practice, the relationship is expressed more accurately by the upper line. It is important to note that the voltage required because of polarization (E_p) [*i.e.*, against the headwinds] increases with the current or the current density.

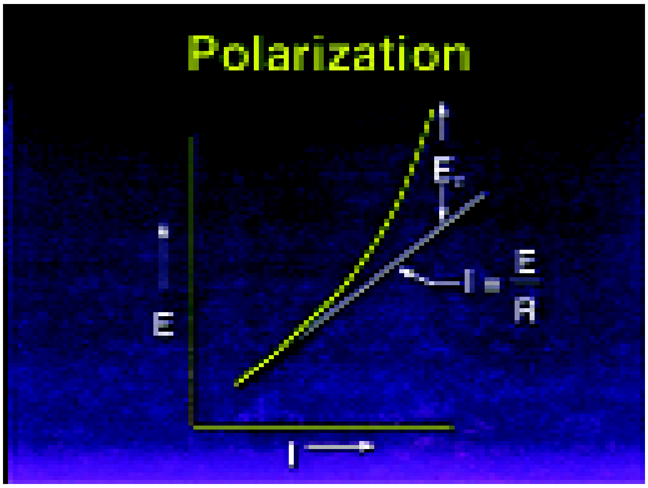


Fig. 1—Polarization.

"The relationship between voltage and current would follow a straight line if we were dealing only with the resistance of the plating bath. [In Fig. 2,] this voltage requirement appears as E_s. An additional voltage E_a is required to overcome polarization at the anode and an additional voltage E_c at the cathode.

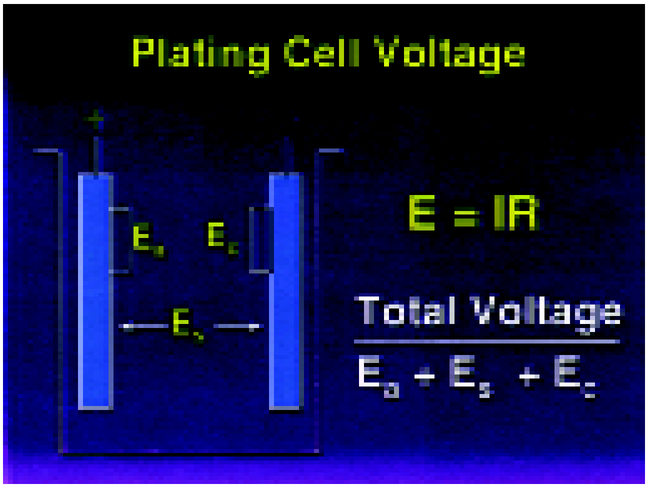
"First, let's consider polarization at the anode. As the metal dissolves anodically, we build up a high concentration of metal ions at the surface of the anode. This requires an additional voltage E_a to dissolve the metal [further]. The situation is quite different at the cathode. As the metal plates on the part, we have a decrease in the metal ions at the cathode film. This requires an additional voltage E_c to deposit the metal. Under normal operating conditions, these polarization factors E_a and E_c do not cause problems to a plater. It simply means that he has to apply a somewhat higher voltage to maintain the current as the current density increases."

Anode Problems

"However, the situation is not always this simple. It is obvious at this point that the normal polarization at the anode and the cathode can be reduced with effective solution circulation. [You sweep away that high concentration of metal ions at the anode and pump in fresh ions at the cathode.] If the voltage required to obtain a given value of current rises abruptly and becomes abnormally high, abnormal anode polarization is indicated. This is primarily associated with malfunctioning of the anodes and can result in serious problems. The anodes are probably operating at too high a current density, which can result in several problems. In most cases, the anode will not corrode anodically at close to 100 percent efficiency because part of the current will be wasted in liberating oxygen. As a result, the metal content of the solution will drop and higher chemical additions will be required to maintain the solution.

"The problem is even more serious in cyanide copper plating. [Although cyanide plating is in more limited use today, the principle is still important to remember.] Oxygen liberated at the anode surface may react with the copper to form an insulating film of copper oxide and the current will eventually cease to flow. If the copper oxide becomes detached from the anode and physically contacts the part being plated, it is reduced to copper metal and becomes welded to the surface. This creates high current density points and produces serious particle roughness.

"Failure to make good electrical contact between the bus bars and the anodes probably represents the greatest single factor in excessive or abnormal anode



Plating Cell Voltage

$E = IR$

Total Voltage

$E_a + E_s + E_c$

Fig. 2—Plating cell voltage.

Hydrogen Overvoltage

At 1 mA/cm^2

Hg	-1.16
Zn	-0.80 (Est.)
Sn	-0.80
Cd	-0.80
Cu	-0.60
Ni	-0.40
Ag	-0.30
Au	-0.15
C	-0.11
Pt	0.00

Low Hydrogen Overvoltage In A Cyanide Zinc Plating Solution Produces Large Amounts Of Hydrogen Gas At The High Current Density Areas In The Hull Cell

Fig. 3—Hydrogen overvoltage on metals.

polarization. This can lead to variations in thickness of deposits, especially in manually operated installations.

"A relatively simple test can be conducted to establish if a significant number of anodes is not making contact with the bus bars. Apply an electrical clip to a Hull cell panel and connect an ammeter (5–10 A range) in series using an insulated or covered copper wire. Record the current on the ammeter. Take readings at several positions throughout the length of the tank and repeat the operation on the parts facing the other anode bus bar. **All readings should be approximately equal**. If you find wide variations, check the anode contacts by cleaning the bus bar in the position where low values of current were obtained and repeat the current survey."

[Another concept, giving many platers fits, is hydrogen overvoltage and its potentially damaging consequence, hydrogen embrittlement. Hydrogen embrittlement remains one of the major concerns in quality assurance today. In many cases, with fasteners and brackets in particular, it is a structural concern. Not all of the plating current goes to laying down the metal. Unfortunately, we have to consider that fraction of the current that goes toward evolving hydrogen at the part surface as well. It has consequences of which we must remain aware. Once again, Dr. Swalheim's "AES Update" promotes a much better understanding of this phenomenon.]

Hydrogen Overvoltage

"Another type of polarization, [shown in Fig. 3], hydrogen overvoltage, may occur at the cathode or surface of parts being plated. Primarily associated with [but not limited to] zinc plating, it is simply the polarization involved in the evolution of hydrogen. In order to understand the term, we can consider hydrogen overvoltage as a two-step process. First, atomic hydrogen is formed and then the atoms combine to form molecules of hydrogen. The hydrogen overvoltage on platinum is zero. This is because the hydrogen atoms combine very rapidly to form hydrogen molecules [on the platinum surface].

"However, the hydrogen overvoltage on zinc is -0.8 volts. In other words, it requires a potential higher than 0.8 volts to deposit hydrogen. You will also note that the single electrode potential of zinc is -0.76 volts. The voltages required to discharge hydrogen and deposit zinc from a sulfate solution are quite similar, so hydrogen tends to codeposit with zinc.

"Before discussing problems associated with hydrogen overvoltage, let's examine how the values vary with different metals [again shown in Fig. 3]. These are only approximate values because a number of factors influence hydrogen overvoltage, such as smoothness of the surface, type of electrolyte, current density and temperature.

"One of the problems associated with hydrogen overvoltage is hydrogen embrittlement in plating high-carbon steel. The problem is caused by the carbon. The value for hydrogen overvoltage on carbon is lower, however, than the value for pure zinc. This is significant because hydrogen will tend to deposit in preference to zinc. The damage to the high-carbon steel part is done before the hydrogen is released as a gas. The culprit is atomic hydrogen. It travels through the crystal lattice of the part and becomes absorbed in the metal, causing serious embrittlement. In some cases, thin-gauge high-carbon steel parts will even fracture during the plating operation because of the high stress. If the part becomes embrittled, the only remedy is to heat treat the part at 190° C (375° F) for a period up to 24 hours to drive off the hydrogen. [Indeed today, this operation is specified to assure that the condition has been alleviated.]

"Most platers are fully aware of the problems in plating cast iron, in which the problem is associated with another form of carbon—graphite. Hydrogen overvoltage on graphite is also low. Although steps can be taken to minimize exposure of graphite on the surface, one solution is to apply a copper 'strike.' Copper will plate at a lower voltage and cover the graphite on the surface. You can then proceed to plate the part with zinc.

"Problems in plating high-carbon steel and cast iron parts have been minimized to some extent with the development of the bright zinc acid plating baths. Problems with hydrogen overvoltage are not as serious."

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