Catalytic Anodes for High-Speed Electroplating and Electrogalvanizing

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This comparison of insoluble anodes for high speed plating and electrogalvanizing emphasizes the advantages of catalytic anodes *over* lead alloys. Valve metals with a coating of oxide mixtures including a precious metal oxide comprise catalytic anodes with effective catalytic action and high electronic conductivity over a wide range of current densities. Cell voltage and energy consumption are reduced. The fabrication method affects the activity and stability of the anode.

he growing importance of high-speed electroplating and electrogalvanizing¹² has led to the careful consideration of the processes occurring at the anode as well as the cathode. A soluble anode appears advantageous because metal ions in solution should be maintained at the desired concentration. However, non-uniform dissolution, passivation and faradaic inefficiency are known to occur.³ The inter-electrode gap necessarily increases and the anodes must frequently be replaced, which complicates the design and operation of an electrolytic system with soluble anodes.

Gas evolves at insoluble anodes. Chlorine evolution from a chloride electrolyte would pose significant problems in cell design and operation and safety. Thus insoluble anodes are presently used with sulfate solutions. Two types of insoluble anodes are: (1) lead or lead alloys such as lead-silver and load-calcium and (2) a precious metal or catalytic type consisting of a valve metal such as titanium or tantalum coated with a metal or metal oxide usually selected from the platinum group (Fig. 1). A valve metal forms a nonconducting surface during electrolysis if not protected by a barrier.

Catalytic Electrodes

Catalytic or electrocatalytic electrode materials influence in a positive manner the mechanism or kinetics of the electrode process.' These terms have a broader meaning today, which probably evolved from the requirements for commercially viable electrode materials.' Thus a catalytic electrode is characterized by a high surface area, high electronic conductivity, long term stability or low cost in addition to its catalytic function. Viable catalytic electrodes are typically a compromise between activity, stability and cost.

Henri Beer⁶ showed in the 1960s that precious metal oxides thermally deposited on valve metals exhibited excellent performance as chlorine-evolving electrodes. Subsequently the so-called dimensionally stable anode (DSA*) had a major impact on electrochemical technology particularly the chlor-alkali industry.

The ruthenium oxide-titanium oxide coating used for commercial DSA electrodes is an example of metal oxides with metallic or quasi-metallic conductivity. The commercial success achieved with this type of coating prompted extensive research and development on both single and mixed oxide structures during the past two decades." These studies focussed particularly on oxides with a rutile crystal structure such as RuO₂, IrO₂, PtO₂, Mn0, and mixtures with TiO, and SnO,. Other oxides of interest include spinels (Co₃O₄ and MCo₃O₄ where M is Ni, Cr or Mn), perovskites (NiM₂O₄ where M is La, Pr or Nd) and platinates (Li, P,0, or SrPd, O,). Incorporation of the valve metal or non-catalytic oxide may also be important because it has been shown that the activity of the electrode is dependent on the ratio of the surface concentrations of the precious and valve metals."

Although successful for electrolyzing brine solutions, the RuO₂-TiO₂ coating is not commercially viable in sulfate solutions. Coating dissolution or passivation of the valve metal substrate causes early electrode failure. With the incorporation of tin dioxide¹⁰ or iridium dioxide" to stabilize the coating, the RuO₂-IrO₂electrode has been successfully used in commercial electrolyzers.¹² The superior stability of iridium oxide, relative to other precious metal oxides, during oxygen evolution has led to the development of other commercially available electrodes, including one that incorporates tantalum oxide. "

The concept of an intermediate, barrier layer between the substrate and the catalytic coating for inhibiting or preventing passivation has also been extensively explored. Several types have been described in the literature. Examples include a Sn/Sb oxide¹⁴ and another that incorporates titanium nitride or titanium carbide¹⁵ and polymer coatings. "



Fig. 1 — Cross-section diagram of a typical catalytic anode.

^{*}DSA is a registered trademark of DST, S.A., Zug, Switzerland

Fabrication Methods

Techniques used to fabricate catalytic electrodes include thermal deposition, diffusion bonding, plasma spraying, electrolytic and electroless deposition and vacuum sputtering. Thermal decomposition of a metal salt is the most common. A thin layer of an appropriate metal salt, usually a halide or organometallic compound, is applied to the preconditioned valve metal substrate by roller coating, dip coating, brushing or spraying. The salt is thermally decomposed under controlled conditions after drying. To obtain the required thickness, several coats are applied and each is followed by thermal cycling. Catalysts such as the spinels or platinates are prepared by high-temperature, solid-state methods. The catalyst is then applied to the substrate as a fine powder dispersed in a suitable binder.

Control of the thermal cycle is critical for both coating stability and electrochemical activity. ? In a crystalline ruthenium dioxide coating, a high degree of disorder is beneficial for promoting activity and electronic conductility. " The valve metal substrate also influences the structure and morphology of the coating. The chemical and physical properties of the surface can affect the adherence of the catalytic coating.¹⁸

The Oxygen Evolution Reaction

In acid and neutral solutions the reaction occurring at the insoluble anode is the evolution of oxygen:

$$2H_2O \rightarrow O_2 + 4H' + 4e$$
 (1)

and the standard reversible electrode potential is 1.23 V vs.the normal hydrogen electrode (NH E). Both the pH and the activity of water affect the reversible potential for this reaction, so that at 25° C,

$$E_r = E_r^0 - 0.06 \text{ pH} - 0.03 \log_{10} a_{H_sO}$$
 (2)

where E", is the standard reversible potential.

The electrode process is kinetically irreversible, particularly in acidic solutions. At high current densities, significant overpotentials are observed, which is apparent in the behavior of both the lead-silver anode and the catalytic anode** used to develop the electrode potential data in Figs. 2 and 3. These data were obtained in sulfuric acid at 50° C; a current interruption technique was used to eliminate the ohmic contributions to the measured electrode potentials, At high current densities (5 to 10 kA/m²), the overpotential for oxygen evolution at the catalytic anode is approximately 400 to 450 mV, but is substantially lower than that at the lead-silver alloy, The lower Tafel slope (i.e. the slope of the curve of the overpotential vs. the log of current density) reflects a change in the mechanism of the electrode process for the catalytic anode, suggesting true electrocatalysis.

Electrogalvanizing processes typically use concentrated sulfate solutions with a pH of 2.0 to 4.0, In these solutions, polarization curves are shifted to less anodic potentials (Fig. 3), as predicted by equation (2) above. However, the kinetics of the electrode reaction do not appear to be affected by the changes in the electrolyte.

The stability of lead in aqueous solutions is attributed to the formation of a protective surface film of lead oxide. However, this film does not entirely prevent dissolution of the metal. Consequently, electrolytes with lead anodes will contain detectable levels of lead ions. The thick surface film of the lead oxide does not strongly adhere to the anode, so



Fig. 2—Comparison of the polarization behavior of a lead-silver alloy anode and e catalytic anode.







Fig. 4-Polarization data for a fresh and aged lead-silver alloy anode.

lead is continually eroded during operation. Lead and lead oxide particles can codeposit with zinc and may adversely affect the properties of the galvanized steel,

The formation of a surface film on the lead-silver alloy anode is indicated by the abrupt change in the polarization behavior after a short period of continuous operation (Fig. 4). The large increase in overpotential may be attributed to

^{**}TIR-2000, Eltech Systems Corporation, Chardon, OH

the impedance of the oxide surface layer. It also appears that a steady state was attained, in terms of surface layer thickness, because the polarization characteristics did not change markedly with continued operation of the leadsilver anode (Table 1).

The catalytic anode, on the other hand, shows comparatively stable performance under similar operating conditions (Table2) and maintains substantial advantage in terms of anode overpotential and operating cell voltage. Table 2 data show that the potential of the anode does not change with time. For example, at 3 and 6 kA/m², the increase in potential over 850 hr is only 0.04 and 0.08 V, respectively.

A representative profile of the change in potential with time for a catalytic anode is shown in Fig. 5. The slope of the first section (AB) of the curve in Fig. 5 will be dependent on electrolyte composition and operating conditions such as current density and temperature. The sharp increase in potential in section BC is an indication of the failure of the anode. If polarization is continued, particularly at high current densities, the potential will rise quickly to 8 or 10 V and the valve metal substrate will dissolve.

Extended Operation

Several factors can contribute to the failure of the catalytic anode. For a given system, any one or all of three factors may be involved: (1) loss of catalyst by dissolution or erosion; (2) electrolyte impurities that cause substrate damage and erosion and exfoliation of the oxide coating, poisoning or blinding of catalyst sites or selective dissolution of the catalyst and (3) passivation of the valve metal substrate.

Oxidation and dissolution of the metal oxide can occur at the high anodic potentials experienced by the electrode. The stability of the platinum group metal oxide is dependent on effective conversion from the salt with emphasis on the critical nature of the thermal cycle during the fabrication of the electrode. Microscopic examination" and physical characterization indicate that the coating is porous. Thus the rate of erosion or mechanical loss will depend on both adherence to the substrate and particle to particle bonding within the coating. The conditions of high electrolyte flow rate (accompanied by high shear force), rapid gas evolution at the surface and the formation of gas inside the porous structure may all contribute to erosion and mechanical loss of the coating.

Certain ions (discussed below) and organic materials in the electrolyte can shorten the life of the anode. These effects have largely been determined at chlorine-evolving anodes and a different electrode reaction or different conditions may lead to a dissimilar effect.

Fluoride ions react with the valve metal at the coating substrate and weaken the adherence of the coating. Free fluoride or HF levels should therefore be minimized (<1 or 2 mg/L). There is some evidence that calcium or aluminum ions in the electrolyte may be beneficial by forming complex ions with fluoride ions and nullifying their activity.

In highly alkaline solutions, both the coating and substrate will corrode and/or dissolve. This environment is unlikely for most high speed electroplating processes, however.

Calcium and barium ions form fine (possibly colloidal) particles of insoluble sulfates that appear to deposit electrophoretically on the anode surface. An accumulation of such particles will blind the catalyst sites and can lead to exfoliation of the coating. Both manganese and lead can

Current density, <u>Anode potential vs. NHE*</u> kA/m ² initial 160 hr 800 hr 850 hr	Polar	ization B	ehavior of a	Pb-Ag An	ode
density, <u>Anode potential vs. NHE*</u> kA/m ² initial 160 hr 800 hr 850 hr	C				and a second
kA/m ³ initial 160 hr 800 hr 850 hr	density,		Anode potenti	al vs. NHE"	
	kA/m ²	Initial	160 hr	800 hr	850 hr.
0.75 1.54 1.90 1.58 1.69 15 1.61 1.97 1.77 1.80	0.75	- 1.54 1.61	1.90	1.58	1.69 1.80
3.0 1.74 2.16 2.07 2.10 45 1.79 2.33 2.29 2.26	3.0	1.74	2,16	2.07	2.10
6.0 .1.81 2.51 2.45 2.39	4.5 610	1.81	2.61	2.45	2.39
(.) 1.80 2.39 2.32 2.30	1.5	1.00	2.09	2.76	2.00

After polarization at 4 kA/m².

		Table 2		
Polar Current		de ordenij	l vs. NHE*	
kA/m ²	Initial	160 hr	\$00 hr	850 hr
0.75 1.5	1.5 1.54	1.44 1.47	1.49 1.54	1.52 1.58
3.0 4.5	1.69 1.62 1.64	1.51 1.54 1.57	1.60 1.64 1.67	1.63 1.68 1.72
7.5	1,67	1.59	1.69	1.75
*After polarizat	ion at 4 kA/m			

deposit as oxides on the anode surface. The deposition of non-conducting a-MnO₂effectively blinds or poisons the electrode; β -PbO₂ is conductive but would provide a significant impedance.

Surfactants tend to accelerate passivation during limited tests, perhaps by enhancing the rate of penetration of water or an anionic species to the valve metal substrate. The response to other additives or impurities species cannot be predicted unless similarities to those discussed above are expected. Because it would be an insurmountable task to develop information on all of the additives used in a plating bath, it is essential to examine each system individually.

Passivation is accompanied by the formation of a surface layer that stabilizes a metal that is dissolving or corroding.



Fig. 5-Change of potential with time for a catalytic anode.

PLATING AND SURFACE FINISHING

This layer must be electronically conductive or become electronically conductive" to provide a useful catalytic electrode. Other anodic processes such as oxygen evolution can then be sustained at such a film-covered metal. An example is the behavior of lead in aqueous, acidic solutions²⁰, with the formation of an insoluble film of lead sulfate which is subsequently converted to conductive a-Pb0,.

The valve metals such as aluminum, titanium and tantalum form nonconductive oxides that normally cannot become conductive. The performance of a catalytic anode that uses a valve metal substrate is critically dependent on the maintenance of electronic conductivity in the coating and across the substrate-coating interface. The coating preparation conditions for an anode such as that used to generate the data in Table 2 favor the formation of the stoichiometric oxides of both titanium and the platinumgroup metal, as is indicated by the crystal structures of the oxides. Hence the electronic conductivity of the coating is probably entirely due to the platinum-group metal oxide. However, there is evidence that a non-stoichiometric oxide of the valve metal is formed at the' interface during fabrication. Passivation is then the conversion of the conducting oxide to a nonconducting titanium dioxide.

The mechanism of the formation of the insulating layer is not well defined, but may involve either (1) diffusion of the oxygenated species, such as a water molecule or an oxyanion, into the pores of the coating or (2) diffusion of oxygen gas molecules or intermediate species to the metal surface. Any of the above species react with titanium ions and the non-stoichiometric oxide at the interface. The nonconducting dioxide may form as growing islands, thereby increasing the local current density at other areas and creating a non-uniform current distribution. The consequences of this may be particularly noticeable in cells with a narrow anode to cathode gap.

Summary

For electrolytic processes involving the anodic evolution of oxygen, catalytic anodes such as the DSA electrode are capable of stable, extended performance over a wide range of current densities. The fabrication process and its impact on the electrochemical activity and stability of a catalytic anode is most important. Experience has shown that passivation is the primary failure mode not loss of the catalyst, when the anode is used to evolve oxygen at high current densities. This is particularly true if the fabrication process is carefully controlled.

The catalytic anode is sensitive to some impurities that can be encountered in the electrolyte. However, the anode does not contribute lead ions, which are deleterious to some cathodic processes such as copper and zinc electroplating. By comparison with lead or lead dioxide, the catalytic anode can substantially reduce the cell voltage and the energy required for electrolytic processes. Different electrode geometries and cell designs can be adopted by using catalytic anodes.

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