CATALYTIC ANODES IN ELECTROWINNING - INHIBITION OF POISONING BY MANGANESE IONS

PART II - GALVANOSTATIC STUDIES

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ABSTRACT

The investigation of the catalytic anodes caused by Mn$^{2+}$ ions in electrowinning electrolytes has been studied under galvanostatic conditions. Galvanostatic anode potential rise in presence of Mn$^{2+}$ ions indicates the deterioration in the catalytic activity as a result of MnO$_2$ formation on the electrode surface. The addition of arsenic phosphorous or arsenic compounds is found to restrict the rise in anode potential.

Current efficiency studies made for MnO$_2$ deposition in presence of arsenic or phosphorous compounds show the inhibiting tendency of these surface active substances on MnO$_2$ formation. Surface characteristics of passivated electrodes has also been used using Scanning electron microscopes.

Key words: Catalytic anodes, electrowinning, galvanostatic studies, Inhibition of Mn$^{2+}$

INTRODUCTION

In recent years there have been many attempts to reduce power consumption in the production of metals by electrowinning process. The power requirement can be decreased by effecting a reduction in the cell voltage which in turn can be reduced by decreasing the oxygen overvoltage. Considerable work has been done on the development of improved anodes for electrowinning of metals. A straight forward reduction in oxygen overpotential is being realised by the substitution of dimensionally stable anodes for the conventional lead alloy anodes. Noble metal oxides like Ruo$_2$, Sb$_2$O$_3$, and Se$_2$O$_3$ show excellent characteristics as catalysts for oxygen evolution. Excellent corrosion resistance, increased purity of the cathode product and reduced maintenance cost are some of the added advantages.

The impurities and additives present in electrowinning electrolytes impose some restriction on the application of catalytic anodes for metal win- ning operations. For example, the presence of cyanides in solution is detrimental for the operation of catalytic anodes as the deposition of poorly conductive manganese oxides during electrowinning process, gradually cover the surface resulting in increased cell voltage.

This paper investigates the problem of deterioration of catalytic anodes by manganese ions studied under galvanostatic conditions. The effect of certain soluble compounds of arsenic and phosphorous on the inhibition of MnO$_2$ formation has been studied.

EXPERIMENTAL

 Valve metal support particles were degreased with trichloroethylene and impregnated with the activating solution in an amount equalizing to 1.0 wt. % Ru by weight of support particles. The impregnated particles were dried at 120°C and then heated to 450°C for 1 hour, in an air stream.

The electrolysis thus prepared was embedded in the surface of lead sheet to substantially cover the surface of the substrate. RuO$_2$ film electrodes of 2 cm$^2$ area on caustic substrate with Ru content of 0.5 mg cm$^{-2}$ were prepared by thermal decomposition technique. Platinum electrode of 1.2 cm$^2$ area was employed for current efficiency studies of MnO$_2$ deposition. Anode polarization studies were carried out under galvanostatic conditions in 1M H$_2$SO$_4$ containing upto 20 g l$^{-1}$ Mn(II) ions at a current density of 400 mA cm$^{-2}$. As(III) addition in the form of sodium meta arsenite from 0 to 600 ppm and addition of Fe(II) in the form of Fe$_3$PO$_4$ from 0 to 1000 ppm were employed. Long term polarization studies with electrodes of 45 cm$^2$ area were carried out at a current density of 40 mA cm$^{-2}$ for a period of 8 hrs. Potentials were measured against saturated calomel electrode (SCE) and converted to normal hydrogen electrode (NHE). Scanning electron micrographs of RuO$_2$ film electrodes polarized at 40 mA cm$^{-2}$ in 1M H$_2$SO$_4$ with and without Mn(II) and Fe(II) have been taken.

RESULTS AND DISCUSSION

Fig. 1 indicates potential-time curves for oxygen evolution on RuO$_2$ film electrode. In presence of Mn$^{2+}$ the anode potential gradually
The effect of PdV and As(III) on the anode potential under oxygen evolution conditions is shown in Fig. 2.

Fig. 2: Anode potential-time curves for oxygen evolution on RuO₂ film electrode of the 0.5 mg cm⁻² loading in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) with additions of As(III) or PdV. The reduction in rate of anode potential by MnO₂ deposition with 200 ppm As(III) is 15 mV for 8 hrs, and it is around 30 mV for 600 ppm As(III) and 1000 ppm PdV additions. The influence of arsenic and phosphorus compounds on the inhibition of MnO₂ formation can be explained on the basis of preferential adsorption of these compounds on the electrode surface.

Table 1 shows current efficiency for MnO₂ deposition with different amounts of As(III) additions, under the conditions of 1M H₂SO₄ containing 20 g⁻¹ Mn(II) at a current density of 100 mA cm⁻², with the increases of As(III) additions, the current efficiency for MnO₂ deposition decreases from 12.8% to 0.23%.

TABLE 1: Current efficiency for MnO₂ deposition in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) with arsenic (III) additions.

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<th>As(III) addition (ppm)</th>
<th>Current efficiency for MnO₂ deposition (%)</th>
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<tr>
<td>0</td>
<td>12.809</td>
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<td>50</td>
<td>7.768</td>
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<td>200</td>
<td>3.220</td>
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<td>600</td>
<td>0.231</td>
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Fig. 3 shows the scanning electron micrograph of RuO₂ film electrode polished in 1M H₂SO₄ which judicious multi-layered pure form structure of RuO₂. Fig. 4 is the SEM of RuO₂ film electrode polished in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) ions where massive crystallite deposition of MnO₂ is seen. Fig. 5 is the SEM of RuO₂ film electrode polished in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) + 1000 ppm PdV. Absence of the characteristic massive crystallite structure indicates the inhibition of MnO₂ formation.

The gradual increase in the anode potential can be explained by the gradual coverage of the active surface by deposition of chemically poorly conducting manganese oxides.

Table II gives current efficiency data for MnO₂ deposition with PdV additions. In this case the current efficiency decreases from 12.8% to 0.86%.

TABLE II: Current efficiency of MnO₂ deposition in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) with phosphorus (V) additions.

<table>
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<th>Phosphorus (V) addition (ppm)</th>
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<td>50</td>
<td>8.281</td>
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<td>500</td>
<td>7.153</td>
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<td>700</td>
<td>0.863</td>
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Fig. 3 shows the scanning electron micrograph of RuO₂ film electrode polished in 1M H₂SO₄ which judicious multi-layered pure form structure of RuO₂. Fig. 4 is the SEM of RuO₂ film electrode polished in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) ions where massive crystallite deposition of MnO₂ is seen. Fig. 5 is the SEM of RuO₂ film electrode polished in 1M H₂SO₄ containing 20 g⁻¹ Mn(II) + 1000 ppm PdV. Absence of the characteristic massive crystallite structure indicates the inhibition of MnO₂ formation.
CONCLUSION

Poisoning of the catalytic sites by MoO₄²⁻ in metal-oxide electrolyte has been studied. Anodic polarization studies under galvanostatic condition with platinum, RuO₂ film electrodes and RuO₂ sponge electrodes indicated the inhibition of MoO₄²⁻ formation by anodic and photolysis compounds. The inhibition may be due to preferential adsorption of these compounds on the electrode surface.

REFERENCES


FIRST NATIONAL CONFERENCE ON ELECTROCATALYSIS.


JOINTLY ORGANIZED BY SANST, ECOR AND M.S. University of Baroda.

OBJECTIVE
To consolidate the presently available knowledge and project future trends.

SCOPE
1. Theory of electrocatalysis
2. Electrochemical reactions on:
   - metallic surfaces
   - Semiconductors
   - Nonmetallic materials
3. Characterization of electrode surfaces by
   - Spectroscopic method
   - Electrochemical method
4. Electrode materials
   - Hydrogen
   - Oxygen
   - Cathode electrode reactions
5. Electroanalysis in:
   - Electrochemical energy conversion
   - Electroanalytic processes
   - Electroanalytical
6. Photoelectrochemistry and photovoltaic energy conversion.

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