

Critical anode potential in chlorate production

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INTRODUCTION

Chlorate is produced in undivided cells, where hydrogen gas is formed on the cathode and chlorine is formed on the anode. Chlorine is then dissolved in the electrolyte and reacts to form chlorate through a number of reaction steps. It has been shown [1-3] that anodic polarization curves on DSAs[®] of RuO₂/TiO₂ bend to a higher Tafel slope at approximately 1.2 V vs Ag/AgCl. Eberil *et al* [1] refers to this potential as the critical potential (E_{cr}) and explains the bend as Ru(VIII) formation. Operating above E_{cr} leads to an increasing rate of ageing of the anode (i.e. the anode loses its ruthenium faster). This work aims to investigate how different electrolyte parameters, for example chloride and dichromate concentrations, affect the critical potential. Cornell *et al* [2,3] have previously investigated the effect of these parameters at pH 6.5 (a typical pH of industrial chlorate electrolyte) and found that E_{cr} decreased with increasing chloride concentration. However, at pH 6.5 oxygen evolution is produced through different possible side reactions, which causes pH gradients in the diffusion layers. At pH 2, where no significant oxygen evolution takes place, bulk pH is close to pH at the electrode surface. Polarization curves at different chloride- and chlorate concentrations, all with electrolyte pH 2, have been recorded and compared to those earlier made at pH 6.5 [3]. Total molar concentration was kept constant, so that the ionic strength was constant.

EXPERIMENTAL

Rotating disks were punched from commercial DSAs[®] and placed into holders suited for an electrode rotator Model 636 from EG&G. Polarization measurements were made using a PAR 273A potentiostat. Correction of iR -drop was made with the current interrupt technique. The "standard" chlorate electrolyte used contained 550 g l⁻¹ NaClO₃, 110 g l⁻¹ NaCl, 3 g l⁻¹ Na₂CrO₇ with no added NaClO at 70 °C. The electrode was rotated at a speed of 3000 rpm. Any deviations from these conditions are given in the text.

RESULTS AND DISCUSSION

Increasing chloride concentration gave a decreasing potential. It lowered the reversible potential and increased the exchange current density. Analyzing where the polarization curves bend to a higher Tafel slope showed that E_{cr} depends on chloride concentration (Figure 1). It can be seen that there was a linear dependency between E_{cr} and the logarithm of the chloride concentration with a slope of approximately 90 mV/decade C_{Cl} , which is similar to that found for pH 6.5 [3]. Figure 2 shows the apparent reaction order with respect to chloride, at pH 2 compared to the results of Cornell *et al* [3] at pH 6.5. At potentials between 1.14 and 1.19 V vs Ag/AgCl, the reaction order was relatively constant at 1.3–1.4. At potentials above this the reaction order decreased with increasing potential until it became 1.0. This agreed with the reaction order above the critical potential at pH 6.5 [3], and with the reaction order found by others [4].

CONCLUSIONS

The critical potential, E_{cr} , depends linearly on the logarithm of chloride concentration at pH 2. This supports the results achieved by Cornell *et al* [3] at electrolyte pH 6.5, which indicated that E_{cr} depended on chloride concentration. The reaction order at pH 2, with respect to chloride is about 1–1.5 at potentials between 1.14 and 1.19 V vs Ag/AgCl. At potentials above 1.24 V the reaction order is close to 1.

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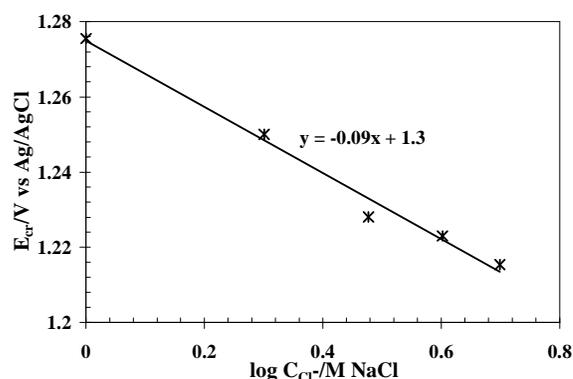


Figure 1. Critical potential, E_{cr} , as a function of the logarithm of chloride concentration, pH 2.

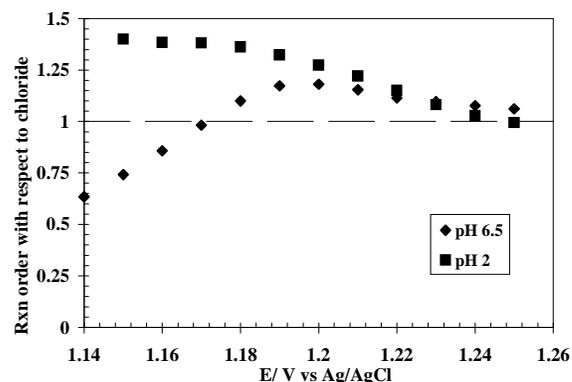


Figure 2. Reaction order with respect to chloride concentration as a function of potential for (■) pH 2 and (◆) pH 6.5 [3].

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