

Anodic Reactions in the Chlorate Process

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Introduction Although the synthesis of chlorate is one of the most important inorganic electrosynthesis processes, there is a limited number of publications relating to the anodic reactions on a DSA[®] at chlorate process conditions [1-5]. The main reaction is the same as in the chlor-alkali process, but the conditions at the anode surface differ from those in the chlor-alkali process regarding pH, chloride-, chlorate-, hypochlorite- and dichromate concentrations, mass transfer, temperature etc. This work aims at characterizing the electrochemical reactions taking place on a DSA[®] at chlorate process conditions. Studies have been made at varying electrolyte concentrations, and some examples are given below.

Experimental Rotating discs were punched from commercial ruthenium dioxide catalyzed DSA[®]s and fit into holders suited for an electrode rotator Model 636 from EG&G. Polarization measurements, mainly polarization curves and cyclic voltammograms, were recorded using a PAR273A potentiostat. Correction for iR-drop was made by a current interrupt technique, where potential transients were sampled by an Integra 20 transient recorder and fit into polynomial expressions to evaluate the iR-corrected potentials. Instrument control, data collection and evaluation have all been made using the LabVIEW program package. The "standard" chlorate electrolyte used contained 550 gpl NaClO₃, 110 gpl NaCl, 3 gpl Na₂Cr₂O₇, no added NaClO and was at pH 6.5 and 70°C. The electrode was rotated at 3000 rpm. Any deviations from these conditions are given in the text.

Results and Discussion Polarization curves at varying chlorate- and chloride concentrations are given in Figure 1, where potentials are given relative to the Ag/AgCl electrode. The total molar salt concentration was kept constant to fix the ionic strength. At anode potentials below *about* 1.1V the dominating electrochemical reaction is oxygen evolution. The anions chloride and chlorate retard the reaction, and chloride has the strongest effect on the potential. At potentials above *about* 1.1V the dominating reaction is chloride oxidation. The reaction order with respect to chloride is one (1.0-1.1) in the potential region 1.175-1.225V. Oxygen evolution is a minor reaction in this region, but affects the polarization curves at pH 6.5. As the chloride concentration is increased the current efficiency for chlorine evolution increases, which lowers the anode potentials and the slopes of the curves.

In Figure 2 the pH of the electrolyte has been varied, and the anode potential recorded at a constant current density of 30A/m². In 200 gpl NaCl without Na₂Cr₂O₇ the electrolyte buffer capacity is low. Any oxygen evolution is self-retarding, as protons formed in the reaction acidify the electrolyte in the vicinity of the anode and thereby increase the equilibrium potential for the reaction. At alkaline conditions, above pH 9, oxygen evolution is enhanced and the anode potential drops rapidly as pH is increased. As dichromate is added to the

solution the buffering effect promotes oxygen evolution already at a pH of about 5, where the potential decreases to a plateau at 0.9 V. At alkaline conditions, above pH 9, the potential drops rapidly. A similar behavior is observed in chlorate electrolyte, although with higher overpotentials for oxygen evolution due to the high anion concentrations.

Conclusions The reaction order with respect to chloride is one, similar to that reported for acidic chloride solutions. At a pH of 6.5 oxygen evolution is a side reaction that is enhanced by the buffering effect of dichromate.

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References

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Figure 1. iR-corrected polarisations curves for a DSA[®] at 70°C, pH 6.5, 3 gpl Na₂Cr₂O₇.

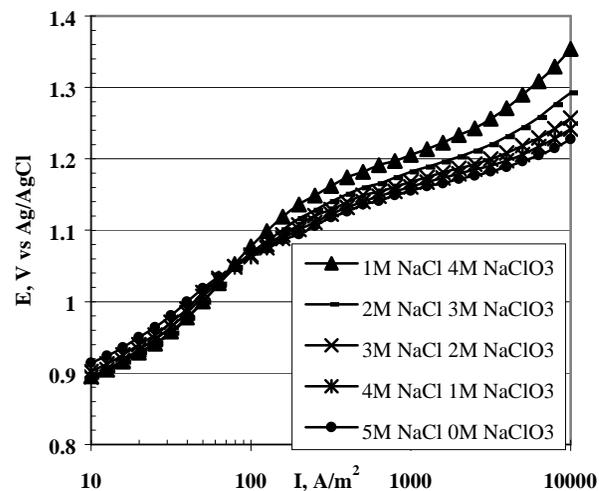


Figure 2. Anode potential against pH at 30 A/m² for chlorate electrolyte and 200 gpl NaCl solution with and without dichromate. Electrode rotation rate 3000 rpm.

