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Electrolytic preparation of bromates using RuO_2 based anodes

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The performance characteristics of $RuO_2 - TiO_2$ and $RuO_2 - SnO_2$ anodes for the preparation of bromates have been studied and discussed.

Key words: Bromates, electrolytic preparation, RuO_2 based anodes, polarisation measurements

INTRODUCTION

The electrochemical production of bromates using graphite and lead dioxide anodes is well known [1,2]. The poor life characteristics of $RuO_2 - TiO_2$ anodes [3] in alkaline solutions hamper their utility in bromate cell. This necessitates some investigations to find a durable RuO_2 based electrode for this reaction. In this paper, the performance of $RuO_2 - SnO_2$ vis-a-vis $RuO_2 - TiO_2$ for bromate preparation has been presented.

EXPERIMENTAL

The relative catalytic activity of the RuO_2 type electrodes were evaluated, both by polarisation measurements and in laboratory scale bromate cell. The usual H-type cell and instrumentation were employed for the galvanostatic polarisation measurement. The laboratory bromate cell was of 10A capacity with stainless steel cathodes.

RESULTS AND DISCUSSION

The steady-state polarisation curves (Fig. 1) indicate a better catalytic activity for bromine evolution on $RuO_2 - SnO_2$ than $RuO_2 - TiO_2$. This is because the SnO_2 component itself catalyses the bromine evolution synergistically, just as reported for chlorine evolution [3]. Both the electrodes give a Tafel slope of about 30 mV. As the pH of the solution is increased, the Tafel slopes show an increase up to pH 10. This is because the preferential discharge of OH^- is likely to suppress the Br^- oxidation above this pH, so that O_2 evolution becomes favoured. Increase in temperature shifts the polarisation curves to less positive potentials and the Arrhenius plot (log i vs 1/T) gave an apparent activation energy of about 7.3 and 12 k cal. mole^{-1} when the overpotential is zero and 50 mV. This indicates that the reaction proceeds with the same mechanism on both the electrodes. The accelerated life test in 1M NaOH at 1A.cm^{-2} at 303–308K gave 48 and 108 hrs for $RuO_2 - TiO_2$ and $RuO_2 - SnO_2$ respectively after which the electrodes failed.

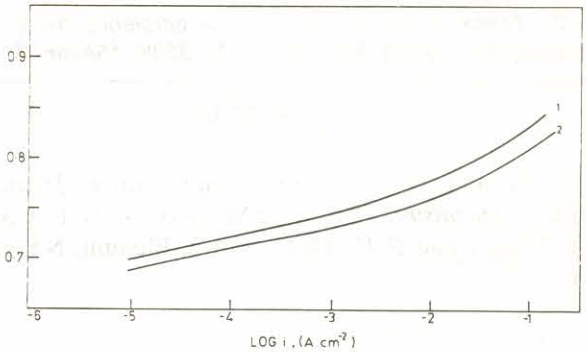

Fig. 1: Polarisation curves in 3.5N KBr, 303K, pH 7.0 for (1,1') $RuO_2 - TiO_2$ and (2,2') $RuO_2 - SnO_2$

The electrolysis of KBr at various pH, temperatures and current densities (Figs. 2 and 3) supported the above measurements. Addition of 2 g/l of dichromate increased the C.E. from 75 to 97% on $RuO_2 - TiO_2$. Highest efficiencies were obtained at pH values between 8.5 and 9.5 which support the fact that the reaction $2HBrO + BrO^- \rightarrow BrO_3^- + 2Br^- + 2H^+$ is favoured at this pH range. Increase in temperature increased the C.E. as the above reaction, as well as the hydrolysis of Br_2, is accelerated by temperature. At optimum conditions of 3.5N KBr + 2 g/l $K_2Cr_2O_7$, pH 9.0, 333 K and 1.5kA.m^{-2} the current efficiencies were 97 and 98.5% on $RuO_2 - TiO_2$ and $RuO_2 - SnO_2$ respectively.

CONCLUSION

Though much difference on the current efficiencies does not exist from the increased service life of $RuO_2 - SnO_2$ as against $RuO_2 - TiO_2$ in 1M NaOH, the former electrode may be more suitable for bromate electrolysis.

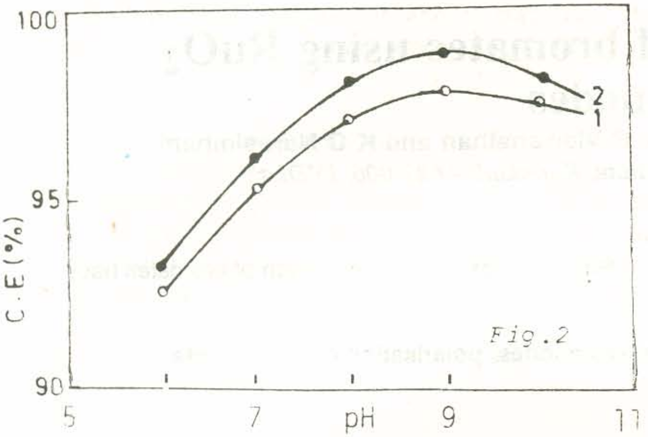

Fig. 2: *Effect of pH on the current efficiency for bromate formation: 3.5N KBr + 2 g/l $Na_2Cr_2O_7$, 333K, 15A.dm^{-2}*

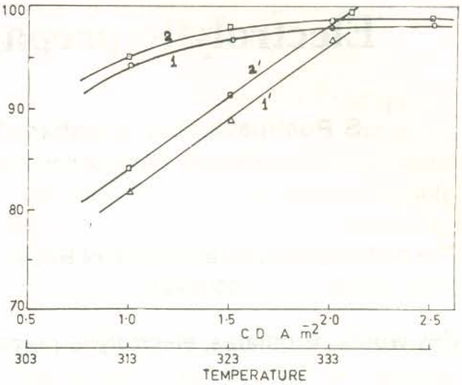

Fig. 3: *Effect of current density (1,2) and temperature (1', 2') on current efficiency, conditions as in Fig. 2, pH 9.0.*

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