

Inhibition effect of magnesium and calcium chloride additives on anodic chlorine evolution at platinum electrode in concentrated potassium chloride aqueous electrolytes

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The effect of MgCl₂ and CaCl₂ additives on kinetic parameters of Cl⁻ anodic oxidation in an acidified KCl solution (pH 2) at platinum electrode with reduced (Pt_{red}) and oxidized (Pt_{ox}) surface has been studied. Pretreatment of the electrode surface included 20-fold cycling of the electrode potential (E) from –0.3 to +1.6 V followed by its fixation at E = –0.3 V (Pt_{red}) and +1.6 V (Pt_{ox}). The addition of calcium and magnesium cations to 4 M KCl electrolyte was found to lead to 1.17 and 1.45-fold decrease in the exchange current (i₀) at the Pt_{red} electrode after replacement of the equivalent part of KCl to 1.24 M MgCl₂ and 1.28 M CaCl₂. Correspondingly, on the Pt_{ox} surface the addition of MgCl₂ and CaCl₂ results in 1.21 and 1.66-fold i₀ drop. At the same time the coefficient b in Tafel equation increases from 55 to 68 mV at Pt_{red} and from 47 to 64 mV at Pt_{ox} in the presence of MgCl₂, and does not change in CaCl₂-containing electrolyte. The main reasons of the inhibition effect of MgCl₂ and CaCl₂ additives seem to be deviations of Cl⁻ ion activity in an electric double layer and a specific adsorption of calcium and magnesium cations on the platinum surface.