Chloride Ion Concentration Effects on Passivity
Breakdown in Magnesium

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Because of its poor corrosion resistance in chloride containing electrolytes, magnesium (Mg) is not typically considered to exhibit passive behaviour and passivity breakdown in a manner similar to traditional passive metals such as stainless steel and aluminium. However, using a combination of conventional potentiodynamic studies and in-situ scanning vibrating electrode technique (SVET) experiments, we seek to demonstrate that passivity and its chloride-induced breakdown plays a pivotal role in the corrosion behaviour of Mg. In this work, the localized corrosion characteristics of specimens comprising two different iron impurity levels of 40 (high purity, HP) and 280 ppm (commercial purity, CP) are investigated under conditions of varying pH and chloride ion concentration. When unpolarised HP-Mg is immersed in near neutral, chloride-containing electrolyte at concentrations of ≥ 0.1 mol dm^{-3}, spontaneous breakdown occurs within hours, characterized by the propagation of dark filiform-like tracks. In-situ SVET scanning shows that these features comprise local anodes at leading edges of advancing filiform-like features, while the dark corroded regions left behind are revealed as cathodically activated with respect to the uncorroded surface. Post-breakdown localised corrosion behaviour is typified in Figure 1, where a current density distribution surface map of a HP-Mg specimen obtained after 10h immersion in 0.1 mol dm^{-3} NaCl (aq) at pH 7 is shown. Furthermore, it is shown that as more cathodically activated corroded surface is revealed, local anodic current density values increase accordingly.

When immersion experiments were repeated at pH values of ≥ 10, no filiform-like corrosion was observed for periods of up to 24 h for NaCl (aq) concentrations of up to 2 mol dm^{-3}. In-situ SVET scanning showed that the passive HP-Mg surface was not wholly electrochemically inert and that a weak distributed anode was coupled with several focal cathodic regions on the exposed metal. Potentiodynamic studies carried out at a fixed pH of 11, using varying sodium chloride concentrations in the range 10^{-3} to 2 mol dm^{-3}, showed clear evidence of passivity breakdown in the anodic braches of the polarization curves, which became progressively well-developed as chloride concentration, [Cl$^-$]was decreased (see Figure 2). Average values of breakdown potential (E_b), taken at the point of sharp inflection in anodic polarization curves for multiple repeat experiments, showed a clear dependence on [Cl$^-$], according to the relationship $E_b = A + B \log_{10}$ [Cl$^-$], where A and B are constants. Under the conditions used for these experiments, values of -1.60 V and -0.11 V/decade were obtained for A and B respectively. It is proposed that the relationship of E_b with [Cl$^-$] derives from chloride ion influence on the solubility product (K_{sp}) of magnesium hydroxide, where K_{sp} is known be a function of $\log_{10}$ [Cl$^-$]. In contrast to these findings at pH 11, similar potentiodynamic experiments repeated at pH 7 for the same [Cl$^-$] range did not show any evidence of passive behaviour in HP-Mg.

Finally, the influence of iron impurity level on passivity is demonstrated. CP-Mg specimens, comprising 280 ppm

Fe, undergo spontaneous breakdown under unpolarised conditions when immersed in chloride containing electrolytes of ≥ 0.1 mol dm^{-3} at all pH levels up to 13. However, at pH 13 an appreciable change is detected in the localized corrosion patterns, with a transition to filiform-like corrosion observed, as opposed to expanding circular features visualized by SVET at pH ≤ 12. The different passive behaviour of the two types of Mg will be discussed in terms of the ease of protective film repair over exposed cathodic sites.
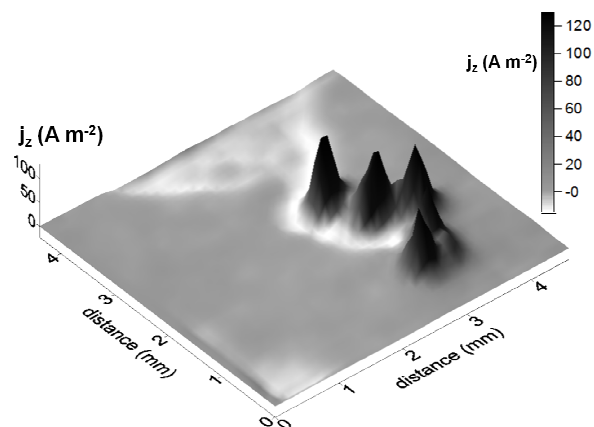

Figure 1: SVET-derived normal current density (j_z) distribution map obtained for an unpolarised HP-Mg specimen after 10h immersion in 0.1 mol dm^{-3} NaCl (aq) at pH7.
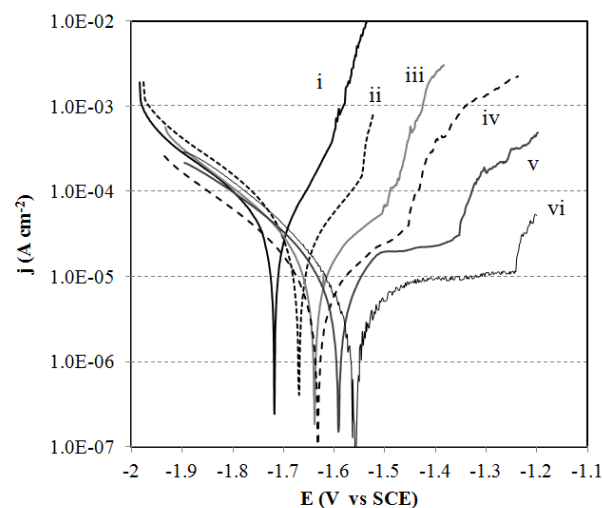

Figure 2: Typical anodic going polarization curves obtained for high purity Mg at pH 11 in aerated sodium chloride containing electrolyte at varying concentrations of (i) 2, (ii) 0.5, (iii) 0.1, (iv) 0.02, (v) 5×10^{-3} and (vi) 10^{-3} mol dm^{-3}.