

A Mechanism Describing Salt Film Formation on Aluminium during Anodic Polarization in Alkaline Lithium-Salt Solution

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Salt film formation during the anodic polarization of active metals is a well-known and widely investigated phenomenon [1-8]. Their growth mode [1-3], composition [4, 5], electrical properties [4, 5] and role in processes such as electro-machining [6], localized corrosion [7] and as a precursor to passivation [8] are well established. The mechanism of formation of the lithium aluminium double salt, lithium aluminium hydroxy carbonate (lithium hydrotalcite), during anodic polarization of aluminium in alkaline lithium carbonate is, however, not so well established; literature pertaining to the kinetics of its formation is scarce [9, 10]. This is somewhat surprising given it has been highly recommended as a replacement for Cr(VI) based surface treatments [11].

In the present work we have investigated the kinetics of salt formation using an aluminium wire disk electrode via a step-potential method. Current - time profiles recorded at various potentials between -1.6 and -0.4 V v Hg/Hg₂SO₄ in lithium hydroxide solutions (pH 13.2), at constant lithium and carbonate levels, demonstrated film growth occurs not via a concerted mechanism, but rather through a multi-step process. Similar profiles determined at constant potential (-0.4 V v Hg/Hg₂SO₄) as a function of the lithium and carbonate levels revealed the process actually proceeds via a four-stage mechanism. Each stage possessed a distinct dependence on solution lithium content, whilst only the latter two stages appeared sensitive to the carbonate level. Protective film formation does not take place in corresponding lithium-free solutions.

The results of our kinetic study were interpreted in terms of a model that postulates film growth occurs via the following sequence:

- (i) Formation of a pre-cursor salt formed via precipitation of lithium and aluminate ions from the supersaturated solution at the electrode surface. The pre-cursor is assumed to be a stage 3 intercalation compound of Al(OH)₃, namely Li_{0.33}Al₂(OH)_{6.33}.
- (ii) Progressive insertion of lithium ions, along with charge-balancing carbonate ions, into the host resulting in the formation of the stage 1 intercalation compound lithium hydrotalcite - LiAl₂(OH)₆(CO₃)_{0.5} - via the consecutive formation of kinetically stable stage 2 and 3/2 intercalates.

Glancing angle XRD provided some evidence in support of the model.

A mathematical description of the postulated reaction sequence, in which the kinetics of salt precipitation determine the surface aluminate concentration, and,

consequently, the dissolution rate, during stage (i), whilst film composition and thickness determine these quantities during stage (ii), allowed the successful reproduction of experimentally determined current - time profiles; see figure 1. In this description Avrami's approach [12-14] to nucleation and growth of crystalline phases was employed to estimate the extent of phase conversion and hence the lithium content of the film at any time during intercalation.

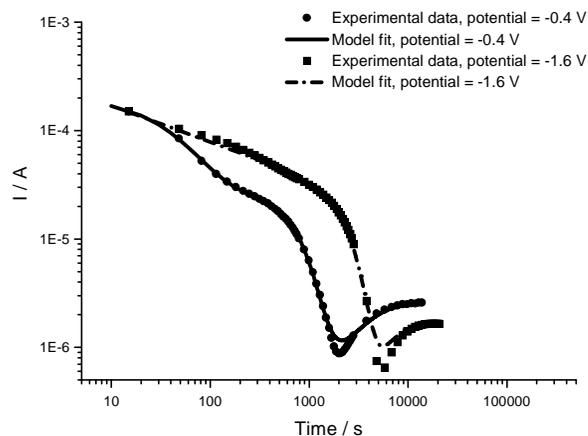


Figure 1: model fit of experimental current - time data for an aluminum disk electrode (area = 0.008 cm²) recorded in 0.1 mol dm⁻³ NaOH + 0.1 mol dm⁻³ LiOH + 0.1 mol dm⁻³ Na₂CO₃, at various potentials - see legend for details.

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