



The Mechanism of Hydrogen Evolution During Anodic Polarization of Aluminium



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ABSTRACT

In this work, a model to account for the superfluous hydrogen evolution mechanism during anodic polarization of Al is proposed. The model is based on the assumption that the simultaneous presence of an anodic current, produced at some distance from the corrosion front, and of conditions that promote local depassivation such as, for example, the presence of chlorides, induces localized rupture of the pre-existing oxide/hydroxide film. This local depassivation leads to the formation of regions where the electrolyte is either in contact with the metal or separated only by a poorly protective salt film. Here, due to the large potential difference available, hydrogen evolves. The model is validated via electrochemical polarization assisted with in-situ image visualization of pure Al and Al/Cu system in experimental conditions that promote stable oxide film formation or induce local film rupture. Hydrogen streams from the active corrosion sites, increasing upon anodic polarization, are observed only in the presence of a depassivating media (chloride) and a remote cathodic current, provided either via galvanic coupling to copper or via external polarization.

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1. Introduction

The aqueous corrosion behaviour of aluminium alloys is considerably affected by alloying elements and resulting microstructure. Although alloying additions generally increase the mechanical performance, they can also lead to the formation of a variety of second phase particles that might have a more or less noble electrochemical potential compared with the alloy matrix [1–3]. A typical example is formation of Cu rich second phases in series 2xxx which become predominant cathodic reaction sites. As a result of localization of the cathodic reaction, local pH variations and higher solubility of aluminium oxide with increased pH, a local dissolution of the adjacent alloy matrix is observed [3]. Such a phenomenon is often named ‘trenching’, and it can be seen as a localized anodic reaction, the dissolution of the matrix nearby a cathodic particle, induced by the localization of the cathodic reaction on the particle.

For metals having low oxidation potential, such as aluminium but also iron, chromium, magnesium and their alloys, the cathodic reaction of hydrogen evolution is thermodynamically possible during free corrosion, but the rate might be controlled by the presence of protective or partially protective oxide, hydroxide or

mixed film on the metal surface. Thus, understanding the details of the process of hydrogen evolution at the active anodic regions on metal and alloys of practical technological interest is essential for the understanding of their corrosion behaviour and for the design of anticorrosion treatments and corrosion resistant alloys. Hydrogen evolution has been observed at the free corrosion potential from propagating pits on steel [4], aluminium [5–8] and aluminium alloys [9–12], and from the active corrosion front on magnesium and magnesium alloys [13–20]. When hydrogen evolution is observed from active corrosion sites at the free corrosion potential, increase in hydrogen evolution during anodic polarization is often reported. This observation is often named ‘negative difference effect’ or ‘superfluous hydrogen evolution’. This terminology is due to the fact that the increase in the rate of hydrogen evolution during anodic polarization is contrary to the prediction from electrochemical theory, i.e. a decrease of the cathodic reaction (hydrogen evolution) rate with increasing anodic polarization [12,21,22]. The increase in hydrogen evolution with anodic polarization has been investigated in detail for aluminium, due to the wide use in batteries and sacrificial anodes, where the negative difference effect is detrimental, since it reduces the faradaic efficiency.

In order to rationalize the observed increase in hydrogen evolution during anodic polarization, various interpretations have been proposed and they can be broadly grouped in three categories: i) based on the assumption that metal cations with

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lower valency are generated during anodic polarization [7,10,21,23,24], ii) based on the assumption that cluster of metal atoms detach from the corroding surface and oxidize in the electrolyte [22] iii) based on the idea that at the active corrosion front the surface film is absent or not protective and at these location hydrogen evolution is possible due to the large potential difference available [5,9].

The first interpretation is largely based on the comparison of the amount of metal oxidized (or hydrogen evolved) with the anodic charge applied to the corroding electrode [7,10]. Given that the oxidized metal (or the hydrogen evolved) generally exceeds what would be predicted by Faraday's law calculation for a valence of aluminium ions of three, it is postulated that some of the metal atoms oxidize to ions with a valence lower than three. Such low-valence ions then undergo further oxidation (by reducing a

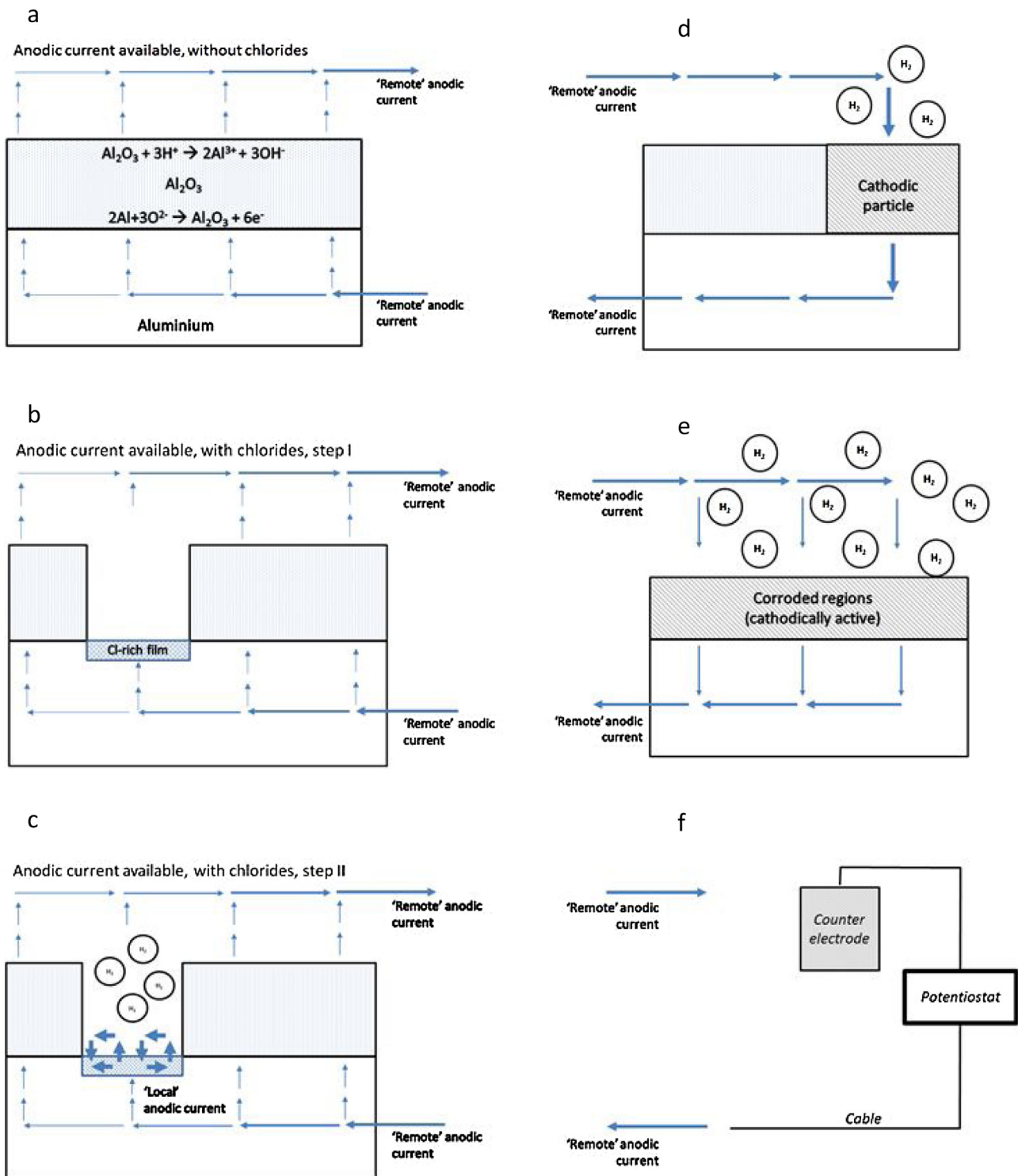


Fig. 1. a) Film growth due to the availability of 'remote' anodic current in the absence of chloride ions. b) Local depassivation in the presence of a 'remote' anodic current and of chloride ions, resulting in the formation of a salt film and c) hydrogen evolution at the corrosion front, producing local anodic current. Generation of 'remote' anodic current from d) cathodic particles on uncorroded regions or e) cathodically activated corroded regions or e) external circuit.

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