

# Investigating the Origins of Chromate Inhibition on Corrosion of Aluminum and Its Alloys by Electrochemical Noise Measurements

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Chromate compounds in aqueous solutions are well known to improve the corrosion resistance of many metals and alloys. However, health and environmental hazards associated with hexavalent chromium have been increasingly recognized, and as a consequence much research has been initiated world-wide to find more environmentally-friendly alternatives to chromate. No suitable replacement is yet identified at present, because the mechanism of chromate inhibition still remains unclear and thus no methodology to develop new alternatives is established. A deeper understanding of the mechanism of corrosion protection by chromate is of utmost importance for the replacement of chromate. The objective of this study is to clarify the origins of chromate inhibition on corrosion of aluminum by electrochemical noise measurements.

Figure 1 shows a 1200 s trace of the current and open-circuit transients from two 0.76 mm diameter coupled Al electrodes in 60 ml of a 0.05 M NaCl solution. Fabrication of the electrode and details of the experimental procedure have been described in elsewhere [1,2]. The electrode surfaces were wet-ground on a 600 grit silicon carbide abrasive paper just before the measurement. The current transient shows intermittent positive and negative spikes and the potential transient displays accompanied events such as a sharp drop, followed by a relatively slower rise. These events are ascribed to initiation, propagation, and repassivation of metastable pits. When 5 ml of 0.05 M NaCl and 0.05 M  $K_2CrO_4$  solution was added to the cell at 610 s, most of these events in both transients seem to disappear, indicating that the addition of  $CrO_4^{2-}$  hampers pit initiation.

Another marked feature in Figure 1 is that the open-circuit potential falls from  $-0.69$  V(SCE) to a minimum value of  $-1.05$  V(SCE) at about 250s after the chromate addition. In general, chromate is regarded as an oxidizer which passivates a metal surface by increasing the corrosion potential several tenth volts [3]. However, we demonstrated that the open-circuit potential of aluminum in a chloride solution decreases rapidly and significantly after the addition of chromate ions, while in contrast, the potentials of iron, steels and copper rise after adding chromate. This implies that the prevailing notion that chromate is a passivator is applicable to iron, steels and copper; however it may not be primarily true for aluminum. Potentiodynamic polarisation tests demonstrated that the cathodic reaction is markedly inhibited by the addition of chromate to electrolyte. This observation is in accord with that recently reported by Frankel *et al* [4]. The present experimental results suggest that chromate primarily inhibits the cathodic reaction of oxygen on the aluminum surface, resulting in

the suppression of anodic dissolution.

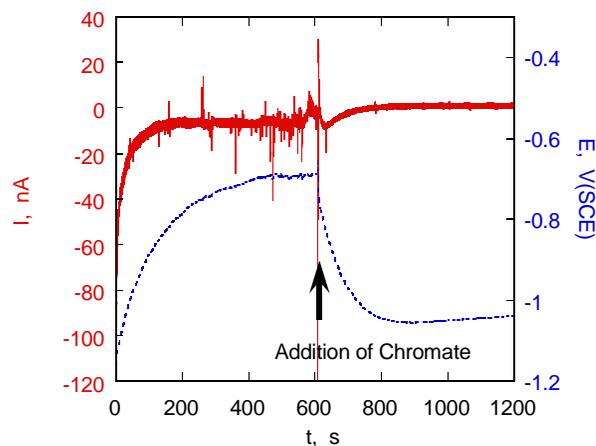
The intriguing questions arise as to how chromate in solutions inhibits the oxygen cathodic reaction on the metal surface. Some plausible notions are considered: (1) Adsorption of chromate ions ( $CrO_4^{2-}$ ) on the metal surface hampers the oxygen cathodic reaction [5]. (2) Reduction of Cr(VI) to Cr(III) occurs on the surface and the resultant  $Cr_2O_3$  inhibits the oxygen cathodic reaction [4]. It is also important to clarify (a) the effective quantity of chromate ions for inhibition, (b) the kinetics of the adsorption/reduction reaction, and (c) preferential reaction sites on the surface (*e.g.*  $Al_2O_3$  film, catalyzed sites, or flaws in the oxide film). These questions will be addressed in this communication.

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## References

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**Figure 1** The current (solid line) and the potential (broken line) transients from coupled Al electrodes in 60 ml of 0.05 M NaCl. At 620s the solution was changed to 0.05 M NaCl and 0.004 M  $K_2CrO_4$ .