



Letter

Multilayered coatings: Tuneable protection for metals

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ABSTRACT

The role of oxide bi-layers in controlling the onset of corrosion has been explored. A high-throughput electrochemical approach was employed to determine the breakdown potential of aluminium metal over-coated with combinations of silicon, titanium, aluminium and magnesium oxides. Bi-layered coatings consisting of two 100 nm thick metal oxide layers provided increased protection against breakdown, and combinations with vastly different iso-electric point of solid (IEPS) were found to exhibit improved barrier properties in comparison to single-component oxides. Furthermore, the most protective oxide bi-layers were produced when a high IEPS oxide was deposited directly onto the metal surface and subsequently over-coated with a low IEPS oxide. The barrier properties of bi-layer coatings appear to be tuneable, with notable dependencies on surface charge and thickness.

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1. Introduction

All industrially relevant metals are thermodynamically unstable and rely upon the addition or formation of protective coatings to slow the kinetics leading to oxidation. Alloys that rely upon passive oxide layers, such as stainless steel and aluminium, tend to suffer from pitting corrosion at the sites of localised breakdown of the protective oxide. There are numerous works describing the importance of chloride ion transport through oxides and passive films and their role in nucleating pitting events [1,2]. Previous studies have also suggested that the surface charge of the oxide can alter the protective nature of the oxide [3]. The formation of oxide bi-layers has also been shown to influence the barrier properties [4–7].

Previous work by McCafferty demonstrated that the pitting potential of oxide-covered aluminium in chloride-containing solutions can be affected by the iso-electric point of the oxide (IEPS) [3]. This led to a proposed model for pit initiation that relied upon the surface possessing a positive charge that would tend to attract chloride anions, thus leading to their transported to the metal interface via oxygen vacancies in the oxide. The initiation of pitting was therefore proposed by McCafferty to be controlled by three factors: (1) the oxide surface charge, (2) the heat of adsorption of chloride ions onto the oxide, and (3) the density of oxygen vacancies in the oxide coating.

Sato [6] also explored the influence of oxide surface charge on controlling the transport of charged species through oxide layers. Oxide precipitation of metal multivalent oxyanions (i.e. metal phosphates/molybdates) can lead to fixed negative charges and the oxide becoming cation selective. In contrast, the precipitation of metal monovalent complexes (i.e. hydroxychlorides) lead to fixed positive charges and anion selectivity. In this manner Sato proposed that the specific adsorption of multivalent anions to the oxide–solution interface imposes a bipolar oxide structure. The bipolar structure possessing an anion-selective inner layer and cation-selective outer layer was demonstrated to block anodic ion transport.

Hayashi et al. [4] studied changes in the electrochemical nature of stainless steel upon the deposition of various oxides. They demonstrated that oxides of approximate thickness of 1 μm led to decreased current densities, where oxides possessing a low reported point of zero charge (PZC)¹ showed the best performance. In addition, the maximum anodic current density was studied for double-layered oxides deposited onto stainless steel. In changing the sequence of the coatings, the passive current density was decreased for samples possessing an oxide of higher PZC near the metal surface, and an oxide with a lower PZC at the outer coating. The coating order was found to have a distinct effect on the passive current density, however no correlation was found between the critical passivation

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¹ Note: The definition of point of zero charge (PZC) is by definition the same as iso-electric point (IEP). IEPS denotes iso-electric point of solid.

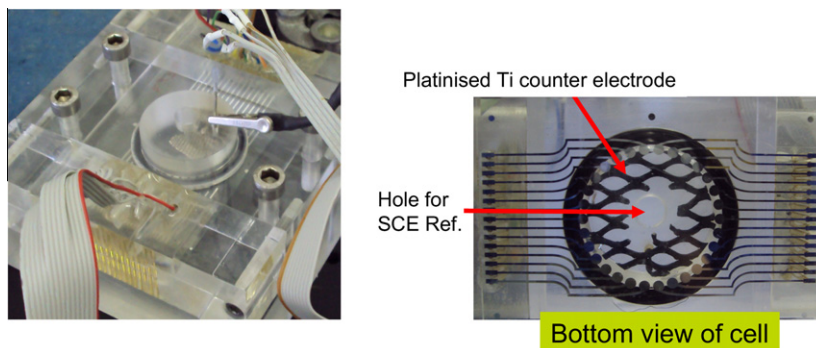


Fig. 1. Multielectrode array testing apparatus.

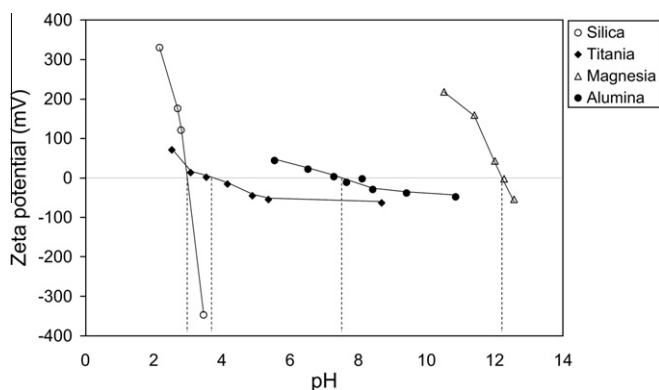


Fig. 2. Zeta potential as a function of pH for 200 nm oxide coatings. IEPs is determined as the pH where $\zeta = 0$.

Table 1
IEPS data for various oxides.

Oxide	IEPS (this study)	IEPS (literature) [10]
SiO ₂	pH 3.0	pH 0.5–3.7
TiO ₂	pH 3.6	pH 3.5–6.7
Al ₂ O ₃	pH 7.4	pH 5–9.4
MgO	pH 12.3	pH ~ 12

current and the PZC and no thickness values were reported for the bi-layer coatings.

Recent work by Macdonald and coworkers, in expanding upon the point defect model (PDM), has also shown the importance of the oxide bi-layer in controlling passivation phenomena [8]. Whilst recognizing the bi-layer structure of oxides, the original PDM only considered the role of a thin-barrier layer at the metal interface. The mechanisms by which bi-layered oxides influence corrosion phenomena are not totally understood at present, but as we demonstrate in this work, can be used to good advantage and are amenable to implementation by industry. The present work demonstrates that the deposition of bi-layer coatings of differing IEPS may offer new opportunities to engineer protective coatings based upon two controlling factors: surface charge and thickness.

2. Material and surface charge characterisation

Physical vapour deposition was utilised to deposit a circular array of aluminium metal electrodes onto a double glass-slide substrate (as seen on the right image of Fig. 1). Multilayer combinations of metal oxides were subsequently deposited over

the aluminium array. The oxides were chosen due to their previously reported surface charge properties, which span the IEPS range from approximately pH 2 (SiO₂) to pH 12 (MgO). The IEPS was characterised for the deposited oxides by measuring the zeta potential, ζ , as a function of pH by the streaming potential approach [9] and determining the pH at which $\zeta = 0$. The flow of an indifferent electrolyte (0.001 or 0.01 M NaNO₃ pH adjusted using HNO₃ and NaOH) through a narrow capillary between two oxide-coated glass slides creates a measurable potential difference along the length of the capillary. The measurement of this potential as a function of the applied pressure enables the determination of the zeta potential (as the slope of $\Delta V/\Delta P$) according to Eq. (1):

$$\zeta = \frac{\Delta V}{\Delta P} \frac{\eta \lambda}{\varepsilon_0 \varepsilon_r} \quad (1)$$

where P = pressure (Pa), V = streaming potential (V), ε_r = dielectric constant (80.2), ε_0 = relative permittivity ($8.854 \times 10^{-12} \text{ J m}^{-1}$), η = solution viscosity (Pa s) and λ = conductivity (S m^{-1}). Determined values of the ζ and IEPS in this study (see Fig. 2²) in comparison to reported values in literature are given in Table 1.

3. Electrochemical characterisation and discussion

The barrier properties of each oxide system were characterised by measuring their breakdown potential. The breakdown potential was determined by performing potentiodynamic polarization scans ($-1 \text{ V}_{\text{SCE}}$ to $+1.5 \text{ V}_{\text{SCE}}$ at 1 mV s^{-1}) simultaneously for each electrode in the 30-electrode circular array. Each coating combination was placed over at least 15 individual electrodes, enabling a rapid assessment of the variation in the coating performance.

Fig. 3 shows a sample of raw polarization data for oxide coatings over a small number of electrodes. The data shown as red is that of 6 replicate 100 nm MgO coatings on aluminium, demonstrating that breakdown potentials for MgO coatings were reproducible at $-0.72 \text{ V}_{\text{SCE}}$ for this particular experiment. The black data shows that the addition of a 100 nm SiO₂ coating, deposited over the top of the MgO coating significantly increased the breakdown potential. It is also noticeable in this instance that the spread in the breakdown potential is significantly increased upon the deposition of the additional coating. Reasons for the increase in the spread are presently unknown and will be examined in future works. The dotted line shows the average breakdown potential for the aluminium array in the absence of an additional oxide coating. In the case shown in Fig. 3 the addition of 100 nm MgO layer decreased the measured pitting potential, however, in Fig. 4 we demonstrate that the deposition of 100 nm layers of the various oxides

² Note that values of ζ are unusually high for silica given that 0.01 M NaNO₃ was used for this determination. Errors in the magnitude ζ however do not influence the position of IEPS and therefore the value of IEPS = 3.0 are thought to be accurate.

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