Reply to comments on ‘Electrochemical transients during the initial moments of anodic oxidation of aluminum’


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1. Introduction

We appreciate the opportunity to respond to the comments by D.D. Macdonald. Before proceeding, there are regrettably several unresolved typographical errors in the equations found in the published version of the paper. We take this occasion to point out some of the more important ones: in Eq. (8) (numbering as in original paper), the term $R_s$ should be $iR_c$; in Eq. (10), $i_a$ should be $i_{c0}$; in Table 1, $I_{a0}$, $I_{c0}$ and $I_{L0}$, should be $i_{a0}$, $i_{c0}$ and $i_{L0}$; in Eq. (11), the factor $F$ should appear in the numerator in the argument of each exponential function. In the following discussion, Macdonald’s objections are considered in turn. Equation numbers from his comment will be used, unless otherwise stated.

2. Nature of the reactions at the film–solution interface

The assumption of equilibrium at the Al–Al$_2$O$_3$ interface is in fact supported by our prior measurements of steady-state anodic currents [1], in which the potential at the metal–film interface was found to agree with the tabulated equilibrium potential (see Fig. 2 in Ref. [1]).

Macdonald maintains that the reactions at the film–solution interface in our model do not conserve the volume of the oxide film under steady-state conditions, and hence would lead to film destruction or growth, in violation of steady-state. His argument, based on the Point Defect Model (PDM), is that the lattice non-conservation reaction (3 in his Fig. 1) at the metal–film interface must be accompanied by another non-conservative reaction (7) at the film–solution interface. However, in the context of the PDM, the oxygen vacancies generated by reaction (3) could migrate through the film and then combine at the film–solution interface with metal ion vacancies formed by reaction (4), so as to annihilate lattice positions. In this way, it is not necessary to include reaction (7) at steady-state, since reaction (4) would be non-conservative. Additionally, it is noted that our film–solution interface reactions are supported by the detailed experimental study of Våland and Heusler [2], from which our kinetic expressions were obtained. In particular, metal ion dissolution and oxygen transfer are shown to be independent reactions, in agreement with the work of others on iron [3,4].

We can also demonstrate conservation of film thickness using a stoichiometric argument, which circumvents the PDM’s application of lattice defect concepts to amorphous oxide films. Consider steady-state dissolution, in which metal atoms ionize at the metal–film interface, metal ions dissolve at the film–solution interface, and both metal and oxygen ions migrate through the film. For aluminum oxide films, constant proportions of the ionic current in the film are carried by metal and oxygen ions, denoted by the cation and anion, transport numbers $t_+$ and $(1-t_+)$, respectively [5]. Thus, for every Al atom ionized at the metal–film interface, $(1-t_+)$ Al$^{3+}$ ions remain at the interface, the remainder being conducted outward through the film. Since 3/2 $(1-t_+)$ inwardly conducted O$^{2-}$ ions also arrive at the interface, a quantity 1/2 $(1-t_+)$ Al$_2$O$_3$ is formed there. Meanwhile, at the film–solution interface, an Al$^{3+}$ ion is ejected by dissolution, while at the same time, $t_+$ outwardly conducted Al$^{3+}$ ions arrive at the film surface, and 3/2 $(1-t_+)$ inwardly conducted O$^{2-}$ ions leave the interface. These processes result in the removal of 1/2 $(1-t_+)$ Al$_2$O$_3$, the same amount of oxide as that which is formed at the metal–film interface. For
anodic alumina films, $t_+$ has been found to be 0.4 [5]. Using this value, Fehlosi et al. showed that within experimental error, the volume of oxide formed at the metal–film interface is equal to that of metal ionized [6]. Thus, assuming that this transport number also applies to native films, both metal and oxide volumes (‘lattices’ in Macdonald’s terms) are conserved during steady-state dissolution. Since our paper indicates that electrochemical transients during growth of native films follow behavior expected for anodic films, we find no reason to doubt such an assumption.

Macdonald criticizes our calculation of the open circuit potential from the simulation results (Eq. (10) in our paper), since the cathodic reaction kinetics are not considered explicitly. We will explain this calculation in somewhat more detail than that in the paper, since, as mentioned above, $i_{0o}$ was erroneously written as $i_a$ in this equation. At the open circuit condition prior to a potential step, the film thickness is at the initial value $\delta_0$ which was determined by fitting the transient data. Also, since the film thickness remains constant with time at open circuit, reaction (2) is in equilibrium, and hence the overpotential for oxygen transfer $\eta$ is zero. At $\eta = 0$, the kinetic expressions at the film–solution interface (Eqs. (3–4) in our paper), dictate that the metal dissolution current density $i_{c} = i_{0c}$, and the oxygen transfer current density $i_{h} = 0$. By current continuity (Eq. (9) in our paper), the conduction current density in the film $i_s = i_{0o}$. These values of the film thickness and current density determine the potential drop $\phi$ in the film, and hence the open circuit potential. The cathodic kinetics do not enter explicitly in this calculation, but would influence the open circuit potential by determining the value of $\delta_0$. The purpose of calculating the open circuit potential in this way was to provide an independent check on the film thickness. From this point of view, the agreement in Table 2 in our paper is reasonable, except for the as received foil.

3. Diagnostic criteria

It may be helpful to briefly summarize the portion of our paper in which the diagnostic plot of Zhang [7] was considered. Zhang claimed that the diagnostic function $f(i) = \sqrt{|i|/i}$ would be a horizontal line on such a plot if the PDM was followed, but not so with their version of the HFM. Further, they show that $f(i)$ from experimental current transients does in fact produce a horizontal line. We agree with these claims, but dispute the significance which they attach to this result.

As Zhang points out, the HFM which they test is based on the early papers of Verwey and Mott [8,9], in which the potential drop at the film–solution interface (represented as the overpotential $\eta$ in our paper) is assumed to be constant. This assumption is not made in our simulation, where, following Vetter and Gorn and others [2–4], the kinetics of interfacial reactions (1) and (2) are explicitly included. As in these papers, the conduction rate law in our model is an exponential current–field relation, commonly referred to as the ‘high field conduction’ equation [10,11]. The conduction rate parameters were taken from experimental measurements on anodic alumina films [12], since we were testing the hypothesis that nm-thick native oxide films can be modeled as anodic films. In our view, it is not appropriate to compare the PDM with the Verwey–Mott model, since it differs from the PDM in two ways: its description of conduction and the absence of film–solution interfacial reactions. Hence, the failure of these models to represent $f(i)$ may be due to either factor. In fact, we showed in our paper that the Verwey–Mott model’s failure was due to its lack of interfacial reactions, and that the high-field conduction equation was valid.

Fig. 7 in our paper shows that $f(i)$ from our simulated current transients is a horizontal line, despite our use of the high field conduction law rather than the PDM. Thus, the horizontal diagnostic plot is not a unique property of the PDM, as suggested by Zhang [7]. The last two paragraphs of Section 4.3 in our paper explore the reasons why both our simulation and the PDM produce horizontal lines. Eq. (6) (Eq. (11) in our paper) speaks directly to this issue. In Macdonald’s comment, he separates $E_1 = E_0 \delta + \eta$ in Eq. (6) into two exponential terms, resulting in Eq. (7), which expresses $i_L$ in terms of two exponential functions of $\delta$. He then claims that this expression reveals a hidden dependence of $i_L$ on $\delta$, which was not evident in Eq. (6), and goes on to imply that this dependence undermines our model. We note, however, that all three exponential functions in Eq. (7) depend significantly on time. During the current decay, the decrease of the first function, exp($\pi_c^L FE_0 \delta/RT$), compensates nearly exactly for the increase of the second, exp($\pi_c^L FE_0 \delta/RT$). That this is so can be seen by referring back to Eq. (6), where $E_0 \delta + \eta$ was written as $E_1$. From Eq. (8) in our paper, it can be seen that $E_1 = E - E_{AL/Al_2O_3} - iR_s$, so that, in our potentiostatic experiment, the only time dependence of $E_1$ is associated with that of the ohmic drop. Since the ohmic drop is small compared to the other terms, $E_1$ is nearly constant. As a result, the time dependence of $i_L$ is confined to the third factor, exp($\pi_c^L FE_0 \delta/RT$), in which only $\delta$ varies significantly with time. Our intention in writing Eq. (6) in terms of $E_1$ was to make this point, since the dependence of the current density on $\delta$ controls the appearance of the diagnostic plot. Macdonald’s criticism is that there is a hidden dependence of $i_L$ on $\delta$ is incorrect.

Zhang shows correctly that the diagnostic plot is horizontal if the current density can be written in the
form \(i = a_1 \exp(-a_2 E_x \delta)\), where \(a_1\), \(a_2\), and \(E_x\) are constants, but \(\delta\) depends on time. Eq. (6) expresses our model in this form. At first glance, there appears to be a contradiction, since in addition to \(E_1\), \(a_1\) contains the variable \(\zeta\), and the field \(E_x\) also depends on time. However, as we pointed out in the paper, examination of the simulation results showed that the time variations of \(\zeta\), \(E_1\), and \(E_x\) were much smaller than that of \(\delta\). This is why the simulation behaves as if \(\zeta\), \(E_1\), and \(E_x\) were constant; the variations of these functions are small enough so that horizontal plots of \(f(i)\) can be produced. Contrary to Macdonald’s assertion, the (approximately) constant \(E_x\) is not an assumption, but a result of the simulation. We are merely pointing out that the two results, constant \(E_x\) and the horizontal line in our Fig. 7, are consistent with one another.

We next considered the reasons why \(E_x\) is approximately constant. This discussion, which is not repeated here, is found in the last paragraph of Section 4.3 in our paper. It is not mentioned in Macdonald’s comment. The most important reason is simply the very high sensitivity of the conduction current density to field, as dictated by the high field conduction rate law. According to experimentally determined conduction parameters for anodic alumina films [12], the field variation is only 5% per decade of current. Since the time variation of our experimental and simulated currents was less than a decade, \(E_x\) was effectively constant. Thus, in our simulation, the nearly constant field arises naturally because of the mathematical properties of the experimentally established high-field rate law. In contrast, \(E_x\) is assumed to be constant in the PDM, on the basis of its depiction of defects in the film [13].

In conclusion, we have effectively answered all of Macdonald’s objections. There is then no basis for questioning the conclusion of the paper, that the transient electrochemical behavior of nm-thick native alumina films is strongly similar to that of thicker anodic films. Concepts derived from studies of anodic alumina—high-field conduction, transient conduction behavior, and interfacial reactions—are apparently applicable to native films as well.

References