The Passive State in Our Reactive Metals-Based Civilization

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Abstract The history of the development of the Point Defect Model (PDM) for the growth of passive films that form on reactive metal and alloy surfaces when in contact with corrosive environments is presented. Three generations of the PDM have been developed, with each addressing issues that have arisen from experiment or theory. The present review updates four previous reviews with more recent information, particularly with respect to the application of the PDM in accounting for phenomena observed in the growth of passive films under controlled electrochemical conditions. These topics include the adaptation of PDM to account for the potentiodynamic polarization of passive metals; for describing the evolution of passive systems under open circuit conditions; in the use of Mott–Schottky analysis to ascertain the electronic character of a passive film and hence to identify the dominant point defect; development of the theory of potentiostatic transients; and a description of the structures of passive films. Finally, the application of the PDM in modeling practical corrosion problems, such as the disposal of high-level nuclear waste, over ultra-long exposure times (10^6 years). This latter application represents one of the greatest challenges ever posed to a sector of the scientific community.

Keywords Point Defect Model · Passive state · Passive film growth
1 Introduction

Passivity of metal and alloys [1–65] is well recognized as being one of the most important phenomena in all of the physical sciences because it allows mankind to enjoy a metals-based civilization based upon the reactive metals. It is, for this reason, that the phenomenon of passivity has been previously termed “the enabler of our metals-based civilization” [1]. Although many models have been developed to describe the passive state, since the original work of Schönbein [8] and Faraday [9] in the 1830s, one model that successfully accounts for all of the known properties of the passive state is the Point Defect Model (PDM), which was first described in the scientific literature in 1981 [31]). At that time, considerable work was underway in the author’s laboratory at Ohio State University on the pitting and stress corrosion cracking of austenitic alloys (Type 304 SS and Alloy 600) that are used in the coolant circuits of thermal (principally, nuclear) power plants. The first generation PDM (PDM-I) [31] was developed as an analytical model (i.e., a model that predicted dependent–independent variable relationships that could be tested analytically, such a $L(t)$, $L(V)$, $i(t)$, $i(V)$, where $L$ is the film thickness and $i$ is the passive current density) that might account for the experimental observations on passivity. Furthermore, we required a model that could be used to predict passivity-related phenomena outside of the current, experimental realm, particularly under aggressive reaction conditions that exist in thermal power plant coolant circuits and that could be tested experimentally.

The Generation I PDM (PDM-I) [31] successfully accounted for some important observations that had not been accounted for by the existing models, including the linear relationship between passive film thickness and voltage after a fixed polarization time and various laws for the kinetics of film growth (e.g., logarithmic and inverse logarithmic laws), which have been defined experimentally [31]. PDM-I also accounted for passivity breakdown in terms of the local condensation of cation vacancies at the metal/barrier layer (m/bl) interface at “weak spots” in the film (locations of high structural disorder, such as the points of intersection of the passive film and precipitates or inclusions). The condensate prevents the barrier layer from growing into the metal substrate, but, because the barrier layer continues to dissolve at the barrier layer/solution (bl/s) interface, local thinning occurs and the film eventually ruptures at that locale, marking a breakdown event. This original treatment of passivity breakdown persists to this day [1]. However, this aspect of the PDM is not reviewed here, but it has been discussed extensively elsewhere [1–3], to which the reader is referred.

Despite its early success, it is important to note that PDM-I exhibited two serious shortcomings that were also inherent in the High Field Models of Guntherschulze and Betz [20–22], Verwey [23], Cabrera and Mott [24], and Fehlner and Mott [25], and in the Place Exchange Model [27,67]; the models could not account for the existence of steady states in either the passive current density or the film thickness, and they failed to account satisfactorily for the development of multi-layer (specifically, bi-layer) passive films. Consequently, a Generation II PDM (PDM-II) [1–3] was developed to address these issues and to provide a more accurate account of the growth and properties of the barrier layer. PDM-II has since been extended to hydride barrier layers, such as those that form on lithium [43] and zirconium [54] in contact with aqueous solution, and is currently being extended to describe the formation of sulfide barrier layers, such as that (Cu$_2$S) which form on copper in sulfide-containing environments. Finally, PDM-II and its successor, PDM-III [3], have defined the conditions that must be present in order for passivity, which is a meta-stable state, to exist on a metal surface and has yielded a simple inequality that determines whether passivity is possible in any given system. A major achievement of PDMs-II and -III is their ability to describe the phenomenon of depassivation in analytical terms and to provide kinetic alternatives, in the form of kinetic stability diagrams (KSDs) [53] to the classical Pourbaix diagrams in describing the passive state.

Space does not permit giving a comprehensive account of all aspects of the development of the PDM here and only some of the more important topics that have been addressed recently will be reviewed. These include an outline of the history of the PDM; the use of Mott–Schottky analysis to determine the electronic type of a film and hence the dominant defect; passive film structure; potentiostatic transients; potentiodynamic polarization; evolution of the open circuit condition; and the prediction of corrosion damage over extremely long exposure times. Some repetition of material reviewed previously [1–6] is inevitable, to maintain consistent arguments, but it has been kept to a minimum. Important topics, such as the differentiation of film growth models, the interpretation of electrochemical impedance spectroscopic data, and depassivation have been included in previous reviews and are not presented here. Therefore, the present paper is best viewed as an update of the 1992 [2], 1999 [1], 2010 [3,4], 2011 [5], and 2012 [6] reviews of the PDM that have been extensively cited in the scientific literature.