

Theory of the Transpassive State

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At sufficiently high potentials, many passive metals enter the transpassive state in which the current/voltage characteristics of the system differ markedly from those for the passive state. For example, the current is often observed to depend exponentially on the applied voltage in a manner that is characteristic of active dissolution. At still higher potentials, oxygen evolution occurs, which in many instances masks the transpassive behavior and indeed is sometime mistaken for transpassive dissolution, because both exhibit Tafel behavior in their polarization characteristics. While the passive state has been explored extensively over a wide range of metals and alloys, relatively little attention has been paid to the properties of the transpassive state. Furthermore, few theoretical treatments of the transpassive state have been reported and those that have tend not to have been based on accepted mechanisms for the passive state. Indeed, the author is of the opinion that a single theory should be capable of accounting for both the passive and transpassive states in any given system, with the transition from one to the other being described in terms of inherent mechanistic phenomena (i.e., it should not be necessary to introduce additional processes in an *ad hoc* manner).

This paper presents an update of the theory for the transpassive state within the framework of the Point Defect Model (PDM) [1], which has been extensively developed to describe the passive state. It is shown that the transpassive state is readily accounted for in the PDM in terms of the oxidative ejection of cations (or oxyanions) from the barrier layer and the oxidative dissolution of the film, resulting in one or both of two fundamental processes: (i) Film thinning, provided that the change in oxidation state is sufficiently large (oxidative dissolution of the barrier layer), and (ii) condensation of cation vacancies at the metal/barrier layer interface over macroscopic areas (oxidative cation ejection).

The theory, in its current state of development, is able to account for the two principal transpassive phenomena that are observed over a wide range of systems; transpassive dissolution (TPD) and electropolishing (EP). TPD is most readily accounted for by the physical destruction of the barrier layer due to potential dependence of the film dissolution reaction at potentials above a critical value, while EP is described in terms of macroscopic condensation of cation vacancies at the metal/barrier layer interface resulting in the physical detachment of the barrier layer from the substrate. Thus, TPD arises as a natural extension of the film dissolution reaction contained within the PDM and EP is simply an extension of the passivity breakdown mechanism contained within the PDM, except that cation vacancy generation occurs via the oxidative ejection of cations from the barrier layer rather than from the absorption of an aggressive anion into an oxygen vacancy at the barrier layer/solution interface. In any event, both TPD and EP arise from the same fundamental process at the barrier

layer/solution interface; the change in oxidation state of the metal species as it passes from the barrier layer to the solution.

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1. D. D. Macdonald, *Pure Appl. Chem.*, **71**, 951 (1999).