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The Effect of Bromide Ions on the Stability of Tantalum Oxide Films †

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Abstract: Among different valve metals, Ta is known to be the most corrosion-resistant metal. This is due to an oxide passivating layer (amorphous Ta_2O_5) forming rapidly on the Ta surface. Tantalum oxide provides excellent stability of the underlying Ta in both the air and a variety of aqueous corrosive media. The passive films of Ta with band-gap energy equal to ~4.3 eV is an n-type semiconductor, and oxygen vacancies were considered to be the prevalent defects. The presence of oxygen vacancies is the basis of a model, the point defect model (PDM) that was developed to describe analytically the physico-electrochemical processes underlying the anodic growth of oxide. The lattice point defects significantly affect the kinetics and mechanism of electrochemical reactions that either enhance the passive state or, under certain conditions, destabilize it. The destabilization of the passive state and its breakdown at a critical potential, $E_{b,}$ was observed in the presence of Br^- albeit the fact that bromides are not the most aggressive halide ions. The mechanism by which bromides act on the passive state of valve metals is not yet well-understood. This study aims to examine the electrochemical behavior of Ta in different concentrations of bromides, where the oxide breakdown occurs locally due to pitting corrosion. Linear and cyclic voltammetry were used for this purpose. It was observed that for 0.25 M KBr the passive state was stable up to 12 V. As the concentration of KBr was increased, current fluctuations appear at E>7 V that sustain even beyond the $E_{b,}$ which was determined at the potential where a sudden increase of the fluctuating current is observed. The E_b shifts toward lower values upon increasing the bromide concentration, in agreement with the predictions of the PDM.

Keywords: tantalum passivity breakdown; bromide-induced pitting corrosion; Point Defect Model

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Conflicts of Interest

The authors declare no conflict of interest.