Accepted Manuscript

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PII: S0013-4686(18)30789-8

DOI: 10.1016/j.electacta.2018.04.057

Reference: EA 31624

To appear in: *Electrochimica Acta*

Received Date: 6 February 2018

Revised Date: 4 April 2018

Accepted Date: 7 April 2018

Please cite this article as: I. Betova, M. Bojinov, C. Lilja, Hydrogen generation during interaction of oxide covered copper with deoxygenated aqueous solution, *Electrochimica Acta* (2018), doi: 10.1016/j.electacta.2018.04.057.

Hydrogen generation during interaction of oxide covered copper with deoxygenated aqueous solution

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Abstract - Copper is considered to react to a very limited extent with oxygen-free water but detection of hydrogen in amounts beyond those predicted by thermodynamic calculations has been reported. It is thus of importance to explore the influence of different factors on the behavior of copper in deoxygenated aqueous solutions. In the present work, we focus on the role of the surface film and associated cuprous species. Electrochemical impedance measurements, in-situ detection of free soluble cupric ion and dissolved hydrogen are employed. The obtained results quantitatively described by a kinetic model, its main feature being the formation of a CuOH intermediate at the cuprous oxide film / electrolyte interface both by oxidation of Cu and reduction of free soluble Cu^{2+}. This intermediate is assumed to play a pivotal role in a sequential surface reaction generating hydrogen gas by reduction of water. The models are successfully parameterized using regression of the model equations to in-situ experimental data, and conclusions on the effect of oxide films are reached based on the evolution of kinetic parameters with time and temperature.

Keywords: copper, hydrogen generation, oxygen-free solution, kinetic model, surface oxide

1 Introduction

According to thermodynamic data for the known solid and aqueous oxidation products in the pure copper-water system, the equilibrium hydrogen partial pressure is of the order of 10^{-4} Pa at room temperature [1,2], i.e. the reaction of copper with water has very low yield. This property of copper is important when predicting the long-term corrosion behavior of copper canisters planned to be used for final disposal of highly radioactive spent nuclear fuel in several countries [3].

On the other hand, experimental studies of copper in pure deoxygenated water have reported the formation of hydrogen gas leading to partial pressures far above the expected equilibrium pressure [4-6], although the results have been debated [7-9]. The hydrogen gas observed in those experiments could to some extent be produced by reactions at the copper / water

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