

Corrosion of Copper in De-Aerated Water by Impedance Spectroscopy

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Impedance spectroscopy is being used to study possible mechanisms for the observed corrosion of nanostructured copper wicks intended for use in heat pipes that provide advanced cooling for high-performance electronics. The heat transfer fluid is de-ionized and de-aerated water.

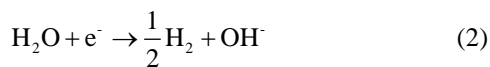
Experiments were performed in 17.6 MOhm cm water de-aerated by N₂ until the oxygen concentration of the gas leaving the cell was measured to be < 2ppb by a Hach Orbisphere 3650 analyzer. Copper working electrodes were polished and degreased prior to experimentation. Impedance data were obtained potentiostatically using a Gamry Ref 3000 at perturbation amplitude of 10mV.

The open-circuit impedance responses of 0.025 cm diameter gold, platinum and copper electrodes are presented in Figure 1. The high-frequency loop can be attributed to the dielectric response of water. All impedance data were scaled with respect to the ohmic resistance R_e. This result shows that, while gold and platinum show blocking behavior, the slight curvature of the low-frequency data for the copper electrode indicates the presence of electrochemical reactions. A model for the impedance response should include the parallel contributions of anodic and cathodic reactions.

In the absence of oxygen, the reactions may include dissolution of copper



and water reduction at the cathode,



As the concentration of corrosion product increases, the cathodic reaction



becomes important. Thus, the impedance model needs to account for reactions (1), (2), and (3).

A simulation was performed using kinetic expressions for reactions (1), (2), and (3).¹ The equations solved included an expression of the open-circuit condition

$$i_{a,\text{Cu}} + i_{c,\text{Cu}} + i_{c,\text{H}_2} = 0 \quad (4)$$

the anodic current density

$$i_{a,\text{Cu}} = i_{0,\text{Cu}} e^{b_{a,\text{Cu}}(V - V_{0,\text{Cu}})} \quad (5)$$

where V_{0,Cu} is the equilibrium potential for the copper reaction, the corresponding cathodic current density

$$i_{c,\text{Cu}} = - \left(\frac{c_{\text{Cu}^{2+}}(0)}{c_{\text{Cu}^{2+}}(\infty)} \right) i_{0,\text{Cu}} e^{-b_{c,\text{Cu}}(V - V_{0,\text{Cu}})} \quad (6)$$

where the concentration term accounts for the concentration of cupric ion at the electrode surface, and

$$i_{c,\text{H}_2} = -i_{0,\text{Cu}} e^{-b_{c,\text{H}_2}(V - V_{0,\text{H}_2})} \quad (7)$$

where V_{0,H₂} is the equilibrium potential for the hydrogen evolution reaction. Kinetic parameters were taken from the literature.²

The concentration of copper at the electrode surface was assumed to be controlled by spherical diffusion from the small electrode,³ i.e.,

$$(i_{a,\text{Cu}} + i_{c,\text{Cu}}) = \frac{4nFD_{\text{Cu}^{2+}}r_0}{A} (c_{\text{Cu}^{2+}}(0) - c_{\text{Cu}^{2+}}(\infty)) \quad (8)$$

Under the assumption that c_{Cu²⁺}(∞) = 0, the corrosion current was calculated to be 1.6 nm/day. While this corrosion rate is too small to have a practical consequence in usual applications, it is large enough to influence the structural integrity of nano-scaled structures.

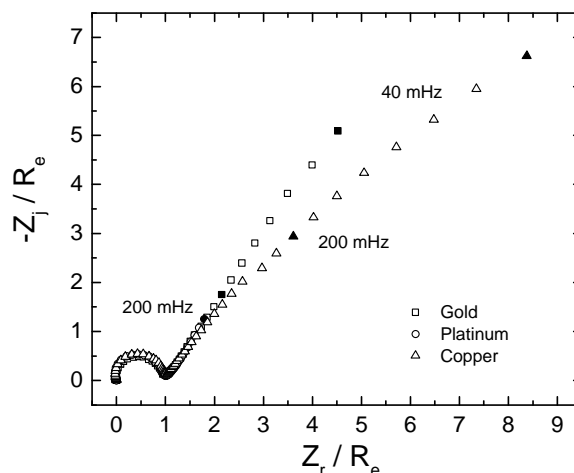


Figure 1. Impedance response of gold, platinum, and copper for the frequency range 100 kHz to 40 mHz.

Acknowledgement

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References

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