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Impedance analysis of copper alloys at the corrosion potential in seawater

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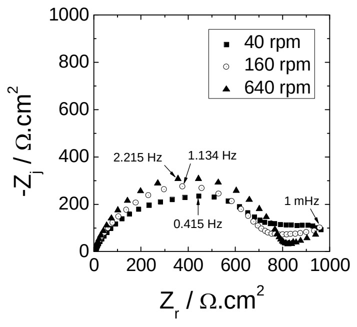
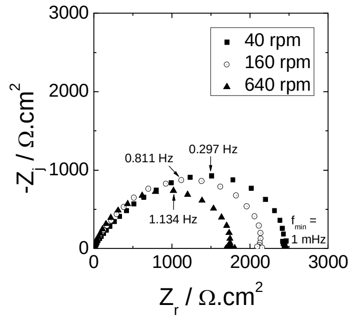
Power plants require cooling circuits with water as the cooling agent; therefore, they are generally located on seacoasts owing to the ready availability of abundant seawater. Copper alloys are commonly used in condensers and heat exchangers due to their high thermal conductivity, good resistance to corrosion and good mechanical workability. It is well known that corrosion of copper and copper alloys depends on mass transport [1]. In this work, mass transport is controlled by means of rotating ring electrodes (RRE) designed from condenser pipes.

The objective of this work was to study the electrochemical behavior of two copper alloys, 70Cu-30Ni (wt. %) alloy and aluminum brass (76% Cu, 22% Zn and 2% Al), immersed in aerated artificial seawater (ASW, pH 8) or filtered natural seawater (FNSW, pH 8), and in particular to analyze the electrochemical impedance (EIS) data obtained at the corrosion potential (E_{corr}) at short immersion time (1 h).

Examples of impedance diagrams obtained with the two copper alloys in FNSW are given in Figures 1(a) and (b).



(a)



(b)

Figure 1: EIS Nyquist diagrams of (a) 70Cu-30Ni and (b) Al brass, plotted at E_{corr} after 1 h of immersion in aerated FNSW, for 3 rotation speeds of the RRE.

Whatever the system, the impedance diagrams can be modeled by the general equivalent electrical circuit illustrated in Figure 2, where R_e is the electrolyte resistance, CPE_{dl} a constant phase element related to the double layer, R_t^a the anodic charge transfer resistance, $Z_{\theta,D}^a$ an impedance that illustrates anodic mass transport and partial blocking effect by CuCl, R_t^c the cathodic charge transfer resistance, and Z_D^c a cathodic impedance that illustrates O_2 mass transport.

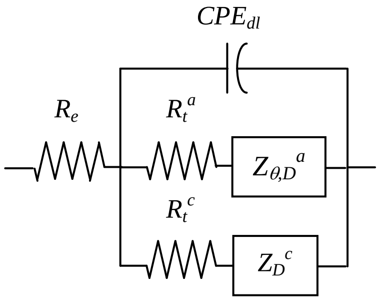


Figure 2: Impedance model.

Depending on the electrochemical system, this general model takes different simplified forms.
In the case of 70Cu-30Ni alloy (Fig. 1(a)), R_t^c can be neglected, and Z_D^c is reduced to a Warburg impedance (W_c). The obtained CPE parameters (α, Q) are similar for the three rotation speeds. The effective capacitance values, calculated by application of Brug formula (surface time constant distribution) [2,3], are around 40 μF.cm^{-2}. Such values are typical of those for a double layer capacitance, which validates the equivalent circuit proposed in Figure 2. Thus, the HF loop of the experimental impedance diagrams illustrates mainly the anodic charge transfer (diameter equal to R_t^a), and its depressed shape is partly due to the CPE and partly due to the cathodic Warburg impedance in parallel; whereas, the LF loop is related to the anodic mass transport and partial blocking effect by CuCl.
In the case of Al brass (Fig. 1(b)), the cathodic branch (R_t^c in series with Z_D^c) can be neglected, and $Z_{\theta,D}^a$ can be approximated by a R//C circuit. Therefore, the single experimental loop illustrates both the anodic charge transfer and the anodic mass transport + partial blocking effect by CuCl.

In conclusion, a single general model was found to analyze impedance data obtained with different copper alloys in different seawater environments. From this model, it was shown that the depressed shape of a loop did not necessarily arise from a CPE behavior.

References

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