Corrosion of Copper in Ammoniacal Solution Containing Cu^{2+} Ions

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Corrosion of copper in solutions containing ammonia and Cu^{2+} ions is a process extensively used in industry. It plays an important role in manufacturing of printed circuit boards, cleaning of copper surfaces and in production of many copper compounds.

In spite of its importance for the industry, the amount of published data dealing with this system is very limited. Although both the thermodynamic[1] and kinetic[2,3] aspects have been dealt with, the investigations have been limited to quite specific conditions or to narrow concentration ranges.

The present work broadens the previous research whereupon some new phenomena are observed. The starting point is a Pourbaix diagram constructed from the available thermodynamic data. Furthermore, we assume that the net corrosion reaction is a sum of the following reactions:

$$\mathrm{Cu(NH_3)_2}^{+} + e^{-} \rightarrow \mathrm{Cu} + 2\mathrm{NH_3} \qquad (1a)$$

and

$$\mathrm{Cu(NH_3)_4}^{2+} + e^{-} \rightarrow \mathrm{Cu(NH_3)_2}^{+} + 2\mathrm{NH_3} \qquad (1b)$$

The validity of the assumption is successfully verified by electrochemical kinetics measurements (Tafel plots, cyclic voltamograms and impedance spectroscopy) as a function of pH, and concentration of ammonia and Cu^{2+}.

Based on these results we propose a mechanism of the corrosion reaction/passivation in a wide concentration range.

A typical example of the present investigation is the effect of pH on impedance spectra in the frequency range corresponding to the electrochemical reaction (Fig 1). We can see that the size of the arc corresponding to the electrochemical reaction is decreasing with increasing pH value. At pH higher than 12, however, the interfacial impedance increases significantly (Fig 2). We show that this is due to changed electrode reaction. The new reaction is the formation of copper (I) oxide:

$$2\mathrm{Cu(NH_3)_4}^{2+} + \mathrm{H_2O} + 2e^{-} \rightarrow \mathrm{Cu_2O} + 8\mathrm{NH_3} + 2\mathrm{H}^{+} \qquad (2a)$$

$$\mathrm{Cu_2O} + 2\mathrm{H}^{+} + 2e^{-} \rightarrow 2\mathrm{Cu} + \mathrm{H_2O} \qquad (2b)$$

which is in agreement with the proposed Pourbaix diagram.

Formation of copper (I) oxide on the electrode surface leads to a partial passivation, as confirmed by large inrease in electrode impedance (Fig. 2). Additionally, the presence of copper (I) oxide has been confirmed by ex-situ observation under scanning electron microscopy and EDS measurements.

Acknowledgements

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References

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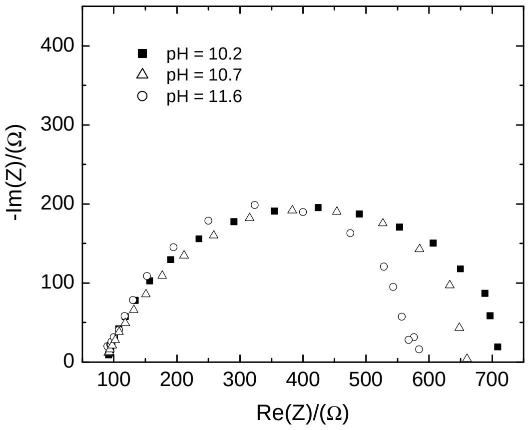

Figure 1. Dependence of electrochemical reaction impedance spectra on pH of ammoniacal solution. The arcs correspond to reactions (1a) and (1b).

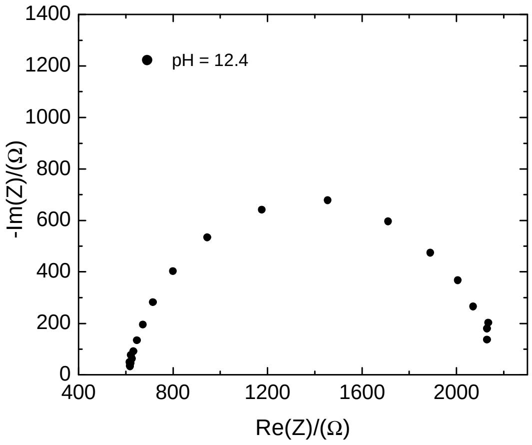

Figure 2. A typical interfacial arc at pH>12 which corresponds to reactions (2a) and (2b).