Study on the corrosion behaviour of metallic copper in aqueous solutions of HNO₃ and HCl and the corrosion inhibiting effects of N and S

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Introduction
Copper metal is used in microelectronics and often embedded into a polymer which may not be entirely free of water. Application of bias can lead to corrosion reactions and local changes in the pH value and can ultimately lead to failure of the device. The effect of anions, e.g. Cl⁻, NO₃⁻, which may be present from former production steps, are investigated.

Influence of c_NaCl and Temperature
Measurements in 0.1 M, 0.2 M, 0.5 M, 1.0 M and 1.5 M aqueous NaCl solution were performed at varying temperature up to 60 °C.

With linear polarization resistance (LPR) the resistance was determined and plotted versus temperature and concentration of NaCl. It can be seen that the influence of temperature is less than the influence of increasing NaCl concentration.

![Fig. 2: Influence of temperature and of concentration of NaCl on the resistance.](image)

Effects of the Inhibitor Cysteine
The addition of the inhibitor cysteine leads to a clearly visible shift of the corrosion potential in cathodic direction.

The corrosion current drops by around a factor of 10.

The ΔG_ads calculated is -31.9 kJ/mol.

With increasing temperature the corrosion potential shifts to more cathodic values and the corrosion potential increases.

The E_ads calculated is 56 kJ/mol.

Experimental Setup
For the measurements, a three electrode setup was used:
CE: Pt
RE: Ag/AgCl sat. KCl
WE: Cu

The working electrode was made of an embedded copper wire with a diameter of 2 mm.

![Fig. 1 Cell setup](image)

Influence of pH-Value and Cl⁻/NO₃⁻
Copper was inserted in 0.1 M HCl, 0.2 M HCl and 0.1 M HNO₃ respectively and measurements were performed after a waiting time of 1 hour.

With higher chloride concentration the corrosion potential shifts to more anodic values.

Copper shows a more anodic corrosion potential in HNO₃ than in HCl of the same concentration.

Optical inspection of the surface reveals the difference in surface appearance after immersion in a blank (dist. H₂O), HCl and HNO₃ solution.

![Fig. 7 Copper sample after immersion in distilled water (left), 0.1 M HCl (middle) and 0.1 M HNO₃ (right).](image)

![Fig. 6: 0.1 M HCl, 0.2 M HCl and 0.1 M HNO₃ in comparison](image)

![Fig. 3: Influence of different concentrations of Cysteine in 0.1 M NaCl solution at 26 °C.](image)

![Fig. 4: Influence of different temperature in 0.1 M NaCl solution with 20 mmol Cysteine.](image)

![Fig. 5: Linear fits for calculation of ΔG_ads (left) and Ea (right).](image)

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