Study of the cathodic processes during the nickel electrowinning from ammonia-ammonium chloride solutions

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The Ezinex® process has been commercialized in Italy for the electrowinning of zinc from zinc ammonia chloride solutions. In this process, zinc is electrodeposited at the cathode and ammonia is oxidized at the anode. Titanium cathodes are used for zinc plating and graphite electrodes are used for anodic oxidation of ammonia. The electro-deposition of nickel from ammonium chloride solutions may offer alternatives to diminish the hydrogen reduction on acid sulfate or acid chloride electrowinning. The nickel deposition at the cathode can be expressed by the reaction:

$$\text{Ni(NH}_3)_4\text{Cl}_2 + 2e^- \rightarrow \text{Ni}^{0} + 2\text{NH}_4^+ + 2\text{Cl}^-$$  \hspace{1cm} (1)

In this paper a fundamental electrochemistry study of cathode processes during the electrowinning of nickel from ammonia-ammonium chloride solutions is presented.

Several solution compositions were used in this study. The base composition was 0.2 M NiCl\(_2\), 4 M NH\(_4\)Cl, with variable amount of NH\(_3\) (added as NH\(_2\)OH). An analysis of the effect of cathode substrate was carried out by cyclic voltammetry, this analysis showed that when a titanium electrode was used better deposit properties and electrochemical behavior was obtained than when platinum and glassy carbon were used. The effect of the ammonium chloride on the electrochemical behavior of nickel from chloride medium was studied (Figure 1). From this analysis was observed that electrodeposition of nickel from ammonium chloride solution exhibits important advantages over the electrodeposition process from simple chloride solutions. The more relevant feature was the non formation of the nickel oxide/hydroxide formed in the chloride media\(^2,3\) (peak A). This fact is mainly due to the formation of nickel complexes and the stabilization of the protons by ammonia. This would be expected to lead to high current efficiency in the nickel electrowinning from ammonium chloride solutions.

The effect of the ammonia concentration and system temperature was determined by voltammetry and chronopotentiometry techniques. This study showed the occurrence of two processes during the electro-reduction process. These processes were considered to be the nickel reduction and the hydrogen evolution.

Finally a study of current density and current efficiency was done at different temperatures and potentials in order to analyze the phenomena involved in the electrowinning process of nickel (Figure 2). From this data we observed that the current density obtained increases as the temperature increases. It was also observed that the current density obtained for each temperature depends on the applied potential, but this does not follow a particular trend (Fig. 2). Hence, for 30 and 50 °C the minimum current density was obtained at -0.9V, while for at 70 °C the maximum current was obtained at this same potential. These results confirm that at least two processes are involved in the electrowinning of nickel, and that the dominant process depends on the applied potential.

![Fig 1. Cyclic voltammetry of 0.2 M NiCl\(_2\) and 0.2 M NiCl\(_2\) - 4M NH\(_4\)OH using Titanium electrode. v = 20 mV/sec.](image)

The data obtained for the C.E. study made clearer the two processes involved in the electrowinning of nickel. At -0.9V the C.E. decreases as the temperature increases and at -1.0V the C.E. increases as the temperature increases. Therefore, the process occurring favorably at -0.9V, which provokes a decrease in the current efficiency with the temperature increment, could be the hydrogen evolution. The nickel electro-deposition is favored at ~1.0 V and increases as the temperature increases, which gives high current efficiencies.

![Fig 2. Effect of the temperature and the applied potential in the current efficiency of the nickel electrowinning. Solution: 0.4 M NiCl\(_2\) and 0.8 M NH\(_3\) in ammonium chloride.](image)

The high current efficiencies obtained from nickel electrowinning from ammonia-ammonium chloride solutions are a good sign of the feasibility of the utilization of a technology similar to the Ezinex® to the recovery of nickel from alternative source.

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