THE MECHANISM OF THE ELECTRODEPOSITION OF NICKEL FROM SULFATE SOLUTIONS

A. T. Vagramyan and L. A. Uvarov

Institute of Physical Chemistry, Academy of Sciences, USSR
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The experimentally measured overvoltage for separation of a metal is a composite quantity, being additively composed of ohmic (η_{ohm}), concentration (η_{conc}), activation (η_{act}), crystallization (η_{crys}), and passivation (η_{pass}) components:

$$\eta = \eta_{ohm} + \eta_{conc} + \eta_{act} + \eta_{crys} + \eta_{pass}.$$

The ohmic overvoltage is dependent on the conductivity of the electrolyte and is also proportional to the electrode dimensions; it can be neglected in the case of point electrodes. The polarization of Ni is independent of the rate at which the polarization curve is developed, the indication being that the concentration overvoltage is negligible at room temperature. The activation overvoltage is determined by the charge and degree of hydration of the ions and should, therefore, be of the same order of magnitude for the metals of the iron group and for Cu, Zn, and Pb. Thus, the activation overvoltage cannot be responsible for the fact that the deposition overvoltage is much higher for Ni than for the metals just mentioned. The crystallization overvoltage can be split down into three components [1]. The first of these can be looked upon as arising from the impedance to the formation of new nuclei. There is, however, little likelihood of forming new nuclei during deposition of a metal on an electrode which has many active surface sectors [2]. The second component is the ohmic overvoltage which arises from distortion of the electric field in the neighborhood of the expanding sectors and is inversely proportional to the number of such sectors. The third component of the crystallization overvoltage arises from delayed diffusion to the active sectors of the crystal with accumulation of adsorbed atoms on the electrode surface. The number of crystallographically active centers depends on the melting point [3], and should be essentially the same for nickel and for silver in which the over-all value of the overvoltage is quite low. Thus, the crystallization components of the overvoltage can be neglected here.

The passivation overvoltage arises from the impedance in ionic discharge caused by adsorption of foreign particles on the electrode surface. The following passivation mechanisms are possible here:

1. The passivation overvoltage is related to the work of penetration of metal ions through the film of adsorbed foreign particles when this film is compact.

2. Foreign particles adsorbed on the active sectors must be displaced before atoms can penetrate into the crystal lattice.

3. The passage of metal atoms into the crystal lattice is impeded by lattice deformations arising from the irreversible adsorption and occlusion of foreign particles.

Study of the equilibrium potential of the nickel electrode has shown [4] that the passivation effects play a major role at low temperatures, but become much less significant at temperatures of the order of 180-250°. This has made it possible to determine the equilibrium potential and the temperature coefficient of potential for the nickel electrode from which the reversible potentials of nickel have been calculated for a wide range of temperatures. It is clear that any passivation effect which exerts an influence on the electrode potential must also affect the electrodeposition of an iron group metal. The present work is a study of the mechanism of the electrodeposition of nickel in which account is taken of the passivation factor. The experimental technique has been described in an earlier paper [4].

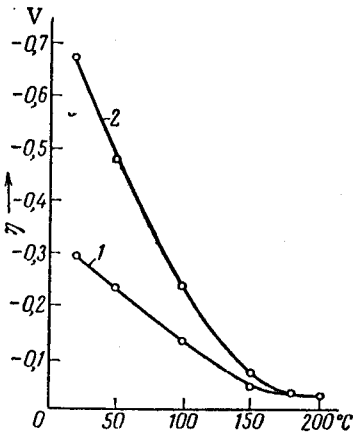

Fig. 1. Relation between the temperature and the polarization of the nickel electrode in a 1 N $NiSO_4$ solution at pH 1.5, i_k = 20 mA/cm^2. 1) Relative to equilibrium potentials; 2) relative to stationary potentials.

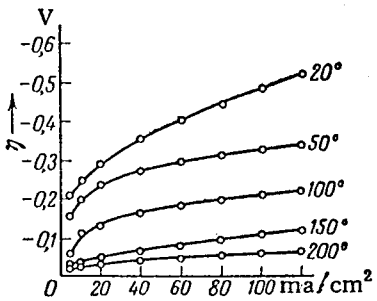

Fig. 2. Relation between the overvoltage for the deposition of nickel and the current density at various temperatures.

The overvoltage is generally determined as the difference between the potential of the polarized electrode and the potential of the same electrode measured with zero current flow. Overvoltages obtained in this manner do not, however, exactly characterize the degree of irreversibility of the electrode-position of the metals of the iron group, since these are readily passivated and their stationary potentials and equilibrium potentials are not identical. It is seen from Fig. 1 that the low-temperature overvoltage of nickel relative to the stationary potential (η_{sta}) is considerably higher than the true overvoltage relative to the equilibrium potential (η_{eq}). The difference between η_{sta} and η_{eq} diminishes as the temperature is increased, the two being identical above 180° where the electrode is reversible. Figure 1 shows that the curve covering the relation of the overvoltage to the temperature (curve 1) is composed of characteristic sections. The overvoltage alters sharply with temperature below 150° and is practically independent of the temperature above this point. The temperature coefficient of the overvoltage is approximately 2 mV/degree in the interval from 20 to 120°, and is equal to zero above 150°.

Figure 2 shows the relation between the overvoltage for the separation of nickel and the current density at various temperatures. There are two sections in each of the low-temperature curves. Over the first section the polarization rises sharply with increasing current density and the principal process is the evolution of hydrogen. Over the second section, the polarization alters only insignificantly with the current density and 60-80% of the current expended is used in separation of the metal. It should be noted that current yield of metal increases with rising temperature and becomes equal to 100% above 150°. An increase in the temperature reduces both the absolute value of the overvoltage and the slope of the polarization curve. In the interval of current densities corresponding to simultaneous separation of both metal and hydrogen, the polarization curve is semilogarithmic at low temperatures, but not at high. Studies carried out by the rapid method show the high-temperature polarization of the nickel electrode to be dependent on the rate at which the polarization curve is developed. The slope of a rapidly developed polarization curve is greater than that of a slowly developed curve. The polarization of the nickel electrode is practically independent of the current density when the polarization curve is developed quite slowly. The explanation of this effect has been found in a study of the structures of electrolytic nickel deposits.

It is a well-known fact that nickel deposits obtained under ordinary conditions are finely crystalline and quite uniform. Studies of high-temperature electrolytic nickel deposits have shown that metal deposition occurs on certain individual sectors rather than over the entire surface of the electrode. Such structure in the deposit causes the current density to be much greater than the apparent density calculated from the geometric surface area of the electrode. Thus, the observed overvoltage corresponds to a considerably higher current density than that indicated in Fig. 2. As a result, the actual reduction of the overvoltage in passing from low temperature to high is much greater than the observed. The weak dependence of the polarization on the current density is explained by the fact that the number of growing sectors increases as the current density rises, with the result that the true current density remains practically unaltered. Thus, at high temperatures, there is an "adaptation" of the expanding surface of the nickel deposit to the polarization current, just as in the case of metal deposition at low overvoltage. When the polarization curve is developed rapidly, the surface fails to increase, self-adjustment does not take place, and the true current density on the growing sectors is greater than it is when the curve is developed slowly. Thus, a higher value of the overvoltage is also obtained here.

For metals with low overvoltage and self-adjustment, the true current density has been shown to be

determined by the ratio of the rates of passivation and material feed to the growing sectors. It can be assumed that the rate of high-temperature deposition of nickel is also determined by the rate of material feed to the electrode. Actually, it is observed that there is a zone of diffusional impoverishment in the neighborhood of the growing sectors on the high-temperature nickel electrode, new crystals forming at considerable distances from these sectors when the current density is increased in the circuit. Preliminary estimates of the concentration polarization have been made on the basis of experimentally determined values of the depth of the diffusion layer; these have shown the concentration polarization for electrodeposition of nickel at 180° under a current density of 10 mA/cm^2 to be about 15 mV.

The marked alteration in the structure of the electrolytic nickel deposit on passing from high temperatures to room temperature (i.e., on passing from nonuniform crystalline deposits to deposits which are compact and finely crystalline), can be considered to result from an increase in the rate of passivation of the surface. This alteration in structure is analogous to that which is observed on introducing a surface-active substance to obtain a uniform electroplate. The high rate of passivation is the principal cause of the high overvoltage which is observed in the electrodeposition of nickel at low temperatures. This is due to the fact that occlusion of foreign particles in the electrolytic nickel deposit and irreversible hydrogen adsorption [5,6] both increase as the temperature falls.

These facts indicate that the passivation of the surface of the nickel electrode in the course of the electrolysis is one of the principal factors determining the rate of deposition of the metal and suggest that there is no essential difference in the deposition mechanisms at high and low overvoltages.

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