SHORT COMMUNICATION

A STUDY OF THE MECHANISM OF THE ELECTROLESS DEPOSITION OF NICKEL*

F. M. DONAHUE and C. U. YU

Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

THE rate-controlling step for the electroless deposition of nickel is not completely understood. The rate law for the process shows a first-order dependence on the hypophosphite-ion concentration (at constant pH)[1,2] and a negative order with respect hydrogen-ion concentration with variable pH.[3] Catalytic mechanisms,[2] thermodynamic arguments (*viz* common ion effects),[3] and slow transport of hydrogen ions[3,4] have been offered to explain the observed results. The experiments reported here are intended to clarify the controlling step in the electroless deposition of nickel and to offer a different approach to the study of electroless plating processes in general.

The basic premise of this study is that electroless plating processes are mixed electrode systems[5-7] wherein the anodic partial process is the oxidation of hypophosphite and the cathodic partial processes are hydrogen evolution and nickel deposition. Thus, at low pH ($\leqslant 4$,)the hydrogen-evolution reaction would proceed at a rate comparable to that of nickel deposition, leading to low measured plating rates; while at high pH ($4 < pH < 6$), the rate of hydrogen evolution would be small compared to nickel deposition, leading to larger measured plating rates. In order to test the hypothesis of the applicability of the mixed potential theory to electroless plating, it was necessary to measure simultaneously the rate of nickel plating and the electrode potential of the sample being plated.

Nickel foil or wire samples were used as one arm of a Wheatstone bridge in order to detect changes in resistance of the foil during the plating operation. A second nickel sample used in the Wheatstone bridge circuit was coated with epoxy and immersed in the plating bath in order to obviate temperature corrections for the plated sample. The experimental sample was cleaned in distilled water, cathodically treated in 6 N HCl, rinsed in water, given a nickel strike, and immersed in the plating bath.

The plating bath contained 0·5 M sodium acetate, 0·5 M acetic acid, and variable amounts of sodium hypophosphite (0·05 to 1·0 M) and nickel chloride (0·05 to 1·0 M). The bath was stirred by a Teflon paddle and thermostated at 90°C. In order to minimize pH changes, the ratio of solution volume to surface area was large and no experiment lasted longer than 4 h.

The change in thickness of the sample was calculated from the measured resistance change†, and the plate thickened linearly with time for all experiments.

---

† Although the plate contained phosphorus, it was assumed that the plate was pure nickel for the calculations. That the rate law derived from these experiments agrees with that observed by others (see below) indicates that this assumption does not seriously affect the results.
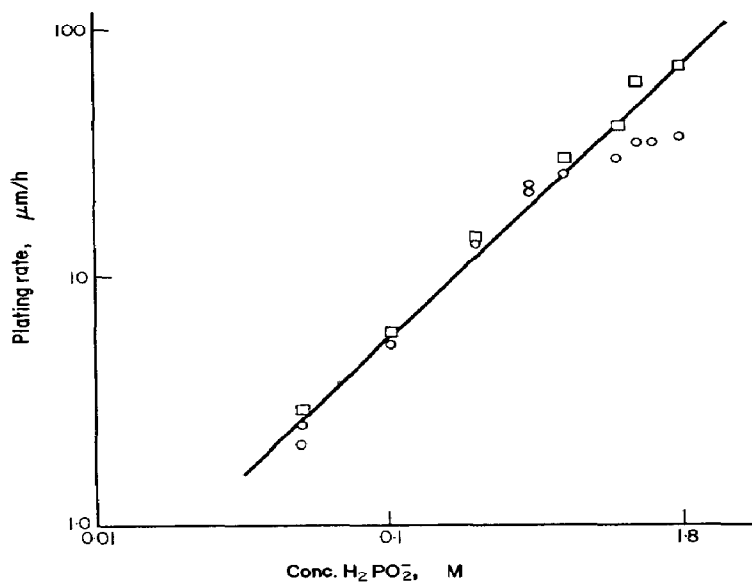
FIG. 1. Determination of reaction order with respect to hypophosphite ion.
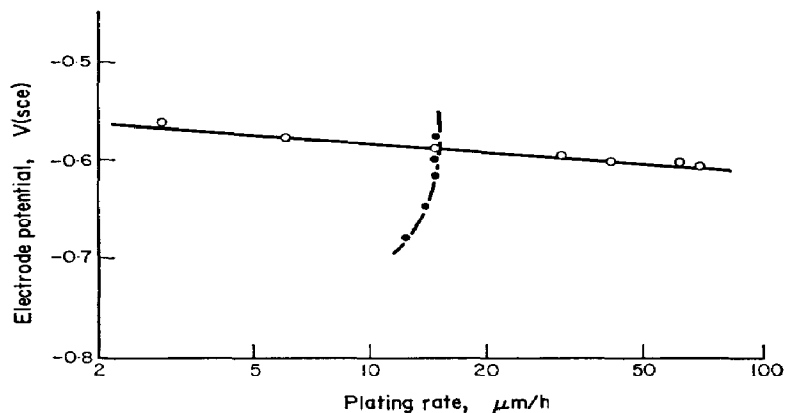○, concentration of nickel ion, 0·1 M; □, 0·8 M.

FIG. 2. "Polarization" curve for electroless nickel plating.
Open circles, variation of hypophosphite-ion concentration; filled circles, variation of
nickel-ion concentration.

Potential measurements were made with respect to a sce in the same solution, with
a Keithley Model 621 Electrometer.

Figure 1 shows the experiments used to determine the reaction order with respect
to hypophosphite ion. The slope of the line, 1·1, verifies the previously observed
first-order dependence. Similar experiments to determine the reaction order with re-
spect to nickel ion demonstrated a zero-order dependence. Consequently, the rate
law obtained in the present work agrees with that given previously.[1,2]

The experiments which differ from the usual approach to electroless plating were
those wherein the concentration of one species was held constant while the other was
varied (as in the reaction-order experiments above) and in which the electrode potential
was measured as well as the plating rate. The open circles in Fig. 2 are those obtained

at constant nickel-ion concentration, 0·8 M, with variable hypophosphite-ion concentration. The points traverse a Tafel line for the deposition of nickel. The Tafel slope (*ca* 30 mV) suggests that the deposition of nickel proceeds by way of a complex ion. The filled circles in Fig. 2 were obtained at constant hypophosphite-ion concentration (0·2 M) with variable nickel-ion concentration. In contrast to the other polarization curve, this is not a Tafel line, but exhibits the characteristics of a process under mass-transport control, or one wherein the reactant for the electrode reaction is derived from a preceding slow chemical reaction. From the observed magnitude of the activation energy,[2] mass-transport control of the cathodic process may be ruled out. Consequently, it is evident that the electrochemical oxidation of hypophosphite ion is preceded by a slow chemical reaction with a first-order dependence on hypophosphite ion. The precise nature of the process could not be ascertained from the present data.

REFERENCES

1. W. G. LEE, *Proceedings of the Second International Congress on Metallic Corrosion*, p. 711. National Association of Corrosion Engineers, Houston, 1966.
2. G. GUTZEIT, *Plating* **46**, 1158 (1959).
3. G. GUTZEIT, *J. electrochem. Soc.* **109**, 1219 (1962).
4. A. BRENNER, in *Modern Electroplating*, ed. F. A. Lowenheim, p. 699. Wiley, New York (1963).
5. K. J. VETTER, *Electrochemical Kinetics*, p. 732. Academic Press, New York, (1967).
6. C. WAGNER and W. TRAUD, *Z. Elektrochem.* **44**, 391 (1938).
7. M. STERN and A. L. GEARY, *J. electrochem. Soc.* **104**, 56, 645 (1957).