XCVII.—*Studies of Electrolytic Polarisation. Part VI. Electro-deposition Potentials of Alloys of Zinc with Iron, Cobalt, and Nickel.*

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IT has been known for some time (Toepffer, *Diss.*, Breslau, 1899; *Z. Elektrochem.*, 1899, **6**, 342; Küster, *ibid.*, 1900, **7**, 257; Treadwell, *Diss.*, Zurich, 1909, see Foerster, *Z. Elektrochem.*, 1911, **17**, 883; von Escher, *Diss.*, Dresden, 1912, see Foerster, *Z. Elektrochem.*, 1916, **22**, 85; Schoch and Hirsch, *J. Amer. Chem. Soc.*, 1907, **29**, 314) that if a gradually increasing current is passed through a solution containing a mixture of zinc and nickel or iron salts, the initial deposit on the cathode consists mainly of the iron-group metal but contains a small proportion of zinc. If the *C.D.* is increased a point is reached—at very low *C.D.*'s at room temperature, but at much higher *C.D.*'s at higher temperatures—at which the cathodic potential increases rapidly until it attains a value very close to that at which pure zinc would be deposited from a solution of the zinc salt only; the deposit under these conditions contains only a small proportion of nickel or iron. It was considered (Treadwell, *loc. cit.*) that the zinc deposited with the nickel increases the resistance to cathodic deposition which already exists in the case of the latter metal, with the result that a much higher negative potential is required to deposit the nickel; the result of the increased polarisation effect is that the deposit becomes richer in zinc until finally it contains only a small proportion of nickel. The results of von Escher suggested that the intensity of this polarisation depends on the hydrogen-ion concentration of the electrolyte, since the rapid rise of cathodic potential was found to occur more readily in a weakly acid than in a neutral solution of ferrous and zinc sulphates; hence hydrogen ions apparently enhance the retardation effect caused by zinc on the deposition of iron (see Grube, *Trans. Faraday Soc.*, 1914, **9**, 214; Foerster, " Elektrochemie Wässeriger Lösungen," 1922, p. 378).

In view of the results obtained previously on the electro-deposition potentials of iron, nickel, and cobalt, and their alloys (J., 1926, 2887, 2897) in solutions of varying hydrogen-ion concentration, it was of interest to investigate the changes of cathodic potential occurring with increasing *C.D.* in solutions of iron, cobalt, or nickel containing zinc ions, along the lines followed previously. The general observations of previous authors (*loc. cit.*) have been confirmed and found to apply to these solutions. Moreover, it has been found that, as in the case of anodic passivity, the *C.D.* may

be reduced considerably below that at which the sudden increase of potential occurs before the corresponding fall of potential results.

<center>E X P E R I M E N T A L.</center>

Electrolytic Solutions and Electrodes.—The solutions were generally made up by adding the requisite amount of zinc sulphate and either ferrous, cobalt, or nickel sulphate to a sodium acetate–acetic acid buffer mixture such as was used in previous work (*loc. cit.*); the total concentration of zinc and iron-group metal was 1 g.-equiv. per litre. The zinc sulphate was a recrystallised commercial specimen and the other salts were of the same quality as had been used before. The cathodes were of copper covered with a layer of iron, cobalt, or nickel, according to the metal in the electrolyte; the exposed area was generally 7·5 sq. cm. The anode was a short piece of platinum wire, and this was separated from the cathode by means of a porous pot when ferrous solutions were being used.

Potential Measurement.—Owing to the instability of the electrode potential in the vicinity of the *C.D.* at which the rapid increase of negative potential occurred, it was necessary to modify slightly the commutator–extrapolation method used in previous work. Preliminary experiments were made at a number of *C.D.*'s in order to determine the rate of fall of cathode potential in the first 0·012 sec. after the polarising current was switched off. The measurements were extrapolated in the usual way (J., 1924, **125**, 250) so that the potential at the instant of switching off the current could be determined and hence the fall of potential occurring in the first 0·002 sec.; this quantity was determined under a variety of conditions and never exceeded about 0·04 volt. In the actual measurements, the commutator was set so as to give the potential of the electrode at an average time of 0·002 sec. after the polarising current was stopped; the correction, found as described above, for the particular condition of the electrode was then added in order to give the values quoted below; these must be very close to the actual electrode potentials while the current was flowing.

As in previous work, the current passing through the electrolyte was increased or decreased by stages and kept constant for 1 minute before the potential was measured; the reference electrode was in every case a calomel half-element containing a saturated solution of potassium chloride and no allowance was made for liquid-junction potential.

Results.—The potentials recorded in Table I were obtained with a mixture of 0·1 g.-equiv. of zinc and 0·9 g.-equiv. of nickel in solutions of varying hydrogen-ion concentration at temperatures of 15° and 95°. (All *C.D.*'s throughout this paper are expressed in

terms of amps. $\times 10^{-4}/cm.^2$, and potentials are on the hydrogen scale.)

TABLE I.

Cathode potentials in 1Zn : 9Ni solutions.

C.D.	V/50·H$_2$SO$_4$.		p_H 2·8.		p_H 4·0.		p_H 5·5.	
	15°.	95°.	15°.	95°.	15°.	95°.	15°.	95°.
2·8	−0·19	−0·16	−0·32	−0·18	−0·41	−0·22	−0·47	−0·25
4·2	−0·22	−0·17	−0·41	−0·20	−0·45	−0·23	−0·50	−0·26
8·4	−0·28	—	−0·52	−0·24	−0·52	−0·25	−0·56	−0·30
12·0	−0·44	−0·21	−0·56	—	−0·56	−0·27	−0·79*	−0·32
20·0	−0·56	−0·23	−0·58	−0·28	−0·57	−0·31	−0·79	−0·34
32·0	−0·58	—	−0·60	—	−0·80*	−0·33	—	—
40·0	−0·80*	−0·26	−0·62	−0·31	—	—	−0·80	−0·42*
80·0	—	−0·29	−0·80*	−0·35	—	−0·35	−0·81	−0·43
160·0	−0·82	−0·30	−0·81	−0·37	−0·81	−0·39	—	−0·43
210·0	—	−0·43*	—	—	—	−0·43*	—	—
320·0	—	−0·43	−0·82	−0·38	—	−0·44	−0·83	—
640·0	—	−0·45	—	−0·42*	—	—	—	—
960·0	—	—	—	−0·43	—	−0·45	—	—

The general conclusions to be drawn from these results are that the potential of the electrode after the sudden increase has occurred —marked with an asterisk in Table I—is independent of the hydrogen-ion concentration of the solution, and that this potential rise occurs less readily, *i.e.*, at higher *C.D.*'s, at high temperatures and high hydrogen-ion concentrations.* Before the rapid increase of negative potential, the deposit on the cathode resembles ordinary electrolytic nickel in appearance and is not easily attacked by acids, but the metal deposited at the higher potentials is grey and dull, like electrolytic zinc, and is readily attacked by dilute acids, leaving a black residue of finely-divided nickel. This zinc-rich deposit obtained at 95° appears to contain relatively more nickel than does the corresponding deposit obtained at 15°, in agreement with the change in deposition potential from − 0·43 at 95° to − 0·80 at 15°. It should be noted that the first alloy, rich in nickel, is deposited at a potential of − 0·56 to − 0·58 at 15° and about − 0·30 at 95°; these are roughly the potentials at which pure nickel would be deposited from a solution of nickel sulphate alone at the concentration used in the mixture (J., 1926, 2887).

All these general observations have been confirmed by a large number of potential measurements made on various solutions of zinc sulphate and nickel, cobalt, or ferrous sulphate; it has also been found that the sudden increase of potential occurs at lower *C.D.*'s the greater the proportion of zinc to iron-group metal in the electrolyte. For solutions at the same hydrogen-ion concentration and temperature and containing the same relative pro-

* The anomalous result with $N/50$-sulphuric acid is probably due to the solution not being buffered.

portion of zinc, the zinc-rich alloy is deposited at lower *C.D.*'s in the case of nickel than in that of cobalt. With iron–zinc mixtures the zinc-rich alloy is only obtained at much higher *C.D.*'s; *e.g.*, in a solution of p_H 2·8 containing 1 atom of zinc to 9 atoms of iron (compare Table I), the sudden increase of potential occurs at a *C.D.* of about 210×10^{-4} at 15° and 640×10^{-4} at 90°. Once this higher potential condition has set in, however, the current may be reduced to very low values, especially at low temperatures, before the corresponding fall of potential is observed.

In order to compare the results obtained with different solutions, it was considered most satisfactory to determine a potential value equivalent to the deposition potential of the zinc-rich alloy for each solution; the nearest approach to this would be the cathodic potential of the electrode when the alloy was being deposited at the slowest possible rate. The following method was therefore adopted : The polarising current was increased to a fairly high value, so as to cause deposition of the zinc-rich alloy, and then reduced gradually; the potential was measured at each stage and found to decrease very slowly and then to remain almost constant before decreasing suddenly. This constant value was regarded as the deposition potential of the alloy of zinc and the iron-group metal. The observations were repeated at a number of temperatures and the results are summarised in Table II. The potential measurements

TABLE II.

Deposition potentials of zinc-rich alloys.

* Zn %. Iron–Zinc.	15°.	35°.	55°.	65°.	75°.	85°.	95°.
2·5	−0·80	−0·78	−0·73	−0·66	−0·58	−0·52	−0·50
5·0	−0·80	−0·79	−0·75	−0·69	−0·59	−0·53	−0·50
7·5	−0·80	−0·79	−0·76	−0·73	−0·69	−0·62	−0·53
10·0	−0·80	−0·79	−0·77	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·74	−0·73
Cobalt–Zinc.							
5·0	−0·80	−0·75	−0·68	−0·63	−0·57	−0·50	−0·41
10·0	−0·79	−0·75	−0·70	−0·66	−0·60	−0·52	−0·43
20·0	−0·79	−0·76	−0·72	−0·69	−0·65	−0·59	−0·49
40·0	−0·78	−0·78	−0·76	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·73	−0·70
70·0	−0·77	−0·77	−0·77	−0·76	−0·76	−0·75	−0·72
Nickel–Zinc.							
1·0	−0·80	−0·65	−0·55	−0·49	−0·45	−0·40	−0·38
5·0	−0·80	−0·69	−0·59	−0·54	−0·47	−0·41	−0·39
10·0	−0·79	−0·70	−0·62	−0·56	−0·50	−0·44	−0·42
30·0	−0·78	−0·74	−0·68	−0·64	−0·56	−0·49	−0·45
50·0	−0·77	−0·75	−0·72	−0·70	−0·67	−0·61	−0·56
70·0	−0·76	−0·75	−0·73	−0·71	−0·68	−0·63	−0·58
90·0	−0·76	−0·75	−0·74	−0·73	−0·72	−0·70	−0·65

* This gives the zinc in the electrolyte as an atomic percentage of the total zinc and iron-group metal.

were very consistent and, as indicated above, independent of the hydrogen-ion concentration of the electrolyte.

Discussion.

It appears very probable, from the results of the foregoing experiments, that the hydrogen-ion concentration of the electrolyte, contrary to the views of previous authors (see p. 641), plays no direct part in any influence which the simultaneously deposited zinc may have on the retardation of the electro-deposition of the iron-group metals. In general, the sudden increase of cathode potential, and the change in the nature of the deposit from an alloy rich in iron-group metal to one rich in zinc, occur at a lower $C.D.$ the smaller the hydrogen-ion concentration of the solution; this is merely due to the fact that a given rate of metal deposition is more easily reached when the solution is less acidic, and not because the hydrogen ions accelerate the deposition of nickel, iron, or cobalt. It is doubtful, too, if the small amounts of zinc deposited with the iron-group metal at the low cathodic potentials appreciably affect the deposition of the latter; for the initial deposition of the alloy poor in zinc occurs almost at the same potential as that at which the iron, cobalt, or nickel itself would be deposited, and, further, if the zinc inhibited the deposition of nickel, we should expect the cathode potential to rise rapidly with increasing $C.D.$ from the instant at which metal deposition first occurs, instead of remaining fairly low over an appreciable range of current (see Table I).

An alternative view is the following (nickel is taken as representing any of the three iron-group metals) : A small quantity of zinc does not appreciably affect the deposition of the nickel, or, in terms of the views expressed in connexion with previous work (*loc. cit.*), it has no influence on the rate of transformation of metastable to stable nickel, although in the zinc-rich alloy this rate of change is probably affected. The initial deposit at low $C.D.$'s will probably contain relatively more nickel than is present in the solution, and as the $C.D.$ is increased gradually the composition of the deposit, as judged from the potential measurements, will not vary appreciably; a point will be reached, however, at which the nickel ions cannot diffuse towards the electrode as fast as they are being deposited. In order to maintain the current, an increased proportion of zinc ions must be discharged and an alloy richer in zinc commences to be deposited; owing to the high overvoltage of hydrogen at a zinc electrode it is fairly certain that hydrogen evolution at this new deposit will be retarded, with the result that the efficiency of metal deposition is increased and still more zinc must be deposited. This process results in the rapid increase in

the proportion of zinc in the deposit and corresponds with a rapid rise in the cathodic potential almost up to that at which pure zinc is deposited; the deposit now consists of an alloy very rich in zinc and rarely contains more than about 20% of iron-group metal. Further increase in the *C.D.* should result in a much more gradual increase in the zinc content of the deposit, and at very high *C.D.*'s this may even decrease slightly owing to the depletion of the electrolyte in the vicinity of the cathode. It might be anticipated that at this point, or as a result of decreasing the *C.D.* whereby the solution near the cathode would once more contain a large proportion of nickel, the original process of the deposition of a nickel-rich alloy would recommence; this does not occur, however, and it is concluded, therefore, that in the zinc-rich alloy the change from metastable to stable nickel is considerably retarded, and so the latter metal cannot be deposited at its ordinary potential. On decreasing the *C.D.* far below the point at which the sudden increase of potential occurred, a corresponding fall is observed; this cannot be due to any change in the concentration of the electrolyte near the cathode because the current value is generally so low that diffusion cannot play any appreciable part, and the " diffusion layer " must be almost identical with the bulk of the electrolyte. The suggested explanation for the fall of potential is that on reducing the *C.D.* the deposit becomes richer in nickel, and consequently the hydrogen overvoltage steadily decreases until a point is reached at which discharge of hydrogen ions can occur so readily that the discharge of zinc ions is no longer necessary to maintain the flow of current. A smaller proportion of zinc in the deposit will cause the hydrogen overvoltage to fall still further and so the cathode potential falls fairly rapidly to a low value at which almost all the current results in the discharge of hydrogen ions, although a small amount of nickel may also be deposited.

At increased temperatures, the rate of diffusion of the electrolyte is increased and the hydrogen overvoltage is decreased, hence the rapid rise in potential occurs at a higher *C.D.* than at low temperatures. Since the normal rate of change of metastable to stable nickel is greater at high temperatures, it is to be expected that the zinc-rich alloy will contain relatively more nickel than at low temperatures; the deposition potentials, in accordance with this, are in most cases much lower than that at which pure zinc is deposited (see Table II; the deposition potential of pure zinc from a *N*-solution at 95° was found to be $- 0.74$ volt).

A close examination of Table II reveals a number of points of interest which cannot be discussed owing to lack of information on the nature and properties of the individual deposits, obtained at

different temperatures, from various solutions containing zinc and either iron, cobalt, or nickel.

Summary.

(1) It has been confirmed that during the electrolysis of a solution containing a mixture of zinc and nickel or iron the cathodic potential at some point rises rapidly and an alloy consisting mainly of zinc is deposited; the same phenomenon has also been observed with solutions of cobalt and zinc.

(2) The current density at which the sudden increase of potential occurs is generally smaller the lower the temperature, the greater the proportion of zinc in the solution, and the lower the hydrogen-ion concentration.

(3) The deposition potential of the zinc-rich alloy has been measured in solutions containing various proportions of zinc and iron, cobalt, or nickel at temperatures ranging from 15° to 95°; this potential decreases with increasing temperature.

(4) The theories of previous authors do not appear to explain adequately the results of the present work, and alternative suggestions have been made; the sudden increase of cathodic potential is attributed to a decrease in the concentration of the nickel, cobalt, or ferrous ions in the vicinity of the cathode, with the result that an alloy richer in zinc and with a high hydrogen overvoltage is deposited.