# SCIENCE

VOL. 82 FRIDAY, JULY 5, 1935 No. 2114

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. MCKEEN CATTELL and published every Friday by

THE SCIENCE PRESS

New York City: Grand Central Terminal

Lancaster, Pa. Garrison, N. Y.

Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

# ELECTROCHEMISTRY'S DEBT TO EDGAR FAHS SMITH[1]

## CATHODE FILM CONTROL IN ELECTROMETAL DEPOSITION

By Professor **COLIN G. FINK**

HEAD OF THE DIVISION OF ELECTROCHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK CITY

THE outstanding and numerous contributions of Edgar Fahs Smith to chemistry and to learning in general cover a number of distinct fields of endeavor, each one of which would have completely occupied the time of a less gifted scientist than Dr. Smith. His publications alone number at least 200: organic syntheses, electrochemistry, atomic weight determinations, history of chemistry, mineralogy, biography, urinalysis, pedagogics, etc. But, as Professor Bogert pointed out at the memorial service for Dr. Smith seven years ago, the "most important contributions of Dr. Smith were those he made to electrochemistry, a domain in which he was a pioneer and soon became a recognized leader of international reputation. In the hands of this master craftsman, the electric current became a tool of undreamed-of usefulness and possibilities, opening up wholly new methods of analysis, separation and determination. About half of all the research papers he published were based upon new applications of the electric current. His introduction of the rotating anode, together with the employment of currents of high amperage and high voltage, marked a new epoch in the development of electroanalysis. His books on electrochemistry quickly became and have since remained the standard texts in this country, while the Harrison Laboratory was soon known throughout the world for its leadership in this branch of chemistry." Out of 169 papers published in various scientific journals every second one deals with an

---

[1] Edgar Fahs Smith Memorial Address, slightly curtailed, given on May 23, 1935, at the University of Pennsylvania, Professor Hiram Lukens in the chair.

electrochemical topic. Dr. Smith's first papers on electroanalysis appeared in 1879 in the Proceedings of the American Philosophical Society and in the *American Chemical Journal.* Other papers on the same topic followed at frequent intervals from that time on, but it was not until 1901 that a radical change in Dr. Smith's method of electroanalysis was introduced. In that year while experimenting on the separation of tungsten from molybdenum, Dr. Smith came upon the idea of rotating the anode. He discovered that "by causing the anode to rotate at a high speed, greater current intensity and higher voltage might be applied with an attending, more rapid precipitation of the respective metals."[2]

Then followed the detailed experiments of F. F. Exner, a student working under Dr. Smith's direction. Exner's Ph.D. thesis was published in June, 1903, and the results recorded "were of such remarkable character that many chemists considered the field of electroanalysis to have been truly revolutionized by them."[3]

Although agitation of the electrolyte by some means or other had been suggested by others besides Dr. Smith, it was he who first suggested the combination of a rotating anode and high cathode current densities. Determinations which had previous to 1901, with stationary electrodes and low current densities, taken two to four hours and more, were now, through the findings of Smith and Exner, reduced to 5 to 10 minutes. Furthermore, the quantities that could be accurately determined were more than threefold the quantities by the older methods.

Copper determinations were now made in four minutes; complete precipitation of cadmium in ten minutes; bismuth, lead, silver, zinc, nickel, cobalt, manganese, iron, chromium, uranium, thallium, indium, platinum, palladium, rhodium, molybdenum, gold, tin, antimony, tellurium, arsenic—almost the entire periodic table of elements all precipitated, either as metal or as specific compound, in small fractions of an hour instead of several hours. But this is not all—separations of one metal from another could be carried out more readily and more exactly with the use of the rotating anode—a number of the separations not being even attempted previous to Dr. Smith.

In the summer of 1903 Dr. Smith sent the writer (then pursuing graduate work at the University of Leipzig) a copy of the thesis of F. F. Exner. It was a keen pleasure to repeat a number of the specified tests of Smith and Exner. And it was this work that inspired us to further investigate the basic phenomena involved and started us on our work on chromium, cobalt, tungsten and other metals. Many changes have been made in the apparatus employed by us during these many years. Furthermore, the interpretation of results is quite different to-day from what it was thirty odd years ago. Our thoughts were originally directed to concentration polarization phenomena, whereas to-day we believe that a film of atomic hydrogen and the proper control of the alkalinity of the liquid cathode surface film are of paramount importance.

As regards our apparatus, we directed our attention from the very start to a rotating cathode rather than a rotating anode, as recommended by Dr. Smith. We are operating our cathode to-day at speeds up to 15,000 r.p.m., as against 400 to 1,000 r.p.m. for the anode used by Dr. Smith and his students. With these high-speed cathodes there seems to be almost no upper limit in cathode current density. We frequently use 250 to 500 amperes per square foot, far in excess of the current densities recommended by Dr. Smith.

Before discussing our present conception of the several steps involved in the electrodeposition of a metal, a few of the more interesting experimental results will be recorded. In all these investigations I have been very ably assisted by a host of young students and associates, in particular, Messrs. D. B. Lake, F. A. Rohrman, R. R. Rogers, C. B. F. Young and C. B. de Maya.

### COPPER DEPOSITION WITH THE HIGH-SPEED CATHODE

(*a*) *Separation of copper traces from nickel solutions:* A solution of copper-free nickel sulfate was prepared and to this was added one part of copper for every 30,000 parts of nickel. The solution had a pH of 5 and was electrolyzed at 25° C. at a current density of 0.3 amperes per square decimeter. A deposit of pure copper was obtained at a current efficiency of 23.5 per cent. The cathode speed was 3,000 r.p.m.

It is interesting to note that at the low current density recorded above copper alone and no nickel will plate out of solution, when the cathode exceeds a certain speed of rotation. Increasing the current density increases the speed limit. There is a critical polarization value that must be exceeded before any nickel will plate out. Furthermore, even with the high-speed cathode, there is a fairly narrow pH range beyond which no copper will deposit. This point will be more fully discussed below.

(*b*) *Recovery of copper from tails waters:* Tails waters from copper leaching and electrodeposition plants contain appreciable quantities of copper, as much as 0.1 grams per liter. Taking into account the millions of liters that run to waste, the copper that is lost amounts to many hundred tons a year. Due to

---

[2] Smith's "Electroanalysis," sixth edition, p. 41.

[3] *Ibid.*, p. 41.

the fact that these tails waters contain, besides the copper, a large number of other salts, notably of iron, and this in the ferric state, it is impossible to electrodeposit the copper on a stationary cathode. In fact, we have had cases where the stationary cathode actually went into solution due to the solvent action of the ferric ions. However, upon applying the high-speed cathode, recoveries of copper up to 86 per cent. were obtained at current efficiencies as high as 70 per cent. To cite a definite case, the tails water contained 0.07 g./L. of copper, 0.13 g./L. of iron, besides small quantities of compounds of Si, Al, Ca, Mg, K and Na. The current density was 15 amperes per square decimeter, temperature 30° C., cathode diameter 5 cm and cathode speed 1,500 r.p.m. Current efficiency 68 per cent.; recovery 85 per cent. In other experiments cathode disks three feet in diameter were used. Recovery of copper from tails waters can be accomplished if a satisfactory balance is struck between cost of rotating the cathode and the price of copper. "Raw material" costs are nil.

### DUCTILE ELECTROLYTIC IRON

Noteworthy are the results obtained with iron. Using the chloride bath, bright ductile deposits of iron were obtained on the rotating disk cathode at current densities of 15 amperes per square decimeter. With low current densities of the order of 0.3 ampere per square decimeter, no iron deposits when appreciable quantities of ferric ions are present. As the current density is increased, a point is reached where the ferric ions no longer stop the deposition entirely and at higher current densities current efficiencies of 80 per cent. and over are obtainable.

Iron present in nickel sulfate plating baths can be removed by the high-speed cathode. This is so contrary to common older theoretical considerations that it is hard to believe. First of all, nickel is the more noble metal, and, secondly, the concentration of nickel may be over a hundredfold that of iron. But on the basis of our modern conception of the high pH film at the cathode surface, as discussed below, results appear all too plausible.

### "GOLD FROM SEA WATER"

This is another case in which the high velocity of the cathode plays a most important part. The higher the velocity the better the recovery from gold solutions containing as little as one part per million (or 1 milligram per liter).[4] In a typical experiment a 5 cm diameter nickel disk cathode was used spinning at the rate of 8,500 r.p.m. in three liters of a 3 per cent. salt solution containing 3 mg of gold. The temperature of the solution was 20° C.; pH, 6.00; current density 2 amperes per square decimeter; voltage 8.5. Over 90 per cent. of the gold was plated out at the end of half an hour. It will be appreciated that the gold concentration toward the end of this period was decidedly less than 1 part per million. But hopes of "recovering billions from the five seas" must be dispelled for the present, since the cost of rotating the cathode is about five times the value of the gold recovered. More profitable is this same procedure in the case of the radioactive metals.

### RECOVERY OF POLONIUM

Messrs. Whitaker, Bjorksted and Mitchell,[5] employing our high-speed cathode method, recovered polonium from aqua regia solutions of radium D containing reduced iron and mercury. A silver disk $\frac{7}{8}$ inch in diameter was used and rotated 1,400 r.p.m. Ninety-eight per cent. of the polonium was deposited in about 90 minutes, the solutions containing only 0.0005 curie[6] of radium D in equilibrium with its products. Acid (HCl) concentrations varied between 1/20 *N* and 4 *N* without any noticeable difference in results.

The usual method of obtaining a polonium source from old radium emanation tubes has been described by I. Curie in 1925 and consists of a series of chemical operations and the polonium salts separated from the rest of the solution by a series of precipitations. In the presence of ferric iron and mercuric ions there is no deposition of polonium with stationary electrodes, but with the rotating disk 38 per cent. of the polonium was recovered in spite of the "ic" ions. Upon reducing the ferric and mercuric ions with sulfurous acid, 98 per cent. of the polonium was recovered.

### THE EFFECT OF CATHODE SPEED ON THE DEPOSITION OF ALLOYS

In general we find that in the deposition of binary alloys the composition of the alloy may be easily varied at will by merely changing the speed of the rotating cathode and regulating the current density. Thus, in the case of codepositing cobalt and nickel, the higher the speed the higher the proportion of cobalt in the deposit. Keeping the speed constant at, say, 1,000 r.p.m. and decreasing the current density, the per cent. cobalt in the alloy increases. As a specific example we obtained 27.2 per cent. cobalt in the alloy at a current density of 2 amperes per square decimeter and 43.4 cobalt at 0.22 amperes per square decimeter. The solution was a normal nickel sulfate solution containing one part of cobalt for every 100 parts of nickel. The pH was 5.5, temperature 20° C.

---

[4] Compare with this the arsenic content of the gastric juices of the average normal person, 30 parts per million, or copper in milk 0.6 p.p.m.

[5] *Phys. Rev.*, 46: 629, 1934.

[6] One curie is equal to 0.59 cubic millimeters of emanation.

Another alloy case is that of zinc-cadmium. Using a solution containing 70 g./L. of zinc, 2½ g./L. of cadmium and 109 g./L. of total sulfate, we found that as the speed of the cathode increased from zero up to 13,000 r.p.m., the per cent. of zinc in the alloy deposit decreased. Furthermore, decreasing the current density decreased the zinc content of the alloy. And increasing the temperature of the solution decreased the zinc content. This all fits in beautifully with our present theoretical interpretation.

### WHAT THE HIGH-SPEED CATHODE ACCOMPLISHES

It is generally accepted by electrochemists to-day that there exists in intimate contact with the submerged surface of either electrode a film of electrolyte quite different in composition from that of the main body of the bath. Immediately upon electrolysis, the alkalinity of the cathode film increases very appreciably above that of the solution proper and at the same time the alkalinity of the anode film decreases appreciably below that of the bath. This can be illustrated—at least as far as the cathode film is concerned, in which we are primarily interested—by electrolyzing a solution of acid sodium sulfate containing a little phenolphthalein. Upon closing the circuit the solution layer in contact with the platinum cathode turns red, although the main body of the bath is still colorless.

This film at the cathode can be regulated as to its thickness, and as to its pH, by various chemical means, but none of these is as simple and as direct—in particular, for orientation purposes when investigating the electrodeposition of a new metal—as the procedure of changing the speed of the rotating cathode and then its current density. In this way desired results have been obtained in short order, as compared with long, tedious, "hit and miss" methods of the past. And credit for this discovery we unhesitatingly give to Dr. Edgar Fahs Smith. The observations made by him in 1901 to 1903 are at the very foundation of all that followed and led up to a clearer interpretation of the steps in metal deposition.[7]

On the basis of numerous experimental results we find that: (1) A cathode film is essential for successful metal deposition, but that—(2) this film must be held within fairly definite limits as to: (a) thickness and (b) hydrogen-ion concentration. (3) The film can be maintained within these limits most easily by the rotating cathode method, a definite cathode speed and cathode current density corresponding to the desired film thickness and film pH. (4) The film thickness and its pH are different but specific for each metal.

It has been shown repeatedly that the higher the cathode speed, the thinner the film, without however reaching zero thickness. Furthermore, the higher the cathode speed, the higher the limiting cathode current density for compact, adherent metal plate. And, finally, the higher the cathode current density, the higher the pH of the film.

A number of cases were observed in which no metal plate was obtained with a stationary cathode and yet from the very same solutions, and under otherwise identical conditions, beautiful, reguline metal deposits were produced upon rotating the cathode. In the presence of ferric salts there may be an actual loss in cathode weight when the speed is zero, and a decided gain in weight when the speed is 1,000 r.p.m. or more.

The best film thickness is not the same for all metals. The more noble metals usually require a thinner film than the baser metals. Similarly the pH range for best metallic deposits is characteristic though different for each metal. Thus, zinc and tin have a fairly wide film pH range, nickel, cobalt and manganese a relatively narrow range. If zinc and nickel are present in solution in equimolecular proportion, and the current density increased to a point to bring about a cathode film pH beyond the range for nickel, zinc alone will deposit out, even though nickel is the more noble metal.[8] On the other hand, as recorded above, a trace of copper may be separated from nickel, providing the film pH is held within relatively narrow limits and the cathode speed exceeds a definite value. Copper will plate out at a higher film pH than iron and thus it is possible to recover copper from solutions high in iron when using the high-speed cathode. Iron, on the other hand, will deposit out to the exclusion of nickel, even though this may be in great preponderance, if the cathode film pH is above the nickel limit.

In the case when both cadmium and zinc are present, the more alkaline the film, the less cadmium is deposited. Thus by increasing the current density or decreasing the temperature or decreasing the cathode speed, the less cadmium was found in the alloy deposited on the cathode—and *vice versa*.

Gold will not deposit from sea water with a stationary cathode due to the excessively high pH of the cathode film and its relatively great thickness. Upon rotating the cathode, both film thickness and film pH are very much reduced and bright, solid, pure gold appears on the cathode.

From all available data it is apparent that with the high-speed cathode and/or high current densities applied, the sequence of electrodeposition of metals is not necessarily in the order of their "classic nobility" but may at will be changed about to suit the requirements

---

[7] How the thickness and the pH of the cathode film can be varied was shown in six figures projected on the screen.

[8] Compare Newberry, *Jour. Am. Chem. Soc.*, 51: 1429, 1929.

under consideration. Thus the following order applies within well-defined limits of cathode speed, cathode film pH and current density: zinc, copper, iron, nickel —that is, first zinc, then copper, then iron, then nickel can be plated out.

In conclusion, we strongly recommend the high-speed cathode to all interested in the electrodeposition of those metals and alloys which have to date not been produced from aqueous solutions in solid, adherent, compact and metallic form.

# SCIENTIFIC EVENTS

## ASCENT OF THE RUSSIAN STRATOSPHERE BALLOON

A SPECIAL cable to *The New York Times,* dated from Moscow on June 26, reports that a surprise flight of a Soviet stratosphere balloon on June 26 reached a height of almost ten miles.

The flight, which was entirely for scientific purposes with no attempt to break altitude records, was reported to have been entirely successful.

The balloon was the U. S. S. R. 1-Bis. It took off from the Kuntzevo military airfield on the outskirts of Moscow at 5:25 and landed at 8 A. M. on a collective farm at the village of Trufanoff, near Tula, 115 miles south of Moscow.

The balloon was the one in which Commander Prokofieff ascended 19,000 meters [62,335 feet] in 1933. Although it had the same gas bag—one of 24,000 cubic meters' capacity, the gondola had been largely reconstructed, strengthened and equipped with the latest scientific equipment.

The balloon contained two Wilson cameras for photographing the path of electrons. These had been built by Professor Alexander Verigo, chief physicist of the Department of Radioactivity and Cosmic Rays at the Geophysical Laboratory in Leningrad, who took observations on the flight. The other equipment included ionization cameras with which he observed the secondary emanations produced by cosmic rays in aluminum and lead, a spectrograph to measure the brightness of the skies and thermographs for measuring outside temperatures.

Besides Professor Verigo those aboard were K. I. Zille, a graduate of the Red Army air academy and one of the most experienced Soviet aeronauts, and J. G. Prilutsky, an engineer, also Red Army trained.

The *Times* states that although there was no announcement of the flight until it had been successfully completed, the balloon and crew had been in readiness to ascend for three days. Clouds and unfavorable winds prevented the take-off until June 26.

From beginning to end of the flight the balloon was in radio communication with the ground. The balloon's radio station was called "Luna" and the earth station "Venus." The radio transmitted word that the balloon was ascending at the rate of five meters (16.4 feet) a second, which slackened to three meters as it reached higher altitudes.

## THE HARVARD DREDGING EXPEDITION ALONG THE ATLANTIC COAST

THE dredging expedition undertaken by Harvard University was done on Georges Bank, about 120 miles east of Nantucket Island, Massachusetts, under the direction of Henry C. Stetson, research associate in paleontology, Museum of Comparative Zoology. It will be continued this summer in the Hudson River submarine channel off New York Harbor and in the submarine valleys off the Maryland coast. One of the Maryland coast valleys is the deepest yet found along the Atlantic shore, dropping 9,000 feet below sea level.

Fossils were taken by the expedition from the sides of the Georges Bank valleys, which extend more than a mile below sea level on the edge of the continental shelf. The evidence uncovered is said to confirm the generally supported theory that the deep ocean valleys cutting into the continental shelf were formed by rivers which flowed into the Atlantic before the continental shelf sank below the ocean.

The boat employed by the expedition was the *Atlantis,* of the Woods Hole Oceanographic Institute, an auxiliary steel ketch, 142 feet overall. The dredge used is of the scraper type, of $\frac{3}{8}$-inch steel plates, with sharp cutting edges.

Eleven successful hauls were made. The middle and upper parts of the valleys between 2,100 and 600 feet were found to be the best areas. Here the walls were either steep enough to prevent the deposition of recent sediment or else the mantle was thin enough to be penetrated. The lower parts of the valleys have gentler grades and the fill of unconsolidated material covers the bed rock so deeply that no rock was found exposed.

In one of these valleys the expedition dredged at a depth of 1,956 to 1,578 feet a coarse sandstone containing fossil mollusks, which Dr. Lloyd W. Stephenson, of the U. S. Geological Survey, has assigned to the Upper Cretaceous period, about 105,000,000 years ago.

From another valley, between 1,968 and 1,740 feet below the sea level, came a greensand, which Dr. Joseph A. Cushman, lecturer on micro-paleontology