
**Contributions to the Knowledge of the Electrolysis of
Aqueous Solutions of Vanadium Salts**

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BY
SIEGFRIED FISCHER, Jr.

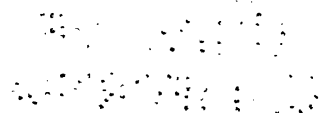
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M. N. W.

CONTRIBUTIONS TO THE KNOWLEDGE OF THE ELECTROLYSIS OF AQUEOUS SOLUTIONS OF VANADIUM SALTS.

By SIEGFRIED FISCHER, JR.

INTRODUCTION—LITERATURE ON ELECTROLYTIC VANADIUM.

Previous to 1882, very little electrolytic work was done on vanadium, but since then much interest has developed in this field. Electrolytic processes may be divided into (1), those using an aqueous electrolyte, and (2), those using a non-aqueous or fused electrolyte. The electrolytic processes for obtaining metallic vanadium, using either aqueous or fused electrolytes, are very few, and most are of theoretical value only. The literature on the subject is very scant, and much of the data reported lacks accuracy.

It is the object of this thesis to determine whether or not it is possible to obtain metallic vanadium from aqueous solutions of its salts.

Electrolysis of Vanadium Electrolytes.

The literature on electrolytic processes for obtaining metallic vanadium is very scarce, but a considerable amount of work has been done by various scientists on the electrolytic behavior of vanadium compounds. The work is of importance, because in treating an ore or a vanadium product by electrolysis, the vanadium will always be in solution as a compound, which must be decomposed by the electric current. The literature may be conveniently divided into

1. General Literature on Electrolysis of Vanadium.
2. Electrolysis of Aqueous Solutions of Vanadium Salts for obtaining Metallic Vanadium.

1. *General Literature.* Der Zustand Einiger Übersäuren und ihrer Salze (the condition of some super acids and their salts in

solution), in the "Zeitschrift für physikalische Chem.," **43** (1903), 160-178. L. Pissarjewsky studied the conductivity, behavior and composition of the potassium salts of the acids HVO_4 and $\text{H}_8\text{V}_6\text{O}_{26}$, and found that these compounds are much too complex to yield metallic vanadium on electrolysis, but simply an oxide.

According to L. Marino—Über das elektromotorische Verhalten des Vanadins (about the electromotive behavior of vanadium), "Zeitschrift für anorganische Chemie," **39** (1904), 152-169, the lower oxides of vanadium behave like those of chromium, while its higher oxides resemble those of phosphorus and arsenic. If vanadium is used as an anode it acts as a reducing agent in solutions of neutral salts of silver, gold, platinum and iridium, reducing the salts to the metallic state, on connecting the anode and cathode leads, while Cu^{++} , Hg^{++} and Fe^{+++} ions are only partially reduced to Cu^+ , Hg^+ and Fe^{++} . Vanadium exerts no reducing action on Zn^{++} , Cd^{++} , Ni^{++} and Pb^{++} . The vanadium enters the solution anodically as tetra-valent ions (V^{++++}). Marino has shown experimentally that, in an alkaline solution, vanadium enters solution as penta-valent ions (V^{+}), while in an acid solution it dissolves as tetravalent ions (V^{++++}). The potential for the reaction $\text{V} \rightarrow \text{V}^{++++}$ was found to be approximately -0.3 to -0.4 volt. The article contains much experimental data, but unfortunately they lack accuracy, due to the experiments being conducted with vanadium which contained 8.66 percent carbon.

Muthmann and Frauenberger showed that vanadium under certain conditions possessed passivity. Pure vanadium in a normal solution of potassium hydroxide shows at the beginning a potential of -0.13 volt; but after ten minutes a maximum value was obtained, namely 0.737 volt. This property of passivity is shown more or less after treating the vanadium with oxidizing agents or after anodic polarization. ("Berichte der königlichen bayrischen Akademie der Wissenschaften zu München.")

Under "Vanadium," in Abegg's "Handbuch der anorganischen Chemie," Vol. III, 683-788, is found valuable information regarding the behavior of the various vanadium ions. Tetravalent compounds may show either acid or basic properties. The acid compounds have formula VX_4 , while the basic are of the type VOX_2 . Under this latter type of ion comes the vanadyl-ion (VO^{++}) and the divanadyl-ion (V_2O_2) $^{+++}$. The cathions (V^{++++}) or

$V(OH)^{+++}$ show weak electric but strong hydrolytic properties. The trivalent ion (V^{+++}) shows strong positive properties. It is different from the ions of the other metals of the same periodic group, as it does not form the compound VH_3 . The electro-positive property of the tri-valent (V^{+++}) ion is not very great, because this ion very readily forms double salts, similar to Al^{+++} , Fe^{+++} , Cr^{+++} and Mo^{+++} . The di-valent ion (V^{++}) possesses still stronger positive character. It forms double salts with $FeSO_4$ and $MgSO_4$, strongly resembling the magnesium group of metals. The di-valent ion is very readily oxidized, and in its reducing power reminds one of the Cr^{++} ion.

In a dissertation entitled "Measurements of the reduction potential of solutions of diverse solutes forming vanadium compounds," published in Leipzig in 1906, T. F. Rutter gives the results on the determination of the electromotive behavior of the chains, $V^{++} \rightarrow V^{+++}$, $V^{+++} \rightarrow V^{++++}$, and $V^{++++} \rightarrow V^{+}$ from solutions containing V^{II} and V^{III} , V^{III} and V^{IV} , and V^{IV} and V^V compounds in changeable quantities. The solutions investigated were compared with a mercurio-sulphate electrode in a 0.5 normal H_2SO_4 solution of potential 0.679 volt. The results obtained are as follows:



0.1n V^{II} ; 0.5n H_2SO_4 (free from V^{III})	Potential 0.909 volts
0.05n V^{II} ; 0.05n V^{III} ; 0.5n H_2SO_4	" 0.889 "
0.033n V^{II} ; 0.066n V^{III} ; 0.5n H_2SO_4	" 0.881 "
0.025n V^{II} ; 0.075 V^{III} ; 0.5n H_2SO_4	" 0.875 "
0.1n V^{III} ; 0.5n H_2SO_4 (free from V^{II})	" 0.464 "

(Mercury electrode used was positive.)



0.1n V^{III} (free from V^{II} and V^V)	Potential 0.462 volts
0.075n V^{III} ; 0.025n V^{IV}	" 0.397 "
0.05n V^{III} ; 0.05n V^{II}	" 0.373 "
0.025n V^{III} ; 0.075n V^{II}	" 0.363 "
0.1n V^{IV} (free from V^{III} and V^V)	" 0.051 "

(Mercury electrode used was positive.)



0.1n V^{IV} (free from V^{III} and V^V)	Potential 0.051 volts
(Mercury electrode, used positively.)	
0.05n V^{IV} ; 0.05n V^V	Potential 0.241 volts
0.1n V^V ; 0.5n H_2SO_4 (free from V^{IV})	" 0.462 "

(Last two experiments, mercury electrode used negatively.)

Rutter also found that vanadium of its own accord could form ions of the type VO^{+} from V^{+++} ; VO_2^{+} , VO_3^{+} , and $V_6O_{17}^{+++}$. Also if the ratio of ($V^{II} \cdot V^{III} = 0.05 \cdot 0.05$) and ($V^{III} \cdot V^{IV} = 0.05 : 0.05$) existed, then the single potentials are respectively $+ 0.21$ and $- 0.30$. This means that the tendency to form V^{II} to V^{III} is greater than the tendency to change H to H^+ ; and the potential to change V^{III} to V^{IV} is greater than that to change Ag to Ag^+ : therefore, vanado-salts liberate hydrogen, and vanadi-salts liberate silver or copper of the solution of copper sulphate used is concentrated and heat applied. Vanadyl salts, according to the author are very weak reducing agents, they being readily oxidized by permanganic acid, chromic acid and hydrogen peroxide, slowly by persulphates, and only slightly by iodine and bromine. Rutter also established the fact that various oxides of vanadium immediately come to an equilibrium. Further information on this subject may be found in an article published by the same author in the "Zeitschrift für anorganische Chemie," **52**, 368-396, on "The Contribution to the Knowledge of the Compounds of Vanadium." This article deals in detail with the extract given from his thesis.

Stahler and Wirthwein prepared vanadic salts (V^{+++}) and followed the progress of reduction by titrating part of the electrolyte at different stages of the experiments with potassium permanganate ("Berichte," **38**, 3978).

A. Bültemann quotes the work of Piccini and Brizzi who, in the "Zeitschrift für anorganische Chemie," **11**, 106, and **19**, 394, published two articles on the reduction of penta- and tetra-valent vanadium salts by means of electrolysis. Both articles show that the penta- and tetra-valent compounds are reduced to the tri- and di-valent state respectively, by electrolysis. Bültemann continued the investigation of the double salts of vanadium, corresponding to the ordinary alums. The preparation of these vanadium alums by electrolysis was based fundamentally on keeping the anode and cathode liquors separated by means of a porous cell. He describes the apparatus used and the various salts prepared. The only one of interest is the vanadium-ammonium alum, $V_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$. The anode liquor used was sulphuric acid of the same concentration as the cathode liquor, which consisted of 100 cubic centimeters of a sulphate solution

of tetra-valent vanadium. The catholyte was prepared as follows: 25 gm. of acid ammonium metavanadate was dissolved in 31.4 grams of concentrated sulphuric acid, and heated on a water bath with 200 cc. of saturated sulphurous acid until all the vanadium was in solution. This solution then had a blue color, indicating the presence of the tetra-valent compound. This process requires time, and much of the water was evaporated. After cooling, the solution was filtered; the filtrate after being made up to 100 cc. was ready for electrolysis. The anolyte was put into the porous cup and placed in a beaker of convenient size, and the catholyte added. A platinum wire, 0.15 cm. in diameter, served as anode. The cathode was circular in shape, having an area of 160 square centimeters, and was made of lead. Good circulation of the electrolyte was required which was accomplished by introducing a current of hydrogen. Used 8 amperes, that is 0.05 ampere per square centimeter. Duration of experiment was 43 minutes; voltage 8 to 9; temperature 80° C. At the end of the experiment, the catholyte was poured off and allowed to cool in a closed vessel. A large quantity of bluish-violet crystals of vanadium ammonium alum separate out.

Bültemann observed that this alum occurs in two modifications, analogous to chromium aluminium. By treating the ammonium metavanadate with less sulphuric acid than called for above, he obtained after electrolysis a brown solution instead of a green one, as before; and the crystals separating out were of garnet color instead of bluish-violet. These red crystals in acid solution changed to the bluish-violet crystals. The garnet crystals may also be obtained by recrystallizing the bluish-violet ones from an acid solution. The alum is fairly stable, but if the solution is in contact with air it readily oxidizes. ("Zeitschrift für Elektrochemie," **10**, 141-143. Contribution to the knowledge of the electrolytic preparation of tri-valent vanadium salts.) This alum may prove of value in obtaining metallic vanadium from aqueous electrolytes (Fischer).

Eugen Renschler prepared the tri-valent vanadium ammonium sulphate similarly to Bültemann, "Zeitschrift für Elektrochemie," **18**, 137 (1912). The preparation of vanadium salts by electrolysis.

Dr. R. Luther found that chloric acid oxidizes more readily by

electrolysis if tri-valent vanadium is present in the electrolyte. With no vanadium present in the acid solution 1.8 volts were required for electrolysis at the start, rapidly decreasing to 0.6 volt; with vanadium present the electromotive force rose to 2.2 volts. When the ClO_3 ion was present there was much less polarization. "Elektrochemische Aktivierungserscheinungen" (The electrochemical activity shown by vanadium compounds), "Zeitschrift für Elektrochemie," **13**, 1907.

Bleecker mentions a method for obtaining vanadic acid electrolytically. Notes on the chemistry and metallurgy of Vanadium: "Metallurgical and Chemical Engineering," **8**, 666-671; and **9**, 209-213, 499-505. The article is divided into three parts: I. The Chemistry; II. Methods of Analysis, and III. The Metallurgy. Sodium vanadate liquor, free from chlorides, is purified by making the solution slightly alkaline with sodium carbonate and heating up to 90°C . The liquor is decanted into an evaporator and concentrated to 30° Baumé, giving a solution which will contain about 200 gm. of vanadic acid per liter, depending upon the amount of sodium vanadate present. Electrolyze in a compartment cell, consisting of a porous cup of 8 liters capacity which contains the vanadium liquor, and a jar holding 5 to 10 gallons (19 to 39 liters), containing a dilute solution of sodium hydroxide. The anode is platinum foil 6 in. x 6 in. (15 cm. x 15 cm.), and the cathode is either iron or copper; preferably the latter. The voltage used depends upon the resistance of the porous cell and is about 6 to 8 volts. The current density will be 30 amperes per square foot (33 amp. per sq. dm.). The sodium ions pass through the porous partition into the cathode compartment, leaving vanadic oxide ions in the anode compartment. Since sodium vanadate is very soluble in water, and vanadic acid practically insoluble, a precipitation occurs on removing the alkali. The presence of mineral acids interferes seriously with the reaction, since vanadium oxide is soluble in dilute acids. If small amounts of chlorine are present in the electrolyte it is partly liberated at the anode, part forms complex vanadyl compounds, giving an impure product. The presence of sulphuric acid causes the precipitation of sodium vanadyl-sulphate containing 73 per cent vanadic acid. Any lime or silica not previously removed by filtration will precipitate in part in the anode compartment just

as the solution becomes neutral. Some impurities enter the product in spite of the best care taken in the manipulation, probably due to the disintegration of the porous cell.

A patent was granted Blecker on a process for the electrolytic separation of vanadium and uranium (U. S. Pat. 1,050,796, Jan. 21, 1913). The solution containing these two elements is heated to 90° C., and treated with sodium hydroxide in sufficient quantities to precipitate the uranium. The precipitate thus formed contains some vanadium hydroxide which is recovered by electrolysis as follows: the precipitate is well washed with water and then dissolved with sulphuric acid. The solution is then made slightly alkaline with sodium carbonate and electrolyzed with an anode of iron, nickel, or copper. The vanadium is recovered as vanadium oxide, an anode product, the uranium remaining in solution.

P. Truchot determined vanadium by electrolyzing a hot, slightly ammoniacal sodium vanadate solution. The solution was decomposed, depositing the vanadium as an oxyhydrate on the cathode. The vanadium content of the solution may be from 0.012 to 0.05 gm. vanadic acid per 200 cc. of electrolyte. Temperature of electrolyte, 80° to 90° C. The voltage employed was 2 to 2.25 volts, and the current density was 0.3 amperes per 8 square centimeter cathode surface. The electrolysis lasted 8 to 10 hours. The successful operation requires that the volume of the electrolyte be kept constant by the addition of water from time to time. The water added should contain a little ammonia. The oxyhydrate is precipitated on the cathode as a brown deposit, and when dried and heated gives vanadic acid. "Les Annales: Chimie analytique applique, 7, 165-167." "Chemisches Zentralblatt," LXXIII, 5, 1423-1424.

R. E. Myers electrolyzed a sodium vanadate solution acidulated with sulphuric acid, using a mercury cathode. The electrolyte changed from a blue to a green color, but no increase in weight was observed at the cathode. ("Electrochemical Analysis by use of a Mercury Cathode," Journal of the American Chemical Society, 26, 1130.)

2. *Electrolysis of Aqueous Solutions of Vanadium Salts for Obtaining Metallic Vanadium.* In a statement made by Blecker