THE ELECTROLYSIS OF SOLUTIONS OF SODIUM NITRITE USING A SILVER ANODE.

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(*A Paper read before* THE FARADAY SOCIETY, *Monday, July* 14, 1919, PROFESSOR ALFRED W. PORTER, F.R.S., VICE-PRESIDENT, *in the Chair.*)

A compound derived from sodium nitrite and silver nitrite has been known for many years. More recently Pick (1) examined a dilute aqueous solution of silver nitrite and potassium nitrite by the Bodländer method, and obtained evidence of the existence of the complex anion $\left\{Ag(NO_2)_2\right\}$.

Marcel Oswald (2) studied the equilibrium of the system water—sodium nitrite—silver nitrite, and gave the diagram for 14° and for 22°. In each case the curve consists of three distinct portions, the middle portion corresponding with solutions in equilibrium with the solid phase $2\left[Na\,Ag(NO_2)_2\right]H_2O$.

It seemed interesting to examine the reactions which might take place at the anode during the electrolysis of solutions of sodium nitrite using a silver anode. The cell employed was formed of a beaker of 600 c.c. capacity inside, which was a porous pot. The cathode was of smooth platinum, and hung inside the pot from a platinum wire in such a manner as not to touch the bottom of the pot. The anode was of Stas-silver and was bent into a cylindrical shape so as to stand on the bottom of the beaker. It was connected with a platinum wire above the surface of the electrolyte. A glass stirrer turned by a motor revolved rapidly close to the anode. The beaker and its contents were placed in a large vessel of cold water.

For most of the experiments the volume of the anolyte was about 100 c.c., and the temperature 12° to 16°.

The sodium nitrite was obtained by re-crystallising the crude material. It was free from sulphate and chloride, and contained 98.6 per cent. of $NaNO_2$, the rest being nitrate.

Solutions of the following concentrations were used as electrolytes, the catholyte and anolyte being of the same concentration—70 gms. $NaNO_2$, 65 gms. $NaNO_2$, 50 gms. $NaNO_2$, 30 gms. $NaNO_2$, and 10 gms $NaNO_2$ per 100 gms. water.

In no case was any silver deposited on the cathode, nor was there any silver compound present in the catholyte; for these experiments the current was often kept constant during more than twenty-four hours. The area of the anode immersed was 2×47.3 cms.^{2}, and currents between the limits 0.07 amps. and 0.46 amps. were used.

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(1) Zeit. anorg. Chemie 1906, *51*, 1.

(2) Annales de Chimie 1914, *1*, 32.

Silver went into solution from the anode, the colour of the anolyte becoming a bright yellow, which deepened during the progress of the electrolyses. No oxygen or other gas was evolved at the anode, but in all cases a gradually increasing solid deposit was formed on the anode, more rapidly the smaller the concentration of $NaNO_2$ in the anolyte. During ten to twelve hours from the beginning of the electrolysis this deposit was firmly attached to the anode, and did not cause any appreciable resistance to the current, but at a later stage a coherent film was formed which was partially in contact with the silver, and the effect of this was to produce a badly conducting system which gradually reduced the current almost to zero.

To examine this material the anode was drained as free as possible from the anolyte, dried in the air and some of the outermost portion of the layer detached. This gave nitric peroxide with dilute acetic acid, leaving a residue of silver; the dried material when decomposed by heat was found to contain 71.1 per cent. of silver. The anode with the material on it was left in water at 28° for some hours, the resulting solution was filtered and surrounded with ice for six hours. Transparent, almost colourless needle-shaped crystals were obtained; when matted together these appeared a very faint primrose yellow. After being dried over concentrated sulphuric acid, they were analysed by heating them; nitric peroxide was evolved, and the silver residue was 70.07 per cent. of their weight—0.2509 gms. of crystals were taken—for $AgNO_2$ per cent. $Ag = 70.13$.

The film, therefore, appears to be principally silver nitrite with which is mixed a small percentage of finely divided silver due to disintegration of the anode.

Silver nitrite is soluble in an aqueous solution of sodium nitrite, but in spite of rapid stirring and low current density—0.072 amp. per 2×47.3 $cms.^2$—the rate of soluton of the silver nitrite during these electrolyses was slower than its rate of formation.

The complex silver anion which is produced and the undissociated compound corresponding with it appear to be derived from the direct action of the NO ions on the anode to a greater extent than from the solution of the silver nitrite since in a given number of hours more silver went into solution when the current was flowing than when it was stopped, although in each case there was silver nitrite on the anode and stirring was maintained. It seems probable that in the immediate neighbourhood of the anode the anolyte becomes saturated with the complex more rapidly than fresh portions of the liquid reach the anode, and that the silver nitrite is deposited owing to the decomposition of the complex.

The NO_3 ions from the nitrate present do not react with the silver anode to the extent necessary to produce a concentration of silver cathions such as would give a deposition of silver on the cathode.

In order to get further evidence as to the effect of NO_3 ions in the anolyte a solution of 30 gms. $NaNO_2$ + 10 gms. $NaNO_3$ in 100 gms. water was used as anolyte, the catholyte was a solution of 30 gms. $NaNO_2$ alone in 100 gms. water.

With a current of 0.072 amp. during seventeen hours there was no increase in weight of the cathode. With a current of 0.30 amp. during forty minutes there was likewise no increase in weight. In each case after the second weighing the cathode was left in dilute nitric acid; when sodium chloride was added to this there was not the slightest turbidity.

A film formed on the anode in the same manner, and as far as could be judged at the same rate as when an anolyte of 30 gms. $NaNO_2$ alone in 100 gms. water was used with the same current. The film was examined in the way previously described. Similar needle shaped crystals were obtained containing 70.08 per cent. silver—0.2100 gms. of crystals were taken—for $AgNO_2$ per cent. $Ag = 70.13$, and as before the film appeared to consist of silver nitrite mixed with a small proportion of finely divided silver.

These results do not indicate any effect on the anode reaction due to the NO_3 ions.

The presence of silver nitrite on the anode must give rise to a concentration of silver ions appreciable by measuring the potential difference of the silver anode relative to the anolyte; the dissociation of the complex anion must also contribute an appreciable concentration of silver ions. Hence measurements of the anode potential were made.

The potentiometer used was of the "Granta" type made by Messrs. Pye of Cambridge, this in conjunction with a standard cadmium cell and sensitive suspended-coil galvanometer enabled direct readings to 10^{-4} volt. to be made. The normal electrode used was made from a strip of Stas silver, which had been plated from a cyanide bath, and a normal solution of potassium chloride saturated with silver chloride. The connecting tube of this electrode was fitted with a glass stop cock and dipped into a saturated aqueous solution of ammonium nitrate. A siphon tube connected this latter solution with the anolyte, one of its limbs being in contact with the anode. The liquid filling the siphon was that used for the anolyte at the commencement of the experiment. The anolyte was stirred continuously during the electrolysis and during all measurements. The electrolysis cell, the beaker containing the ammonium nitrate solution and the normal electrode were immersed in a large volume of water which was kept at a constant temperature of 18° C.

The sodium nitrite used was pure as far as could be ascertained from the results of analysis—a note on the method and the results is appended.

(i) Exactly 100 c.c. of a solution containing 30 gms. $NaNO_2$ per 100 gms. water was taken for anolyte and 50 c.c. of the same solution for catholyte. The current was 0.072 amps. After three hours from the beginning of the electrolysis the E.M.F. of the combination anode in anolyte and normal electrode was measured first while the current was passing and then when it was stopped; two hours later another similar pair of measurements was made, and two hours later a third pair was obtained. During these seven hours the current was constant, but after this period no further measurements were made partly because of possible disturbance due to the film and partly because the effects of migration from the catholyte would become considerable. Before each pair of measurements the anode was strongly heated in a gas-flame.

The results were :—

	Current on.	Current off.
After 3 hours	0.326 volts.	0.275 volts.
,, 5 ,,	0.338 ,,	0.292 ,,
,, 7 ,,	0.348 ,,	0.302 ,,

The silver anode was the positive pole of the combination.

If the potential of the normal electrode Ag/AgCl, N. KCl/at 18° be taken as 0.513 volts, the silver being positive to the solution, the anode potentials corresponding with the figures given above were :—

	Current on.	Current off.
After 3 hours	0.839 volts.	0.788 volts.
,, 5 ,,	0.851 ,,	0.805 ,,
,, 7 ,,	0.861 ,,	0.815 ,,

It has been assumed that the diffusion potential was practically annihilated by the ammonium nitrate. (Cumming.)

(ii) Exactly 100 c.c. of a solution containing 30 gms. $NaNO_2$ + 10 gms. $NaNO_3$ per 100 gms. water was taken for anolyte, for catholyte 50 c.c. of a solution containing 30 gms. NaNO per 100 gms. water. The current was 0.072 amps. A series of measurements precisely similar to those described in (i) was made. The results were :—

	Current on.	Current off.
After 3 hours	0.330 volts.	0.283 volts.
,, 5 ,,	0.339 ,,	0.290 ,,
,, 7 ,,	0.343 ,,	0.294 ,,

The silver anode was the positive pole of the combination. The corresponding anode potentials were :—

	Current on.	Current off.
After 3 hours	0.843 volts.	0.796 volts.
,, 5 ,,	0.852 ,,	0.803 ,,
,, 7 ,,	0.856 ,,	0.807 ,,

These results do not show that in the immediate neighbourhood of the anode the concentration of the silver ions was increased by the presence of the nitrate.

Both in (i) and in (ii) the difference of a number in the first column from the corresponding number in the second is proportional to the rate of work at the time of measurement involved in the transfer of electricity from the anode to the liquid in contact with it. In each case this was approximately constant, being about 0.0035 watts for (i) and about the same number of watts for (ii). This affords some evidence that throughout the period of electrolysis examined the reactions in (i) and in (ii) were essentially the same and that possibly only one species of complex ion was formed at the anode.

To isolate a solid salt corresponding with the complex anion it was found convenient to use an anolyte of concentration 50 gms. sodium nitrite per 100 gms. water and a current of 0.072 amps. The 98.6 per cent. material was employed for this. The electrolysis lasted for fifty-five hours, it was necessary to clean the anode several times during the latter part of this time to keep the current approximately constant. The anolyte was filtered and left to evaporate iso-thermally over concentrated sulphuric acid in an exhausted desiccator. After seventy-two hours a crop of small, well-shaped, bright-yellow crystals was obtained. These were pressed between filter paper, left over concentrated sulphuric acid for five hours and then finely powdered, the powdered material was then left over phosphoric oxide in an exhausted desiccator until the weight became constant—this required about six days. The percentage of silver was determined gravimetrically from a dilute nitric acid solution, the percentage of NO_2 by means of potassium permanganate from an equeous solution: the percentage of silver found was 48.40 and of NO_2 was 41.48, for $Na.Ag(NO_2)_2$ the calculated percentages are 48.41 and 41.29.

If the iso-thermal evaporation was allowed to proceed further crystals were obtained which were not definite chemical individuals. their composition depended on the time at which the evaporation was stopped and ultimately it was easy to distinguish two types of crystals. The results of analysis corresponded with a mixture of NaNO and of $Na.Ag(NO_2)_2$, the proportion of $NaNO_2$ increasing with the duration of the evaporation.

The effect on the reaction of raising the anode potential was also examined. The same material and the same quantities were used as for the measurements in (i). A current of 0.072 amps. flowed for thirty-five minutes through a freshly prepared solution of the pure nitrite before the series of measurements given below was commenced. Before each pair of measurements the anode was washed and heated strongly in a gas-flame; the area of the anode was 2 × 25.4 cms.^{2} and the temperature was 18° C. as before.

Current in amps.	E.M.F. in volts, current on.	E.M.F. in volts, current off.	Rate of work at anode in watts.	Anode potential in volts, current on.
0.072	0.284	0.234	0.0036	0.797
0.16	0.315	0.247	0.0109	0.828
0.25	0.349	0.253	0.0238	0.861
0.35	0.379	0.261	0.0413	0.892
0.45	0.415	0.266	0.0670	0.928
0.55	0.458	0.284	0.0957	0.971

If the anode potential when the current is on be plotted as a function of the current a straight line is obtained; if the rate of work involved in the transfer of electricity from anode to anolyte be plotted as a function of the current a line slightly convex to the current axis is obtained.

The results afford some evidence that the nature of the chemical reaction does not change within the range examined; the very rapid formation of the deposit at higher potentials prevented further measurements.

Experiments with other metals and the same anolyte are in progress.

Note on the estimation of the nitrite. The burette, flask and pipettes used were correct at 15° C. A solution of the recrystallised sodium nitrite of concentration 0.9874 gms. per 500 c.c. was put in the burette and was run in drop by drop to a solution at 65° of 25 c.c. 0.9362 N/10 permanganate + 200 c.c. water + 100 c.c. dilute H_2SO_4 (1 to 8), which was shaken continuously.

This method gave the per cent. $Na\ NO_2$ in the specimen 100.5. Some silver nitrate was prepared from Stas silver and from a solution of this $Ag\ NO_2$ was precipitated. This was recrystallised and analysed gravimetrically by heating it. The per cent. silver found was 70.12, the calculated percentage is 70.13. A solution of this $Ag\ NO_2$ was made of concentration 1.0562 gms. per 500 c.c. It was titrated, as described above, with 10 c.c. 0.9362 N/10 permanganate + 200 c.c. water + 100 c.c. dilute H_2SO_4.

This method gave the per cent. $Ag\ NO_2$ in the specimen 100.7.

I am again indebted to Col. C. T. Heycock, M.A., F.R.S., Goldsmiths Reader in Metallurgy. He has given me every facility, the accurate measuring vessels for volumetric analysis were lent to me by him; on many occasions I have also had the advantage of drawing on his experience and have profited much thereby. I am very grateful to him for his kindness.

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