ELECTROLYTIC PREPARATION OF SODIUM PERMANGANATE

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Manganese, used as an anode in an alkaline solution, gives permanganate, manganate, manganese dioxide and manganous hydroxide, the particular product and the current efficiency depending upon the concentration of the alkali, the temperature of the electrolyte, and the current density. In this investigation we studied the effect of temperature, current density, and concentration of the alkali upon the production of sodium permanganate.

The formation of permanganate at a manganese anode in alkaline solutions was first discovered by Lorenz.¹

Müller² studied the anodic behavior of manganese in solutions of sodium sulphate and sodium di-hydrogen phosphate, with and without the addition of sodium hydroxide. He showed by polarization measurements that hydroxyl ions produced passivity.

White³ states that ferromanganese anodes in sodium hydroxide solutions form manganous hydroxide at low current densities. He found that this could be readily oxidized electrolytically to manganese dioxide but not to permanganate. Neither was he successful in oxidizing the manganese dioxide electrolytically to permanganate. From this he concluded that the electrolytic formation of permanganate is a direct reaction not involving manganous hydroxide or manganese dioxide as intermediate steps. At 95° C he secured the green manganate.

Wilson and Horsch⁴ state that they secured the best current yields of sodium permanganate from ferromanganese anodes in sodium carbonate solutions, at low temperatures and

¹ Lorenz: Zeit. anorg. Chem., 12, 393 (1896).

² Müller: Zeit. Elektrochemie, 11, 755 (1905).

³ White: Jour. Phys. Chem., 10, 502 (1906).

⁴ Wilson and Horsch: Trans. Am. Electrochem. Soc., 35, 371 (1919).

with a current density of about 13 amperes per square decimeter, but they give no quantitative results to show the effect of temperature and current density. The major portion of their article is concerned with the development of a commercial process, the object being to secure a pure solution of the permanganate to meet the Government's requirements, as impurities caused serious deterioration in the resulting soda-lime.

Thompson¹ gives the results of some experiments carried out on a large scale. He used ferromanganese anodes in a 24 percent potassium carbonate solution and secured a current efficiency of 17 percent.

In our experiments we used a manganese anode containing 92.0 percent manganese, the impurities being for the most part iron, silicon and carbon. The anode was made by reducing pyrolusite with coke in an electric arc furnace. Connection with the anode was made by soldering a copper wire onto one edge of it. The anode had a surface of 30 square centimeters on each side. In calculating the current density 45 square centimeters or $1\frac{1}{2}$ times the area of one side was used, since there was only one cathode on one side of the manganese anode. The electrolysis was carried out in a beaker $8\frac{1}{2}$ cm in diameter by $11\frac{1}{2}$ cm high. This was kept within two degrees of the indicated temperature by placing in a water bath. To secure the lower temperatures a cooling coil was also used, which was placed inside the vessel. The cathode consisted of a perforated platinum plate having a surface of 10 square centimeters counting both sides. The electrolyte was in each case 350 cc. The amount of current used was indicated by an ammeter, slight variations being noted. Before each electrolysis the manganese anode was scrubbed with an iron wire brush, in order to have it in as nearly the same condition as possible at the start of each experiment.

The amount of permanganate formed was determined by pipetting out a portion of the electrolyte, which was acidi-

¹ Thompson: Chem. Met. Eng., 21, 680 (1919).

fied with sulphuric acid, heated to 65°C and then reduced by a known amount of a standard solution of oxalic acid, an excess being added which was titrated with a standard solution of potassium permanganate. Since the manganese is oxidized to a valence of seven, one ampere hour should produce 0.7566 gram of sodium permanganate which is equivalent to 265.5 cc of a decinormal solution of oxalic acid.

In some preliminary experiments a porous cup was used. This worked nicely for a time but soon the resistance of the cup would begin to increase and the voltage would rise to a prohibitive figure. On breaking the cup the walls were found to contain a deposit of a brownish black oxide of manganese. Morse and Olsen¹ encountered the same difficulty in making permanganic acid. This led us to attempt the formation of the permanganate without the use of a diaphragm. The electrolyte was a solution of caustic soda containing 10 grams of sodium hydroxide per liter. Using a current of 3.5 amperes (current density 7.7 amperes per square decimeter), at 25°C for one hour the current efficiency was 16.4 percent, while in a similar electrolysis, except with the addition of an excess of calcium hydroxide, the current efficiency was 32.8 percent. That is, under these conditions, the addition of an excess of lime increased the current efficiency about 16 percent. There was a great deal of difference in the appearance of the platinum cathode under the two conditions. Without the lime it was covered with a coating of a black oxide of manganese, probably manganese dioxide, while with the addition of the calcium hydroxide the coating on the cathode was very similar in color to that of manganese. It seems as though the calcium hydroxide formed a film over the cathode which acted as a diaphragm. In the following experiments no diaphragm other than that formed by the calcium hydroxide was used.

The results of Table I are plotted in Plate I. The current efficiency, which is plotted in Curve A, rises rather rapidly

¹ Morse and Olsen: *Am. Chem. Jour.*, 23, 431 (1900).

TABLE I

Effect of Current Density on Current Efficiency
Temperature 25°CElectrolyte—350 cc of NaOH solution containing 10 grams NaOH per liter. To this an excess of $\text{Ca}(\text{OH})_2$ was added
Time of passage of current—one hour

Current strength amperes	Current density amperes per sq. decm	Bath tension volts	Anode discharge potential volts	NaMnO ₄ formed grams	Current efficiency in percent of theory
0.75	1.66	3.4	—1.157	0.0250	4.4
1.52	3.38	4.0	—1.239	0.2351	20.5
2.62	5.82	5.3	—1.415	0.5547	28.1
2.98	6.66	5.5	—	0.6774	30.1
3.5	7.78	5.9	—1.445	0.8593	32.5
3.83	8.52	6.3	—	0.9795	33.8
4.7	10.43	7.0	—1.445	1.1844	33.4
5.7	12.68	7.8	—1.445	1.4626	34.2
6.9	15.33	8.6	—1.485	1.6288	31.2

with increase in current density up to 6 amperes per square decimeter and then less rapidly up to 12.7 amperes per square decimeter, after which it declines slightly. In Curve 8 the anode discharge potential is plotted. This was measured after the current had been passing half an hour. In calculating the discharge potential the voltage of the calomel half-cell was taken as -0.56 volt. The results show that the discharge potential increases with increase in current efficiency calculated from the formation of permanganate. In the case of lead anodes¹ in sodium hydroxide solutions the corrosion decreased when the anode discharge potential increased.

Plate I

¹ Brown, Henke and Smith: Jour. Phys. Chem., 24, 367 (1920).

The results of Table II are plotted in Plate II. Curve A shows the decrease in current efficiency with increase in

TABLE II

Effect of Temperature on Current Efficiency
 Current density 12.7 amperes per square decimeter
 Electrolyte—350 cc of NaOH solution containing 10 grams NaOH per liter. To this an excess of $\text{Ca}(\text{OH})_2$ was added
 Time of passage of current—one hour

Current strength amperes	Temperature degrees centigrade	Anode discharge potential volts	NaMnO_4 formed grams	Current efficiency in per cent of theory
2.93*	8	—	0.8548	38.6
2.78*	16	—1.445	0.7518	35.8
5.70	25	—1.445	1.4726	34.2
5.63	40	—1.363	0.8548	20.1
5.70	60	—1.211	0.1342	3.1

temperature. The efficiency decreases from 38.6 percent at 8°C to 8.1 percent at 60°C . Besides the decrease in effi-

Plate II

ciency the color of the solution was different at 60°C . The color indicated that there was a large amount of manganate along with the permanganate. Also at 40° and 60°C the platinum cathode was covered with a black coating probably manganese dioxide, even though there was an excess of calcium hydroxide present. At the lower temperatures there was no black coating on the cathode.

This indicated that the lime

did not make as good a diaphragm at the high as at the low temperatures. Curve B shows the decrease in anode dis-

* Only one-half of the anode was immersed in the electrolyte.

charge potential with temperature, the discharge potential decreasing with the current efficiency as it did in Plate I, Curve B.

TABLE III

Effect of Concentration of Sodium Hydroxide on Current Efficiency
Temperature 25° C

Current density—12.7 amperes per square decimeter
Electrolyte—350 cc of NaOH solution of concentration indicated in column two below. To this an excess of $\text{Ca}(\text{OH})_2$ was added
Time of passage of current—one hour

Current strength amperes	Concentration of NaOH in grams per liter	Bath tension volts	Anode discharge potential volts	NaMnO_4 formed grams	Current efficiency in percent of theory
5.70	10	7.8	—1.445	1.4726	34.2
5.68	30	3.4	—1.234	0.8424	19.6
5.70	75	2.9	—1.114	0.7167	16.6
5.70	112.5	3.0	—1.076	0.8802	20.5
5.75	150	3.0	—1.034	1.0900	25.0
5.75	180	2.9	—1.034	1.0924	25.1
5.85	225	2.8	—1.005	1.1347	25.7
5.82	300	2.9	—1.005	1.2315	28.0

The results of Table III are plotted in Plate III. Curve A shows the effect of concentration of the sodium hydroxide

Plate III

on the current efficiency. The shape of this curve is peculiar in that there is a minimum with maxima on either side.

Thus at a concentration of 10 grams of sodium hydroxide per liter the efficiency is 34.2 percent and at 150 grams per liter the efficiency is 25 percent, while with 75 grams sodium hydroxide per liter the efficiency is only 16.6 percent. At the low concentration permanganate is formed while at the high concentration of sodium hydroxide manganate is formed. So it may be possible that the curve shown in the figure consists of the branches of the two curves, one where the formation of manganate predominates along with some permanganate, and the other where the formation of the permanganate predominates along with some manganate, and that these two curves intersect at the low point in the curve, that is, at a concentration of about 65 grams sodium hydroxide per liter.

At the higher concentrations of the sodium hydroxide the black coating on the cathode was formed. In an attempt to secure a substance that would give a better diaphragm than calcium hydroxide and thus prevent this reduction, we tried the hydroxides of magnesium, strontium and barium, thinking that the solubility of the hydroxide would determine its efficiency as a diaphragm. However, with the concentration of the sodium hydroxide at 150 grams per liter, the efficiency was practically the same with the different alkali earth hydroxides, that is, about 25 percent, although with the strontium hydroxide we got 26.9 percent current efficiency.

Curve B, which shows the effect of concentration of sodium hydroxide on the anode discharge potential, drops continuously from -1.445 to -1.005 volts, although during the latter part of the curve the current efficiency is increasing. In the other two plates the discharge potential increased when the current efficiency increased. In the first part of the curve in Plate III that is also true, but after the minimum in the current efficiency curve is passed the discharge potential continues to decrease although the current efficiency increases. But during the last increase the amount of manganate in proportion to the permanganate formed increases until at a concentration of 300 grams sodium hydroxide per liter the manganate with practically no permanganate is formed.

This would seem to indicate that when the manganese goes into solutions as permanganate the discharge potential is higher than when it goes in solution as manganate. That is, the discharge potential is higher when the manganese goes into solution with a valence of seven than it is when it goes in solution with a lower valence, which would be six in the case of manganate. A similar occurrence is found when lead is used as an anode in sodium hydroxide solutions.¹ Lead dissolves as a bivalent metal and the discharge potential is low. When dark spots of lead peroxide begin to appear the lead stops corroding properly and the discharge potential increases. Hence it appears that the higher the valence to which the metal is oxidized the higher the discharge potential becomes.

This is further indicated by the following experiment: A solution of sodium carbonate containing 150 grams per liter was used as electrolyte. The current density was 12.7. A porous cup diaphragm was used, the catholyte being a 11 percent sodium hydroxide solution. The temperature was 25° C. The current efficiency was 37.1 percent and the anode discharge potential was -1.61 volts. With strong solutions of the carbonate the permanganate is formed while with strong solutions of sodium hydroxide the manganate is formed. This is also borne out by the discharge potentials. With the carbonate solution permanganate is formed and the anode discharge potential is -1.61 volts, while with the hydroxide solution, containing the same number of grams per liter, considerable manganate is formed and the discharge potential is only -1.034 volts. That is the higher the valence to which the manganese is oxidized the higher the discharge potential.

Conclusions

1. We secured high current efficiencies in the formation of sodium permanganate without the use of a diaphragm.
2. The current efficiency was highest at a current density of about 13 amperes per square decimeter.

¹ Loc. cit.

3. The current efficiency increased with decrease in temperature to over 38 percent at 8° C, and indications are that it would have been still higher at lower temperatures.

4. The higher the valence at which the metal goes into solution the higher the discharge potential.

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