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PERFORMANCE CHARACTERISTICS OF DIFFERENT ANODE SYSTEMS IN EMD DEPOSITION

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A comparison has been made of the behaviour of variety of pretreated/activated anodes, viz., Ti, expanded Ti, Ti/RuO_2-TiO_2, Ti/MnO_2, expanded Ti/MnO_2 during deposition of EMD from sulphate and chloride electrolyte and compared with that of conventional ones, i.e., graphite, bare Ti and platinum with special reference to energy consumption and cell voltage. It is found that cell voltage increases with increase in sulphuric acid concentration in the bath, indicating passivation of the substrate. Ti/RuO_2-TiO_2 anode exhibits a lower cell voltage than bare Ti or Ti/MnO_2 due to lower contact drop between the deposit and the substrate. The employment of expanded Ti/MnO_2 exhibits a cell voltage comparable to that of Ti/RuO_2-TiO_2. In chloride electrolytes, in general Ti/RuO_2-TiO_2 behaves similar to Ti/MnO_2 except that it exhibits a lower cell voltage by about 400-500 mV. Smooth platinum performs poorly due to lower overpotential for chlorine evolution. Chemical manganese dioxide coated anode is more attractive for employment as anode for MnO_2 deposition from either electrolyte.

Keywords: Anode materials, EMD deposition and manganese dioxide

INTRODUCTION

The conventional method of preparing electrolytic manganese dioxide (EMD), otherwise known as battery grade manganese dioxide, is by electrolysing an aqueous solution of a mixture of manganese sulphate (0.5-1.0 *M*) and sulphuric acid (0.2- 0.5 *M*) [1], wherein lead or lead based alloys are used as anodes. The main disadvantage encountered was the contamination of EMD with the heavy metal lead, which is deleterious for its efficient performance in dry cells. Graphite anodes were also employed. However, it became difficult to avoid (a) heavy contamination of the product with the inert material graphite and (b) frequent breakage of the anodes during handling.

Alternatively, a mixture of manganese chloride and hydrochloric acid has been electrolysed between graphite electrodes to get an EMD sample with better physical, chemical, electrochemical and catalytic properties associated with its fibrous (γ_f) nature [2-5]. The graphite consumption was comparatively less and hence contamination of the same with EMD was largely avoided, but not completely.

Hence to prepare high quality EMD particularly for use in alkaline batteries, the process demands an anode/coating of the following characteristics:

1. Should be chemically as well as electrochemically resistant to the electrolyte to minimise the contamination of the final product with substrate material;
2. Should be capable of providing proper keying for the deposition of EMD;
3. Should possess good bending and breaking resistance to withstand the strain of deposition and stripping alternatively;
4. Should have longer life with minimum maintenance;
5. Should exhibit good electronic conductivity and
6. Should be less expensive.

One of the anode materials largely satisfying all the above special characteristics is the titanium which has been properly pretreated/activated. Studies have been made with plain titanium [1], pltainum plated titanium, RuO_2 coated titanium [6,7] and chemical manganese dioxide coated

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titanium [8] for the deposition of EMD. In this paper bare Ti sheet, expanded Ti, CMD coated Ti/expanded Ti, 'mixed-crystal' oxide of Ru and Ti coated on titanium sheet and smooth Pt were employed as anodes and their performance characteristics have been compared with the conventional graphite anode with particular emphasis on energy consumption, life and cell voltage.

EXPERIMENTAL

Mixed crystal oxide of Ru and Ti coated on Ti anode of size 1x50x200 mm prepared by the usual pyrolysis technique was used. Similar size of titanium sheet coated with manganese dioxide described elsewhere [9] and graphite sheet have been employed for comparison. The electrolytic cell consists of a 5 l beaker having an outlet at the top and a lid with provision to introduce an anode at the centre and two side cathodes. Graphite sheets with perforations served as cathodes in all the experiments. The whole set-up was placed on a hot plate provided with simmerstat control so that the temperature of the electrolyte could be maintained constant at a predetermined value. The electrolyte was prepared from LR grade chemicals.

RESULTS AND DISCUSSION

Table I represents the data obtained on electrolysis employing different anode materials and manganese sulphate-sulphuric acid electrolyte system during the preparation of EMD. From experiments 1 and 2, one infers that increase in acid concentration reduces the current efficiency indicating the secondary reaction, viz., copious evolution of oxygen. In addition, average cell voltage increases from 2.08 to 2.2 V with increase in acid concentration from 29 to 49 g/l. This is to be attributed to the gradual attack of the titanium substrate, thereby inducing passivation, which is obvious.

Furthermore, it is evident that Ti/RuO_2-TiO_2 anode exhibits a lower cell voltage than Ti or Ti/CMD.This may be explained by the fact that the precious metal oxide coating, being a metallic conductor, considerably reduces the contact drop between the substrate and EMD, as compared with the other anodes. The employment of expanded Ti with CMD coating exhibits a potential comparable to that of Ti/RuO_2-TiO_2, for the same duration, even with higher acidity. In case of graphite anodes, although the current efficiency is of the same order as with other anodes the energy consumption is the highest due to the contact drop between substrate graphite and less conducting graphitic oxide/EMD deposit.

Table II depicts the data obtained in the electrolysis experiments with different anode materials in chloride electrolyte at two different current densities viz., 50 and 100 A m^{-2}, other conditions remaining the same. From the results of experiments 1 to 4, one could infer that Ti/RuO_2-TiO_2 behaves similar to Ti/CMD, except that it exhibits a lower cell voltage in the range of 400-500 mV. Expanded Ti anode performs with the same current efficiency and that with CMD coating behaves better, although the average cell voltage is 350 mV higher as compared to that of Ti/RuO_2-TiO_2. In case of graphite, the higher current efficiency may be attributed to the porosity of the substrate graphite leading to a larger surface area, thereby making effective current density lower. Consequently, the anode potential is lowered facilitating more of EMD deposition. The poor performance of smooth Pt in chloride electrolyte may be due to the fact that the overpotential for chlorine evolution is less. A similar observation has also been reported for both smooth Pt and compacted graphite, where the reaction Mn^{2+} to Mn^{4+} was

TABLE I: Influence of various anode materials in $MnSO_4$–H_2SO_4 system
$MnSO_4$ = 100 to 150 g/l, current density = 100 A.dm^{-2} and temperature = 371 K

Expt. No.	Anode	Concn. H_2SO_4 g/l	Ave. C.V. V	Duration of electrolysis (hrs)	EMD obtained (g)	Energy kwh/kg	Current efficiency (%)
1.	Ti/RuO_2–TiO_2	29	2.08	144.3	408	1.30	~100.00
2.	Ti/RuO_2–TiO_2	49	2.20	136.0	235	2.16	62.76
3.	Ti sheet/CMD	32	2.40	409.0	1250	1.50	99.00
4.	Bare Ti sheet	50	2.69	16.5*	42	1.90	97.56
5.	Expanded Ti sheet	41	3.03	312.0	800	1.87	100.00
6.	Expanded Ti/CMD	39	2.60	290.0	804	1.50	100.00
7.	Graphite	30	2.76	260.0	631	1.89	90.00

* Passivated after 16.50 hrs

TABLE II: Influence of various anode materials on anode current efficiency in $MnCl_2$–HCl system
$MnCl_2$ = 97 g/l, HCl = 26 g/l and temperature = 353 K

Expt. No.	Anode	C.D. ($A.m^{-2}$)	Ave. C.V. V	Duration of electrolysis (hrs)	EMD obtained (g)	Current efficiency (%)
1.	Ti/RuO2–TiO2	100	2.18	206.00	253.00	44.65
2.	Ti/RuO2–TiO2	50	2.18	281.00	220.00	60.41
3.	Ti/CMD	50	2.57	306.00	280.00	56.30
4.	Ti/CMD	100	2.68	440.00	554.00	44.17
5.	Graphite	100	2.15	1.50	3.90	68.00
6.	Smooth platinum	100	1.69	8.75	Negligible	low
7.	Expanded Ti/CMD	130	2.53	1.50	4.70	60.00
8.	Expanded Ti	130	3.37	146.00	170.00	60.00

retarded [10] as against chlorine evolution. Thus for the production of EMD it is preferable to use low geometrical current densities and anodes of large surface area.

Fig. 1 shows the dependence of cell voltage for Ti/RuO_2-TiO_2 at the start of electrolysis on the number of runs or, in otherwords, the cell voltage at the start of electrolysis on repeated cycling of the anode after each harvesting of the EMD deposit. The cell voltage remains constant upto 11th run, starts steeply increasing at the 12th cycle and reaches approx. 7.5 V, thereby leading to passivation in 13th run, indicating the inadequacy of electrocatalytic activity of the coating. The electrodeposition of manganese dioxide and other possible anodic reactions which may occur and their respective thermodynamic values are presented in Table III.

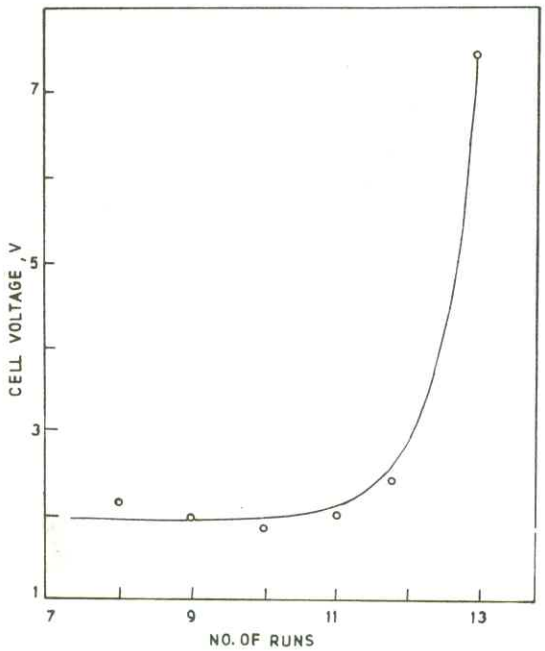

Fig. 1: Dependence of cell voltage on number of runs

According to these values, the most probable one is oxygen evolution in chloride or sulphate solution. However, this is not happening, because of the fact the manganese dioxide coated electrode possesses an overvoltage of 350 to 400 mV [11] for oxygen and chlorine evolution and hence preferentially deposition of manganese dioxide does take place. Although Ti/RuO_2-TiO_2 is the most suitable electrode for chlorine evolution from highly concentrated chloride solutions, still it behaves as a manganese dioxide coated electrode, once initial deposition of EMD takes place in the electrolyte.

Taking into consideration that each continuous electrolysis run lasts for one month, on large scale, which is the usual practice, the Ti/RuO_2-TiO_2 anode could conveniently be employed for 12 successive deposition and stripping, viz., for one full year without any further treatment. On similar experimental basis, it was found that Ti/CMD anode serves for lower number of successive runs (see Table IV).

TABLE III: Probable anodic reactions and their respective potentials vs NHE [11]

Reactions	Potentials (V)	
$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 4e$	1.230	(1)
$2H_2O \longrightarrow O_2 + 4H^+ + 4e$	1.229	(2)
$2Cl^- \longrightarrow Cl_2 + 2e$	1.358	(3)
$Mn^{2+} \longrightarrow Mn^{3+} + e$	1.510	(4)
$Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 8H^+ + 5e$	1.510	(5)
$MnO_2 + 2H_2O \longrightarrow MnO_4^- + 4H^+ + 3e$	1.695	(6)

TABLE IV: A comparison of cost between Ti/RuO_2-TiO_2 and Ti/CMD taking into consideration the following assumptions

	Ti/RuO_2-TiO_2	Ti/CMD
a. Load/m^2	10 g Ru	100 g MnO_2
b. Useful service life, runs	12	2
c. Anode current density employed $A.dm^{-2}$	150	150
d. Cost of chemical/g	Rs.120	Rs.0.20
e. Cost of TiO_2	negligible	—
Cost for coating	Equal for both	Equal for both

Cost of Ru required for getting 1 kg MnO_2 per hour

$$\frac{1000}{1.62} \times \frac{1}{150} \times \frac{10}{12} \times 120 = \text{Rs.}411.50$$

Cost of MnO_2 required for getting 1 kg of MnO_2 per hour

$$\frac{1000}{1.62} \times \frac{1}{150} \times \frac{100}{12} \times \frac{200}{1000} = \text{Rs.}41.15$$

Manganese dioxide coated Ti electrode works out markedly cheaper. Thus Ti/MnO_2 has got the following advantages.

1. Results in noncontamination of the final product of EMD with precious/valve metal oxide/graphite;
2. Results in desired adhesion of the deposit thereby leading to easy removal;
3. Involves less recurring expenditure, as the coating substance could easily be prepared from the intermediate chemical of the process.
4. Lower energy consumption resulting from low contact resistance by the avoidance of the formation of energy wasting barrier layer and dimensional stability.
5. Results in largely circumventing the disadvantages in adopting bare Ti as anode.

CONCLUSION

The comparison of performance of different anode systems for the deposition of EMD indicates that electrocleaned manganese dioxide coated expanded Ti anode lends itself as a good candidate and worth pursuing, particularly from the angle of purity, cell voltage, current efficiency, cost of materials and life.

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