

Electrolytic manganese dioxide from chloride electrolyte: Anode potential measurements

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In the preparation of electrolytic manganese dioxide (EMD) the dependence of anode potentials on conditions of electrolysis, viz., temperature, anodic current density and concentration of hydrochloric acid, has been studied and the behaviour of uncoated and MnO_2 coated graphite in HCl , H_2SO_4 and $\text{MnCl}_2\text{-HCl}$ electrolyte has been compared. It is observed that above 70°C , below an anode current density of 100 Am^{-2} and below a concentration of 20 g/L hydrochloric acid, the deposition of manganese dioxide takes place preferentially. Among the probable electrochemical reactions EMD deposition, oxygen evolution and chlorine evolution occur under the present experimental conditions. The data collected employing an all-glass apparatus also confirm the results.

Electrolytic manganese dioxide (EMD), one of the essential ingredients for the Leclanche' type and alkaline cells, is prepared by electrolysis of a mixture of $\text{MnSO}_4\text{-H}_2\text{SO}_4$ between graphite cathode and lead or graphite or titanium anode¹. Manganese chloride as well as nitrate solutions exhibit a higher conductivity as compared to sulphate. Among them chloride solution is the best alternative taking into consideration the indigenous availability of raw materials as well as cost. Although, lot of fundamental studies have been carried out with respect to sulphate electrolyte², only limited references are available for chloride solutions³. Hence, from the application point of view, an attempt has been made to study the dependence of anode potential under galvanostatic conditions to have a better insight into the problem.

Materials and Methods

A 3 litre glass beaker with a PVC lid having three suitable slots for inserting one anode and two cathodes and provision for inserting a thermometer and a reference electrode, served as the electrolytic cell. Plain and perforated graphite plates of equal size were employed as anode and cathodes respectively. Interelectrode distance was kept as 2.5 cm . Saturated calomel electrode (SCE) or $\text{Hg-Hg}_2\text{SO}_4\text{-1N H}_2\text{SO}_4$ with suitable Luggin capillary served as the reference electrode. The potentials were measured using HIL 2161 digital multimeter and the potentials were converted to hydrogen scale. A 30 V-10 A rectifier was used as the DC source.

The temperature of the electrolyte was maintained at a desired value by placing the glass beaker on a hot plate controlled by Sunvic energy regulator. Each experiment was conducted for a duration of 90 mins. The potentials were recorded every five mins.

The determination of individual current efficiencies for EMD, oxygen and chlorine had been carried out in a fabricated all-glass set-up. The electrolytic cell was made out of B-55 ground joint and capable of holding approx. 200 ml electrolyte. Provision had been made to introduce two cathodes, an anode and a thermometer. An outlet had been provided to suck out the gases liberated. Semicylindrical graphite rods of 1 cm dia served as cathodes, while cylindrical rod served as anode. The experiments were conducted for a duration of 4 h. The gases sucked were passed through the first jar containing a mixture of potassium iodide and thiosulphate solution and then allowed to pass through three others containing alkaline manganese sulphate. From the quantity of iodine liberated and MnO_2 formed in the alkali, the content of chlorine and oxygen liberated were calculated.

Results and Discussion

Influence of temperature

Figures 1 and 2 represent the variation of anode potential with time during electrolysis of $\text{MnCl}_2\text{-HCl}$ at different temperatures. It is evident that increase in temperature of electrolysis decreases the anode potential potential more and more favouring the deposition of manganese dioxide. The

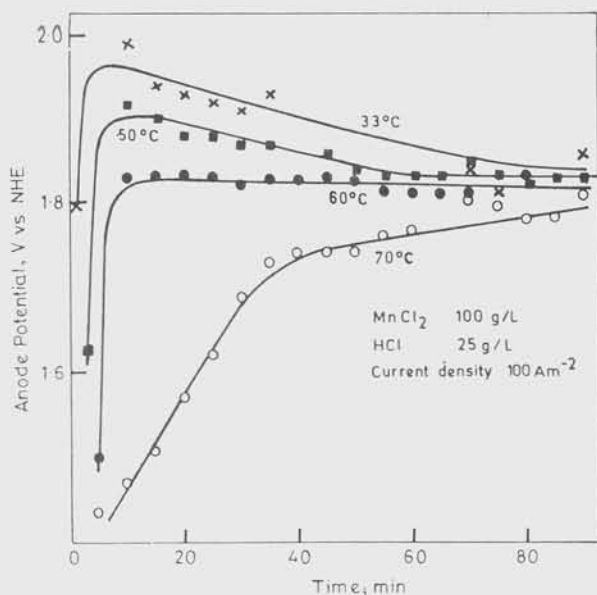


Fig.1—Variation of anode potential with time at different temperatures

dependence of anode potential values on temperature is depicted as an inset of Fig. 2. This clearly indicates that oxygen/chlorine evolution is preferentially taking place along with EMD below 75°C and above 75°C. It approaches the thermodynamic reversible value favouring only EMD deposition.

Influence of anode current density

Figures 3 and 4 indicate the variation of anode potential with time during the deposition of MnO_2 at different current densities. It is found that the rate of change in anode potential is marginal at current densities 30 and 70 Am^{-2} , whereas, it is appreciable with increase in current density from 150 to 500 Am^{-2} . A plot of current density versus anode potential is given as an inset of Fig.3. It is seen that MnO_2 deposition is predominantly taking place up to around 100 Am^{-2} under the said electrolytic conditions, viz. temperature- 80°C, MnCl_2 -102 g/L, HCl-25 g/L. Above 100 Am^{-2} other competing anodic reactions also take place.

Influence of concentration of HCl

The variation of anode potential with time at different concentrations of HCl in MnCl_2 -HCl system is depicted in Fig.5. It is evident that lower the acid concentration lower is the deviation of anode potential with respect to reversible potential

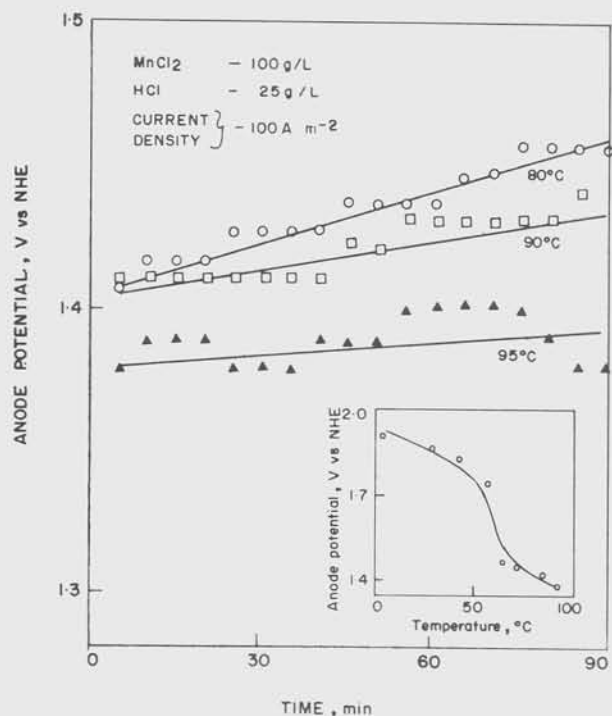


Fig.2—Variation of anode potential with time at different temperatures

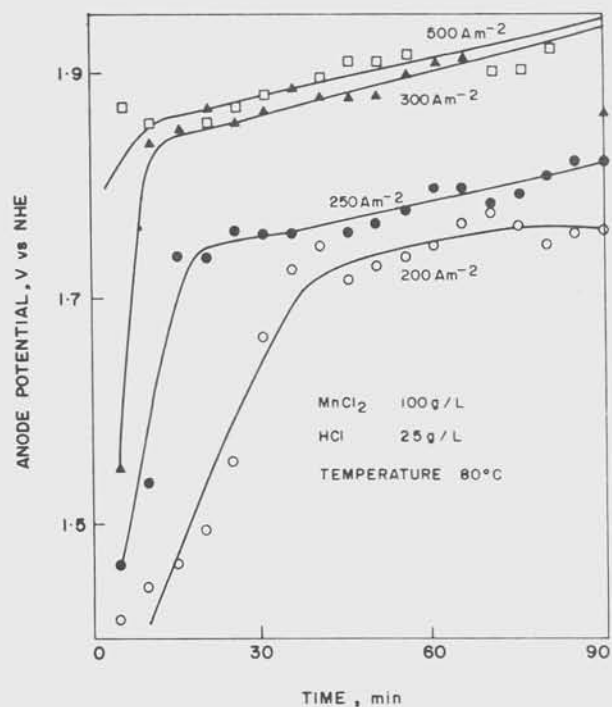


Fig.3—Variation of anode potential with time at different current densities

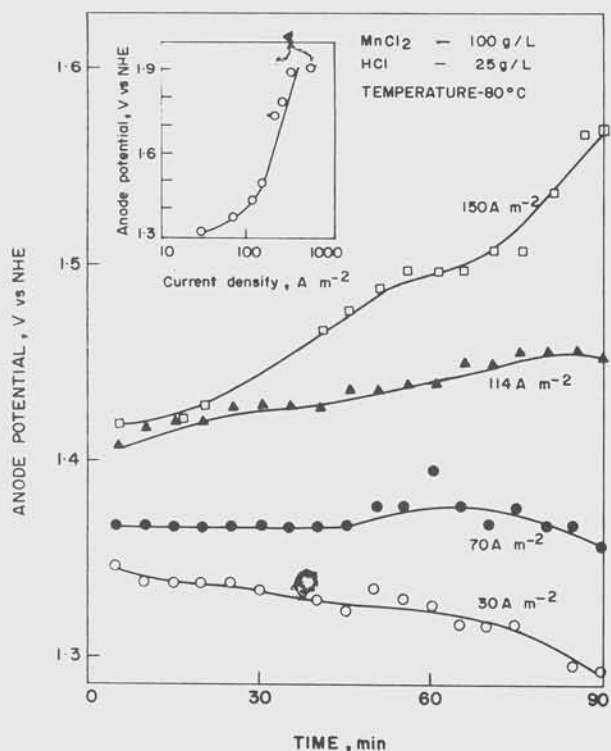
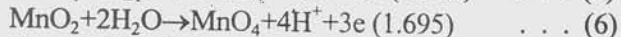
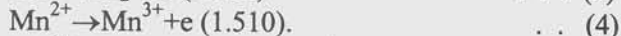
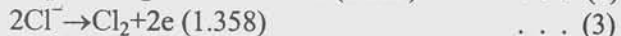
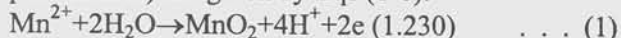


Fig.4—Variation of anode potential with time at different current densities

of the reaction Mn^{2+} to Mn^{4+} , i.e., in neutral solution the reaction takes place at 74 mV higher than the theoretical deposition potential, while it is 156 and 178 mV higher for 20 and 30 g/L HCl respectively under the experimental conditions. In addition, the inset indicates a linear increase of anode potential.

Thermodynamic potentials/overpotentials of the reactions

The anodic reactions that could take place and their respective thermodynamic potentials (in parentheses) are given by Eqs (1-6).



From this it appears that manganese dioxide deposition and oxygen evolution have to take place simultaneously followed by chlorine evolution. In order to allow MnO_2 deposition reaction to take place with near theoretical efficiency in preference to oxygen or chlorine evolution, one has to take

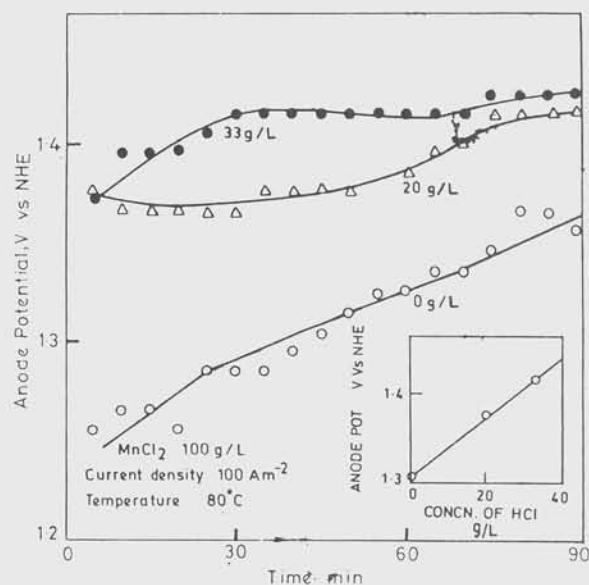


Fig.5—Variation of anode potential with time at different concentrations of HCl

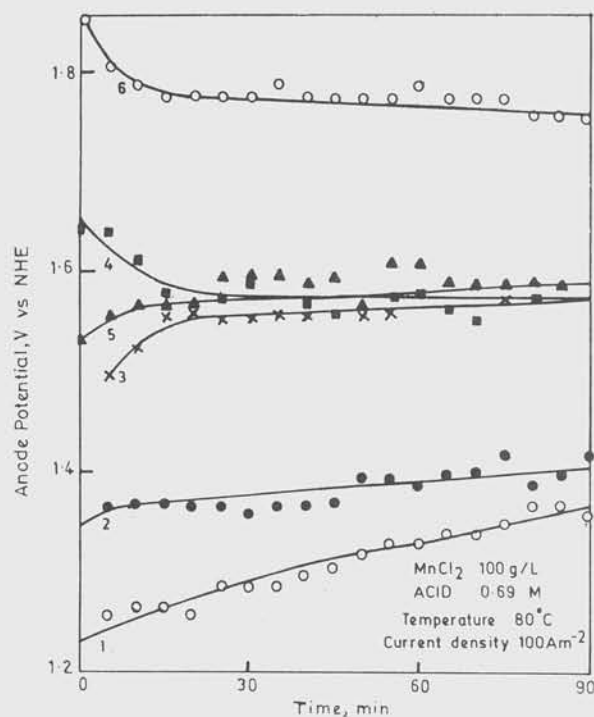


Fig.6—Variation of anode potential with time at uncoated/ MnO_2 coated graphite (1) Graphite in neutral MnCl_2 (2) Graphite in $\text{MnCl}_2 + \text{HCl}$, (3) MnO_2 coated graphite in H_2SO_4 , (4) graphite in H_2SO_4 , (5) MnO_2 coated graphite in HCl and (6) graphite in HCl

Table 1—Data on the current efficiencies for EMD, O₂ and Cl₂
 Anode Current Density: 100 Am⁻²,
 Temperature: 80°C, Concentration MnCl₂: 100 g/L

Concn. of MnCl ₂ g/L	Current efficiency for		
	EMD (%)	O ₂ (%)	Cl ₂ (%)
18.87	83.93	9.71	5.26
25.23	75.49	14.35	7.72
29.57	66.80	15.73	11.08

advantage of the property of overpotentials on the anode and the electrolysis conditions are to be adjusted. Then the predominant reaction is the formation of MnO₂ as per Eq.(1) instead of reactions (2) to (6).

Figure 6 illustrates the variation of anode potential with substrate material. The curves 1,2,3 and 5 represent the variation of anode potential of MnO₂ coated graphite with time in neutral manganese chloride, acidic MnCl₂, H₂SO₄ and HCl respectively. The difference in the steady potential values (at 45th min) of 215 mV between curves 1 and 3 corresponds to overpotential of O₂ on EMD and that of 229 mV between curves 1 and 5 corresponds to the overpotential of Cl₂ on EMD. Curves 1 and 2 indicate that addition of HCl (25 g/L) increases the anode potential though EMD deposition is predominantly taking place. Curves 4 and 6 represent the variation of anode potential with time using bare graphite anode in H₂SO₄ and HCl respectively. The anode potentials in both curves exhibit a gradual fall in first 20 min. and then stabilise. This could be attributed to the initial formation of graphitic oxide⁴ on the surface of the anode, which gradually disintegrates with continuous evolution of gases. The current density that is applied is not sufficient to maintain the potential required for the former reaction, but stabilises to a level characteristic of the electrolysis

conditions suitable for gaseous evolution, which is indicated in the curves after 20 min. The initial fall in potential obviously is not observed with MnO₂ coated graphite or titanium.

Current efficiencies for EMD, O₂ and Cl₂

Table 1 presents the data collected by carrying out the experiments in an all-glass apparatus employing ~100 g L MnCl₂ at 80°C, the anode current density being 100 Am⁻², with varying amounts of HCl. It is observed that major portion of the current is used for formation of EMD and the rest is shared by O₂ and Cl₂ as already discussed.

Based on the above observations, it can be concluded that the electrochemical reactions occur in the order MnO₂ deposition, oxygen evolution and chlorine evolution. EMD deposition with minimum overpotential occurs above 70°C, below an anode current density of 100 Am⁻² and below a concentration of 20 g/L HCl. MnO₂ deposited graphite requires an overpotential of 230 mV for both O₂ and Cl₂ at the optimum conditions.

Acknowledgement

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