

THE LANTHANUM BARIUM MANGANATE, $\text{La}_{(1-x)}\text{Ba}_x\text{MnO}_3$ — A POSSIBLE ELECTROCATALYST FOR OXYGEN EVOLUTION REACTION IN ALKALINE MEDIUM

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Three different non-stoichiometric compositions of lanthanum barium manganate (LBM) have been synthesized and investigated for its possible application as anode catalyst in alkaline water electrolysis. The results of these investigations have shown that LBM is a good electrocatalyst for the oxygen evolution reaction. Of the three oxides examined, $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ has been found to be the best. The above oxide electrodes have been scaled up from 1 cm^2 to 10 cm^2 in apparent area. The electrochemical stability over an operation duration of 500 hrs and the resulting time variation effect on the anode potential have been brought out at normal alkaline water electrolysis conditions of 3 KA.m^{-2} and 80°C when a reduction of $0.1\text{ V} - 0.15\text{ V}$ in oxygen overpotential has been observed on these catalysts as compared to that of smooth nickel electrodes under identical conditions. The electrocatalytic activity of the oxides has been discussed from the point of view of structural distortion and means for further improvement have been suggested.

Key words: Electrocatalysis, perovskite type oxide, oxygen evolution

INTRODUCTION

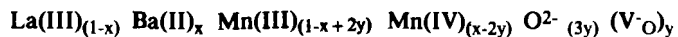
In the energy efficient electrolytic production of hydrogen in large scale as a potential energy carrier, close attention has been recently devoted to the development of highly active, stable and low cost electrocatalysts for both hydrogen and oxygen evolution reactions (OER) from aqueous alkaline solutions at temperatures $80-90^\circ\text{C}$ [1-6]. For the anodic oxygen evolution process, various oxides have been investigated, some of which have been established to be suitable electrocatalysts for the cathodic oxygen reduction process [7-9]. Of the oxides of non-noble metals apart from simple oxides, examined as electrocatalysts for oxygen evolution, two structurally different groups viz. spinels [10-16] and perovskites [17-28] have assumed significance in literature. In the $\text{A}_{1-x}\text{A}'_x\text{BO}_3$ perovskite-type oxide, a large cation such as La (III) exists in the A site. A' is an alkaline earth metal cation such as Ba (II) and B is a transition metal cation. The B site cation is octahedrally surrounded by the oxygen anions in the lattice. The electrical conduction of these oxides is essentially determined by the degree of overlapping between the d-orbital of the B site cation and the p-orbital of the oxygen anions, and by the number of d- electrons which provide majority carriers [29]. As there exists a variety of transition metals in this structure a systematic investigation of their electrocatalytic activities as anodes for the OER has become of interest. The good anodic stability shown by lanthanum barium manganate (LBM) has prompted to carry out the present work. This paper deals with the results of the investigations to characterise the oxide which has been synthesized in three different non-stoichiometric compositions as a possible electrocatalyst for OER in alkaline water electrolyzers. The present studies have been carried out at temperatures upto 80°C . As the results obtained in these studies carried out with thin film coated disc electrodes have not revealed any considerable variation in activities among the three oxides, except the pronounced activity of these oxides when compared with many reported systems [30-32], the electrodes have been scaled up to 10 cm^2 in apparent area and the time-variation effect on the anode potential at common alkaline water electrolysis conditions of 3

KA.m^{-2} and 80°C has been examined. The galvanostatic steady-state polarisation and the linear sweep cyclic voltammetric behaviour have been studied to identify the best of the three oxides.

EXPERIMENTAL

Catalyst materials

The perovskite type oxides were prepared by heating the appropriate mixtures of binary oxides in air on an alumina boat at 1000°C for 100 hours by thoroughly grinding the mixtures once in every 24 hours. The sintered oxides showed a specific resistance of $0.5-1.0\text{ ohm.cm}$ at a pressing pressure of 1.5 ton.cm^{-2} which is fairly close to the reported value [35]. The $\text{AA}'\text{BO}_3$ structure of the oxides was confirmed by x-ray analysis. The whole system of the oxide has the cubic perovskite structure. Ba (II) whose ionic size (1.34 \AA) was substituted in different stoichiometric ratios for La (III) with an ionic size of 1.06 \AA in order to bring about a certain defined quantum of structural distortion without destroying the crystal structure, as this was assumed [33-35] to have higher activity than the perfect structure. In the substitution of La (III) by Ba(II), charge compensation was achieved simultaneously both by conversion of Mn(III) to Mn(IV) and by formation of oxygen vacancies. The composition in the system can be formulated for the oxides, in general, as: [35]



Electrode fabrication

The catalyst powders after thorough grinding were sieved through stainless steel wire mesh (standard sieve size 300 mesh) to get particles of similar size. They were then mixed with polystyrene binder, 10% by weight, in AR benzene and the resulting suspension was uniformly painted onto stainless steel mesh screens (standard 100 mesh). The electrodes were then dried at 80°C for minutes. To ascertain the surface homogeneity, the electrodes were then subjected to a pressure of 10 kg.cm^{-2} by sandwiching them between two smooth stainless steel plates. This process was sufficient to

have a well compacted electrode surface. Then the processed electrodes were cured at 100°C for 1 hr in air. The catalyst loading was $25 \pm 2 \text{ mg cm}^{-2}$ in all the cases. Thin film electrodes were obtained by painting the same dispersion onto smooth glassy carbon (GC) discs. The coated surfaces were as smooth as the GC disc itself and thus they were subjected to straight curing at 100°C for 1 h in air.

Electrochemical measurements

The preliminary investigations were carried out in all-glass three-compartment cell on the thin film disc electrodes under a constant rotation speed of 1200 per minute in oxygen saturated 6M KOH, which was prepared from thrice distilled water and pre-electrolysed for 48 h with purified nitrogen gas bubbling through the electrolyte solution using Ni-mesh electrodes, as Pt-electrode was found to contaminate the solution [36]. The potentials were measured against Hg/HgO reference electrode by appropriately positioning the Luggin in order to have negligible IR. The Linear Sweep Cyclic Voltammetric (LSCV) behaviour of all the systems reported here were obtained by using a PAR model 370 Electrochemistry System.

The polarisation experiments were carried out galvanostatically under steady state conditions using a constant current generator as the DC power supply. A three compartment (1 litre capacity) stainless steel beaker containing 0.8 litre of the above said electrolyte was used as the electrolytic cell. Stainless steel screens sacked in nylon bags were used as two cathodes. As reference, two Hg/HgO electrodes were positioned with the asbestos fibre packed Luggins at a distance of <0.1 mm to either side of the surface of the anode. The currents were monitored using a digital ammeter (IEC model 3501) in 2 A mode and the potentials were monitored using a digital voltmeter (IEC model 3504) in 2V mode. Before each measurement, the anode was held at a current density of 3 kA.m^{-2} for 30 minutes to ensure the presence of oxygen on the surface. The current density was then decreased in steps of 0.10 - 0.25 kA.m^{-2} and at each step, the steady-state value of potential was recorded. The time required to reach the steady state was found to depend on temperature of operation and found to decrease with increasing temperatures. The steady state was attained in all cases within 2 min. and usually 1 min. In order to evaluate the activity of the catalysts more effectively, the polarisation behaviour of the current collector bases were also measured.

The time variation effect of the anode potential was studied by continuously charging the working electrode at the desired current density and periodically replenishing the electrolyte with thrice distilled water to balance the water that was lost due to evaporation and electrolysis. The accelerated life tests have been carried out by raising the charging current density to a specific value at regular intervals of 5 days and recording the change in the anode potential with time over 5 hrs. The stability of the anode at open circuit conditions was investigated by simulation experiments and reverse potential cycling experiments. The former involved interruption of the circuit over time intervals ranging from 10-15 hrs and again closure to understand the effect of such severe but common incidents on the anode potential in industrial water electrolysis, while the latter involved scanning at very slow sweep rate from the oxygen evolution potential (0.7 V in the present case) cathodically to severe reduction potential (-0.2 V) and to record the behaviour by repeated cycling (10 cycles) to monitor the variation in the reduction current with cycling.

The cell geometry and the arrangement of the two Luggins were supposed to keep the IR in 60-70 mV at 3kA.m^{-2} and 80°C. The IR component of the measured anode potential was evaluated as the difference in the potential between the two Luggins and this value was subtracted to arrive at the IR-free potential values. It has been reported that the validity of this assumption was tested by interruptor method [37] and there was fair agreement between

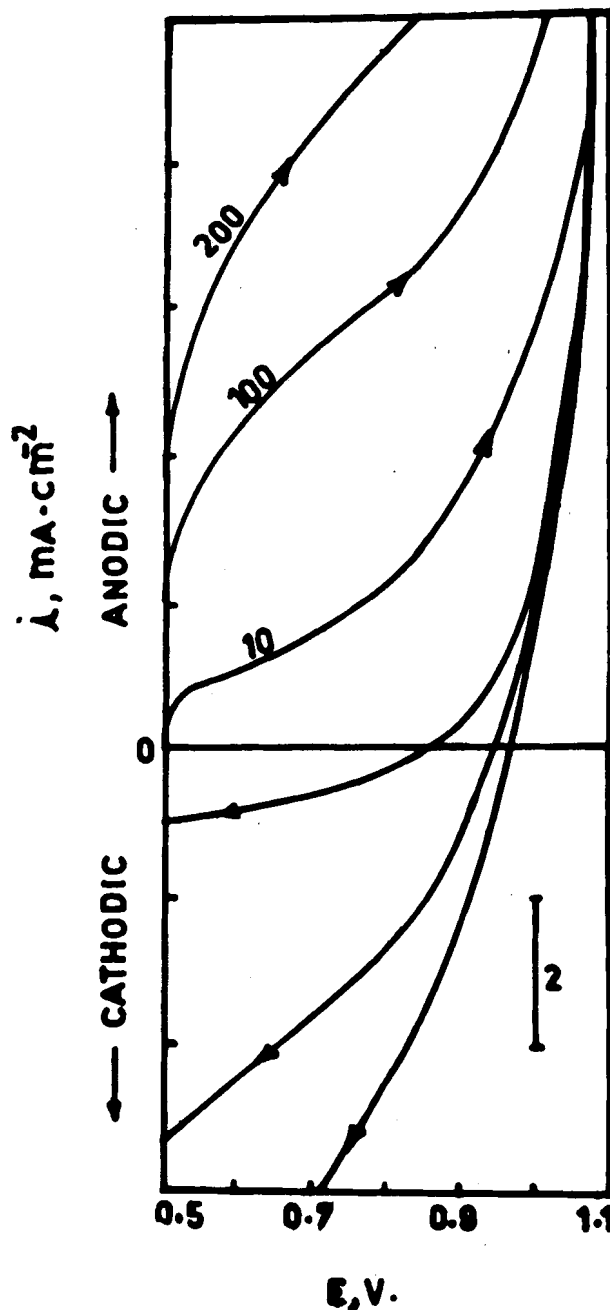


Fig. 1: LSCV behaviour of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ disc electrode in 6M KOH at 28°C under 1200 rpm, effect of sweep rate 10 mV to 200 mV sec⁻¹

the two values. The interruptor method was deliberately not adopted and this method of measurement was chosen in order not to introduce uncontrolled over-compensation of IR by unreproducible switching mode which allows to include into the measurements any increase of potential which might be due to bubble accumulation and curtain effect or by uneven current distribution due to the geometry of the present electrodes.

RESULTS

After a feeble anodic pretreatment of the coated electrodes at 0.01 kA.m⁻² for 30 minutes in O₂ saturated 6M KOH, all the electrodes were found to exhibit a fairly steady reversible temperature-dependent potential values which remained in the range 0.3 V to 0.4 V. The essential requirement of any oxygen evolving catalyst namely the electrochemical stability at extremely anodic potential (1.2 volt) was initially carried out by scanning the thin film disc electrodes under constant rotation speed from 0.5 V to 1.1 V at different sweep rates. The behaviour is shown in Fig. 1 For La_{0.7}Ba_{0.3}MnO₃.

The scaled up electrodes with the three different catalyst powders were scanned from 0.3 V to 1.2 V and the resulted cyclic voltammograms obtained at a sweep rate of 10 mV.sec⁻¹ both at 28°C and at 80°C are shown in Figs.2 and 3, while the latter included the behaviour of the stainless steel base under identical conditions, for the sake of comparison.

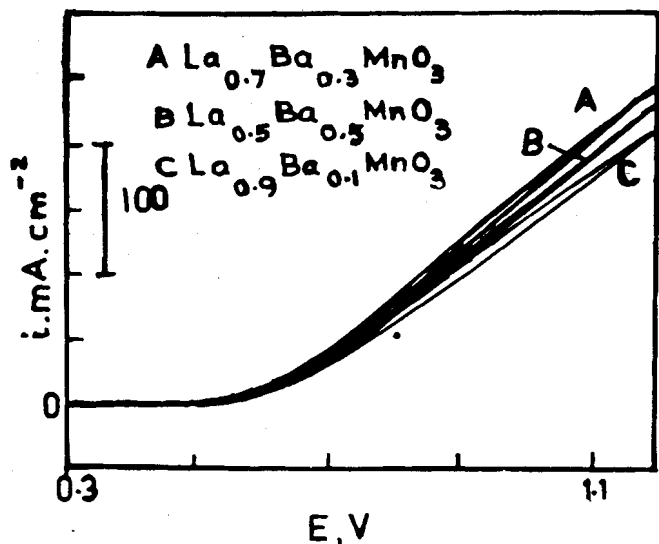


FIG.2 : LSCV behaviour of scaled up electrodes in 6M KOH at 28°C under stationary conditions, sweep rate 10 mV. sec⁻¹

The steady state data obtained on these electrodes at temperatures 28°C, 69°C and 80°C upto a current density of 3 kA.m⁻² were used for the construction of Tafel plots, after correcting the potentials for IR, and the Tafel lines, as exhibited by these catalysts are shown in Fig.4. The electrochemical parameters derived from an analysis of the obtained experimental data are presented in Table I. The i vs E behaviour of these catalysts obtained at 80°C is shown in Fig. 5. As La_{0.7}Ba_{0.3}MnO₃ was found to perform better than the remaining two non- stoichiometric oxides, namely La_{0.5}Ba_{0.5}MnO₃ and La_{0.9}Ba_{0.1}MnO₃, the former was investigated in

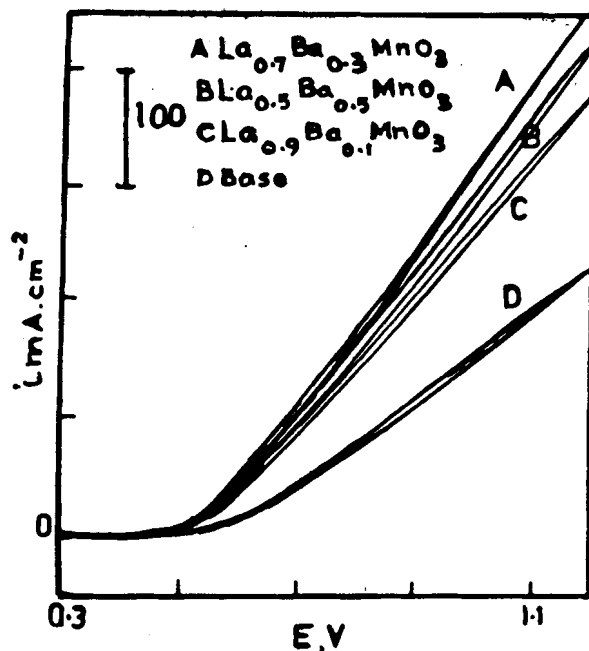


Fig.3 : LSCV behaviour of scaled up electrodes in 6M KOH at 80°C under stationary conditions, sweep rate 10 mV sec⁻¹

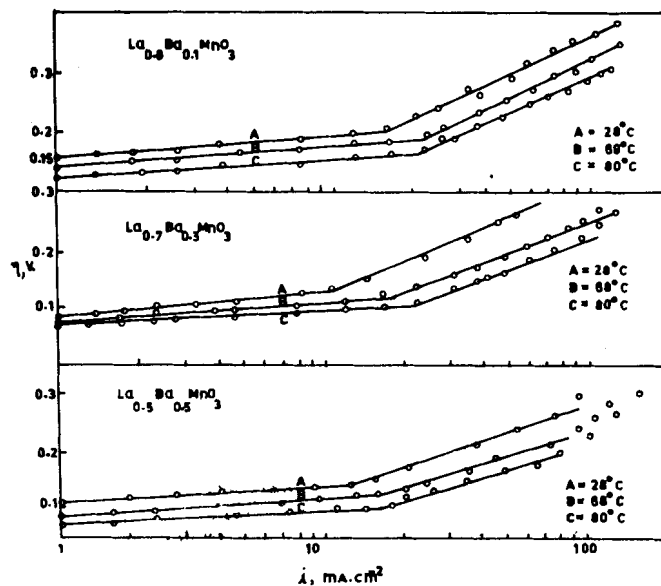


Fig.4 : Tafel plot of the oxide catalysts in 6M KOH under stationary conditions at different temperatures

more detail. The stability in the anode potential on the said catalyst over an operating duration of 500 hrs at 80°C is shown in Fig.6. The steady state polarisation behaviour after continuous operation of the anode in electrolysis over various time durations is shown in Fig. 7. The stability of the anode at open circuit conditions

TABLE-1 : Electrochemical parameters for ore on the catalysts

Electrode	Tafel slope		Exchange current density		Temp °C	η (i = 3 kA.m ⁻²)			η (i = 1.5 kA.m ⁻²)		
	V.dec ⁻¹		A.cm ⁻²			V			V		
	$\eta < 0.15V$	$\eta < 0.15V$	$\eta < 0.15V$	$\eta < 0.15V$		28°C	69°C	80°C	28°C	69°C	80°C
La _{0.7} Ba _{0.3} MnO ₃	0.04	0.185	2.1 × 10 ⁻⁵	2.7 × 10 ⁻³	28						
	0.037	0.170	2.5 × 10 ⁻⁵	4.3 × 10 ⁻³	69	0.57	0.47	0.42	0.38	0.305	0.298
	0.034	0.160	5 × 10 ⁻⁵	6.6 × 10 ⁻³	80						
La _{0.5} Ba _{0.5} MnO ₃	0.035	0.180	1.4 × 10 ⁻⁶	2.9 × 10 ⁻³	28						
	0.032	0.140	2.6 × 10 ⁻⁶	3.4 × 10 ⁻³	69	0.68	0.51	0.43	0.45	0.320	0.306
	0.030	0.138	8.0 × 10 ⁻⁶	3.8 × 10 ⁻³	80						
La _{0.9} Ba _{0.1} MnO ₃	0.040	0.200	2.6 × 10 ⁻⁸	2.2 × 10 ⁻³	28						
	0.040	0.195	6.8 × 10 ⁻⁷	3.5 × 10 ⁻³	69	0.693	0.54	0.48	0.46	0.41	0.332
	0.037	0.190	2.5 × 10 ⁻⁶	4.2 × 10 ⁻³	80						
No sheet smooth	0.080	0.220	1.5 × 10 ⁻⁸	3.1 × 10 ⁻⁵	28						
	0.075	0.215	0.9 × 10 ⁻⁸	0.8 × 10 ⁻⁵	69	0.68	0.59	0.55	0.47	0.415	0.400
	0.060	0.210	2.1 × 10 ⁻⁷	1.1 × 10 ⁻⁴	80						

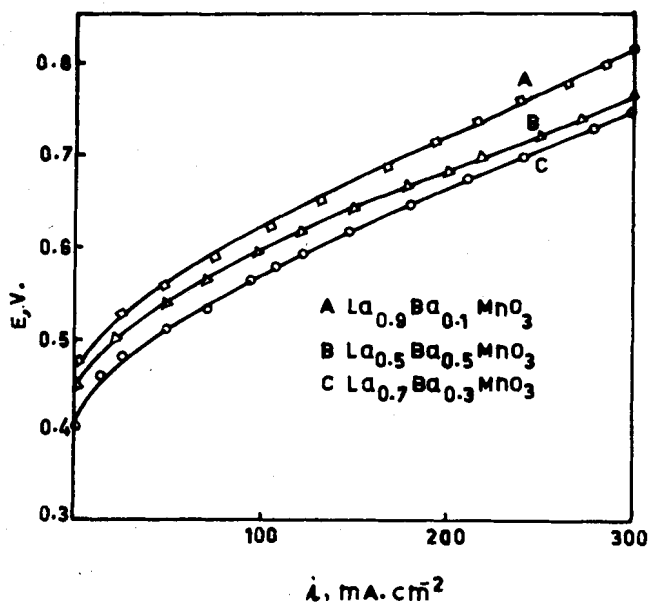


Fig. 5 : Steady-state polarisation curves of the scaled up electrodes at 80°C in 6M KOH under stationary conditions

as investigated by reverse potential cycling experiments and the resulting voltammogram is shown in Fig. 8.

The accelerated life tests resulted in a variation in the anode potential to the tune of 40mV, over a period of 15 days at 6 kA.m² and 80°C. Simulation experiments resulted in a potential fall of 200-250 mV over a period of 2 days.

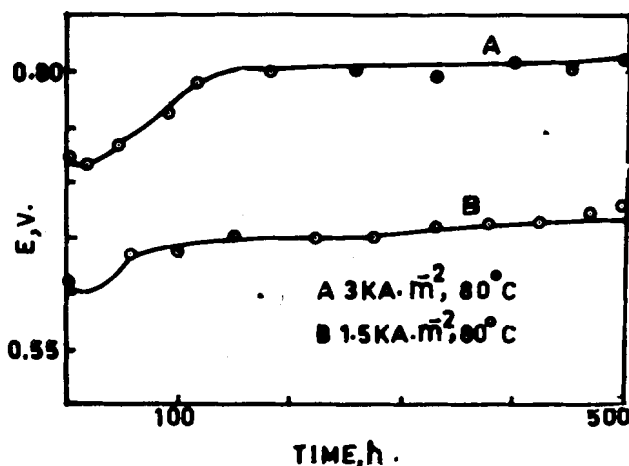


Fig. 6 : Time-variation effect of anode potential on La_{0.7}Ba_{0.3}MnO₃ at 80°C in 6M KOH

DISCUSSION

Cyclic voltammograms

The cyclic voltammograms obtained in the anodic direction from 0.5 V, the potential at which the oxygen evolution gets initiated, to 1.2 V, the potential which is expected to be at high current densities in practical alkaline water electrolysis (at 3kA.m⁻²), indicate a wave in the potential range 0.50 V - 0.55 V, where the current is less and increasing above this potential rapidly. Oxygen evolution begins at this potential with a wave-like appearance especially in the higher potential region. At still higher potential i.e. 1.4 V, the current appears to be limited which is of no practical

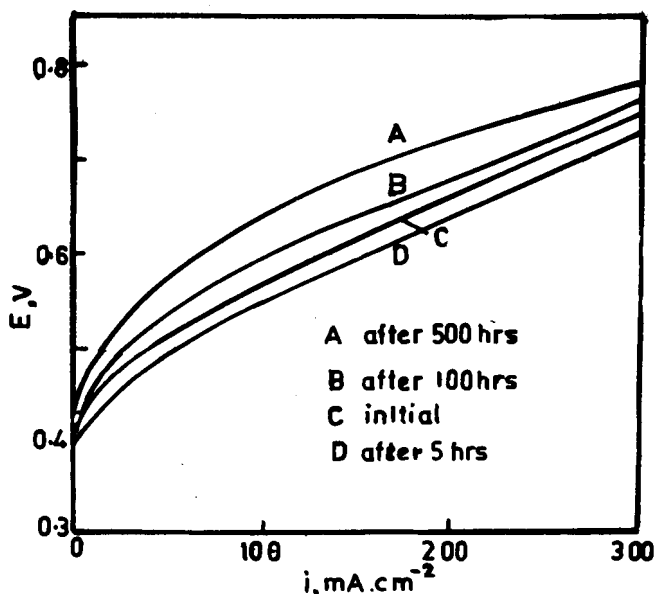


Fig.7: Steady-state polarisation curve of $La_{0.7}Ba_{0.3}MnO_3$ anode after different periods of continuous electrolysis

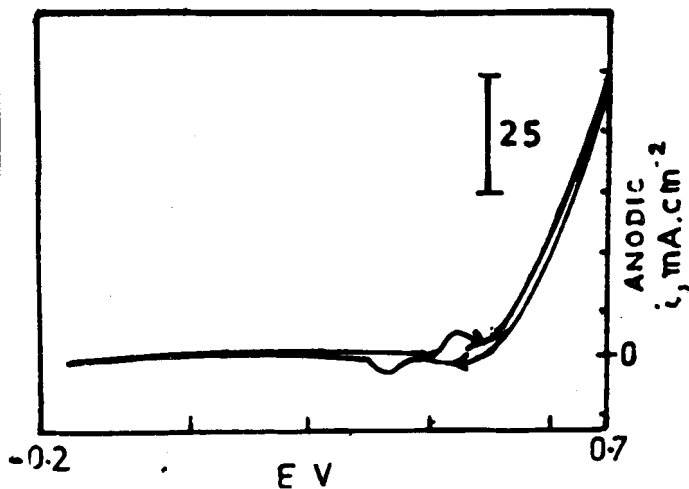


Fig. 8: Reverse potential cycling behaviour of $La_{0.7}Ba_{0.3}MnO_3$ at $80^\circ C$ in $6M KOH$, 10 cycles, $10 mV.sec^{-1}$

interest and hence not shown. In the cathodic branch of the cycle, the currents observed are less when compared with that of anodic branch, and the currents become cathodic from a potential region of $0.85 V - 0.9 V$ as a function of sweep rate. In the cathodic branches of the cycle obtained for oxygen evolution, high currents were observed near $0.4 V$, (the reversible potential value) when the electrode was pre-anodised than the one which was not given any anodic treatment. On the other hand, when the

electrode was cathodically pretreated, the cathodic current observed was found to be very less. This means that the initial anodic wave corresponding to $0.50 V - 0.55 V$ observed may well be treated to be the reverse of the cathodic wave in the voltammograms. This may be due to the formation of higher oxide of the perovskite (Mn), and seems to be a precondition for the onset of oxygen evolution. However, it is premature to throw more light on the mechanism of OER for the present, since it needs further investigations between the reversible potential and the potential at which the oxygen evolution gets initiated, which will be dealt with in future.

From the cyclic voltammograms obtained on the three different non-stoichiometric compositions of the present catalyst, it becomes clear that both at room temperature and at $80^\circ C$, $La_{0.7}Ba_{0.3}MnO_3$ performs well when compared with the other two, although all of them serve as electrocatalysts for OER when compared with many reported systems [30-32]. This result may conveniently be addressed to the control of the quantum of structural distortion, that might have happened by the partial substitution of Ba II for La (III), which is probably the optimum in the case of $La_{0.7}Ba_{0.3}MnO_3$ when compared with that of $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.9}Ba_{0.1}MnO_3$. In other words, these two oxides still possess the electrochemical properties of the major constituent present in them i.e. La_2O_3 in the case of $La_{0.9}Ba_{0.1}MnO_3$ and BaO or La_2O_3 in the case of $La_{0.5}Ba_{0.5}MnO_3$. Further studies on the solid state structure of these oxides have become essential to elaborate this aspect further. It is also clear that the temperature of operation influences the performance very much, that is to the tune of twice the current at the same potential by operating it at $28^\circ C$ and at $80^\circ C$. This reveals the fact that the present catalyst performs the best at $80^\circ C$ for mechanism not investigated at present, which in a way may be of great help to employ it in electrolyzers of recent designs, which go upto temperatures around $150^\circ C$ and more.

Steady-state observations

The galvanostatic polarisation studies carried out under steady-state conditions using scaled up flat electrodes of $4 cm^2$ apparent area in $6M KOH$ for the OER at temperatures $28^\circ C$, $69^\circ C$ and $80^\circ C$ indicate that the Tafel slope is about $40 mV$ per decade in the overpotential region of $0.09 V - 0.15 V$, changing to about $140-180 mV$ per decade above the overpotential region of $0.15 V$ on all the three cases presently under investigation and at all the three temperatures. At overpotentials above $0.32V$, the Tafel region is terminated. The apparent exchange current density values obtained from these results is $10^{-5} A.cm^{-2}$ in the low overpotential region and $10^{-3} A.cm^{-2}$ in the high overpotential region for the best of the three oxides at $80^\circ C$. The value compares well with many electrocatalyst systems [38, 39]. The steady state observations support the fact the $La_{0.7}Ba_{0.3}MnO_3$ performs well when compared with the other two sister oxides, which is in tune with the potentiodynamic observations. The results given in Table I illustrate the fact that effective electrocatalysis from the technological point of view is not well measured by means of i_0 , since all the three oxides have almost the same order both at low and high polarisation potentials. In fact, the $La_{0.7}Ba_{0.3}MnO_3$ gives the far smallest overpotentials for the OER in practical current

density regions but still the order of i_0 remains the same as that of the other two. This anomaly appears in literature often and various authors seem to attribute, the overpotential value at the desired current density region, to be efficient criterion in going for a good choice electrocatalyst for gas evolution reactions [39, 40] on porous electrodes wherein the true specific surface area responsible for the catalytic activity varies considerably on different operating conditions.

The time variation effect on the anode potential of the $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ systems appears to be initially encouraging, as the polarisation potential is found to decrease upto 40-50 hrs, but it shoots up back to the original value after this time. This observation is found to exist both at low and high current density operations. No reason could be given at present for the initial decrease, however, for the practical purposes, the system exhibits good stability over the test duration of 500 hrs. continuous operation. As the observed extent of variation in the anode potential is within the limit of error in the measurement (+ 40 mV) on gas evolving electrodes of the present type, this leads to the inference that the surface of the anode has not undergone any electrochemical instabilities such as changes in the chemical structure. This observation may therefore be treated as a direct measure of the surface stability of the present system. The steady-state polarisation behaviour obtained intermittently while on continuous operation has resulted in variation to a small extent, which is attributed to the variation in real surface area due to the slow disintegration of the oxide particles from the surface with time, which could be observed in the cell and could be minimised by working on the electrode fabrication variables. The result of the reverse potential cycling experiments has brought out a reversible redox process in the potential region 0.3V - 0.5V, which is very near to the reversible potential (0.4V). This is not studied in detail at present. However, the fact that the present system may undergo structural changes because of this redox process at open circuit conditions due to accidental shut down of the electrical circuitry with time, becomes evident. Apart from these, the fact that the present catalyst involves two components excluding the perovskite, may result in preferential cathode behaviour one over the other, which of course may be a cause for this aspect. Therefore, it is necessary to develop methods for protecting the active anodes and cathodes, e.g. devising ways in which a small current is always passed through the cell, even when the system is off-load, a point which is in harmony globally [3,41].

The 40 mV variation in the anode potential over a period of 15 days at $6 \text{ kA}\cdot\text{m}^{-2}$ and 80°C means that the electrochemical surface morphology of the anode has not undergone any significant modification even by doubling the charging current density and thereby the resulting vigorous gas evolution. The 200-250 mV drop observed in the simulation experiments over a period of 2 days is understandable from the redox process which has been discussed in the foregoing section, which again necessitates the need for the protection of the anode and cathode in practical electrolysis, especially when highly reactive composite electrodes are employed.

CONCLUSIONS

1. Of the various manganese perovskites appeared in literature, the lanthanum barium manganate performs well for OER in 6M KOH at 80°C .
2. Of the three different non-stoichiometric compositions studied in the present paper, $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ performs better.
3. By working on the electrode fabrication variables, viz. catalyst loading, current collector specification, binder composition and type etc. improved anodes based on lanthanum barium manganate would become possible for practical alkaline water electrolysis.

REFERENCES

1. B V Tilak, P W T Lu, J E Colman and S Srinivasan, *Electrolytic production of hydrogen*, in *Comprehensive Treatise of Electrochemistry*, (Eds) J O'M Bockris, B E Conway, E Yeager and R White, Vol.2, Plenum Press, New York (1981) pp 1-104
2. J Balej, *Int J Hydrogen Energy*, **10** (1985) 89
3. I Arul Raj, R Pattabiraman, S Dheenadayalan, R Chandrasekaran and V K Venkatesan, *Bull Electrochem*, **2** (1986) 477
4. I Arul Raj and V K Venkatesan, Abstract of technical papers, *Symp. on Electrochemistry in Nuclear Technology*, IGCAR, Kalpakkam, Dec. 10-11 (1986), p 11
5. I Arul Raj and V K Venkatesan, Paper communicated to *Int J Hydrogen Energy*
6. R L Le Roy, *Int J Hydrogen Energy*, **8** (1983) 401
7. I Arul Raj, K V Rao and V K Venkatesan, *Progress in Batteries and Solar Cells*, **5** (1984) 342
8. I Arul Raj, K Venkateswara Rao and V K Venkatesan, *Proc. Symp. Interactions at electrode-electrolyte interfaces*, IIT, Madras, Dec.22-24 (1982) p 127
9. I Arul Raj, K Venkateswara Rao and V K Venkatesan, *Bull Electrochem*, **2** (1986) 157
10. S Trasatti and G Lodi, *Oxygen and chlorine evolution at conductive metallic oxide anodes*, in *Electrodes of Conductive Metallic Oxides* (Ed) S Trasatti, Part B, Elsevier, Amsterdam (1981) p 521
11. A C C Tseung and S Jasem, *Electrochim Acta*, **22** (1977) 31
12. S M Jasem and A C C Tseung, *J Electrochem Soc*, **126** (1979) 1353
13. C R Davidson, G Kissel and S Srinivasan, *J Electroanal Chem*, **132** (1982) 129
14. P Rasiyah, A C C Tseung and D B Hilbert, *J Electrochem Soc*, **129** (1982) 1724
15. J Fischer, H Hoffmann, G Luft and H Wendt, *AICHE J*, **26** (1980) 794

16. H Wendt and V Pizak, *Electrochim Acta*, **28** (1983) 27
17. A C C Tseung and H L Bevan, *J Electroanal Chem*, **45** (1973) 429
18. F R Van Burren, G H J Breers, C Boesveld and A J Bouman, *J Electroanal Chem*, **87** (1978) 381, 353, 389
19. A G C Kobussen and C M A Mesters, *J Electroanal Chem*, **115** (1980) 131
20. A G C Kobussen, *J Electroanal Chem*, **126** (1981) 199
21. Y Matsumoto, J Kurimoto and E Sato, *J Electroanal Chem*, **102** (1979) 77
22. Y Matsumoto and E Sato, *Electrochim Acta*, **24** (1979) 421
23. Y Matsumoto, S Yamada, T Nishida and E Sato, *J. Electrochem Soc*, **127** (1980) 2360
24. G Fiori and C M Mari, *Int J Hydrogen Energy*, **7** (1982) 489
25. T Otagawa and J O'M Bockris, *J Electrochem Soc*, **129** (1982) 2391
26. J O'M Bockris, T Otagawa and V Young, *J Electroanal Chem*, **150** (1983) 633
27. J Balajka, *Int J Hydrogen Energy*, **8** (1983) 755
28. J O'M Bockris and T Otagawa, *J Electrochem Soc*, **131** (1984) 290
29. (Ed) J B Goodenough in H Reiss, *Progress in Solid State Chemistry*, Vol.5, Pergamon Press, Oxford (1971) p 143
30. K Venkateswara Rao, V K Venkatesan and H V K Udupa, *J Electrochem Soc India*, **31** (1982) 33
31. R P Singh, *Proc Fifth Nat Conf Power Sources, Batteries and Fuel Cells*, IISc, Bangalore, Aug. 18-19 (1986) p 38
32. T Kudo, H Obayashi and M Yoshida, *J Electrochem Soc*, **124** (1977) 321
33. A C C Tseung and H L Bevan, *J Electroanal Chem*, **45** (1973) 429
34. M Bursell and G Karlsson, *Electrochem Soc Ex. Abstr.* 79-1 (1979) No.26
35. Y Matsumoto, H Yoneyama and H Tamura, *J Electroanal Chem*, **83** (1977) 237
36. R W Zurilla, R K Sen and E Yeager, *J Electrochem Soc*, **125** (1978) 1103
37. J Newsman, *J Electrochem Soc*, **117** (1970) 507
38. J O'M Bockris, T Otagawa and V Young, *J Electroanal Chem*, **150** (1983) 633
39. Y Matsumoto and E Sato, *Materials Chem Phys*, **14** (1986) 39
40. A C C Tseung and J Botejue, *Int J Hydrogen Energy*, **11** (1986) 125