

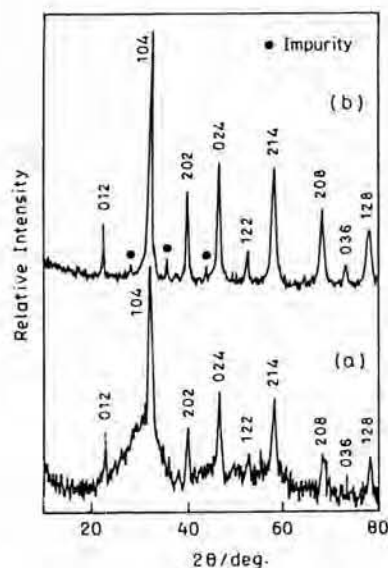


Fig. 1—XRD powder patterns of (a) LaMnO_3 , and (b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

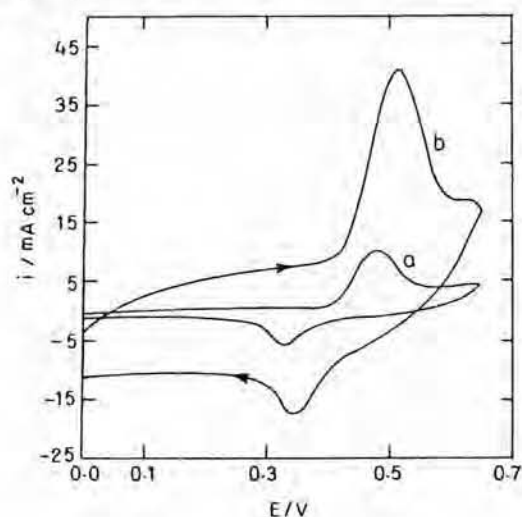


Fig. 2—Cyclic voltammograms of (a) LaMnO_3 and (b) $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ films at 0.02 V s^{-1} in 1 M KOH (25°C).

compartment Pyrex glass cell using electrochemical impedance system (model 273A, EG & G PARC, U.S.A.); the softwares used were M388 Electrochemical Impedance, M270/250 Research Electrochemistry, and M352 Corrosion measurement & analysis. The reference and auxiliary electrodes used were $\text{Hg}/\text{HgO}/1 \text{ M KOH}$ ($E^0 = 0.098 \text{ V}$ vs NHE) and pure Pt-foil ($\sim 8 \text{ cm}^2$), respectively. All potential values in the text are given with respect to the reference, Hg/HgO only. Electrochemical impedance spectra of oxide-film electrodes in 1 M KOH were determined over the frequency range $0.02\text{--}10^5 \text{ Hz}$ at a given DC potential. The double layer capacitance (C_{dl}) and other

Table 1—Unit cell parameters of some perovskite (hexagonal) oxides

Oxide	$a/\text{\AA}$	$c/\text{\AA}$	$S/\text{\AA}$
LaMnO_3	5.505	13.310	~ 575
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	5.450	13.300	~ 579
$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	5.47	13.310	~ 744

circuit parameters were analysed using the Equivalent circuit program due to Bernard A. Boukamp¹⁹.

The procedure adopted in other electrochemical measurements, namely, CV and anodic Tafel polarization, were similar to those given elsewhere¹⁷. The iR-free anodic Tafel polarization curves (where R is the resistance of the electrolyte between the reference and the oxide film including the resistance of the latter) were recorded at a slow scan rate (0.0002 V s^{-1}) using the Tafel technique provided in the corrosion software. For iR compensation current was interrupted at every 10 s during the polarization. The geometrical area of the oxide electrode used in the electrochemical investigation was 0.5 cm^2 .

Results and Discussion

XRD

The XRD powder patterns of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0, 0.3, 0.5$ sintered at 700°C for 5 h were recorded between $2\theta = 0$ and $2\theta = 80^\circ$. Two representative XRD spectra, for the base and 0.5 mol Sr-substituted oxide, are shown in Fig 1. Figure 1 shows that this method produces almost pure LaMnO_3 . However, Sr-substituted manganites showed two weak additional reflections one at $2\theta = 36.11$ and $d = 2.4853$ and the other at $2\theta = 44.615$ and $d = 2.0293$. These weak reflections can be ascribed to the formation of small amount of $\text{La}(\text{OH})_3$ ($d = 2.4915$; JCPDS file No. 38-1481) and La_2O_3 ($d = 2.019$; JCPDS file No. 40-1279) as impurities. The crystallite of each oxide follows more or less the hexagonal crystal geometry. The unit cell dimensions a and c were estimated using $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ and $a = b \neq c$. Values of a and c , thus calculated (Table 1) agree well with those reported for LaMnO_3 ($a = 5.523$ and $c = 13.324$; JCPDS-ICDD file No. 32-484). Table 1 shows that Sr-substitution slightly reduces the a -value, while c -value appears to be unaffected. Values of the crystal size (S) (Table 1) enhanced with 0.5 mol Sr-substitution. S was estimated using the Scherrer formula described elsewhere^{20,21}.

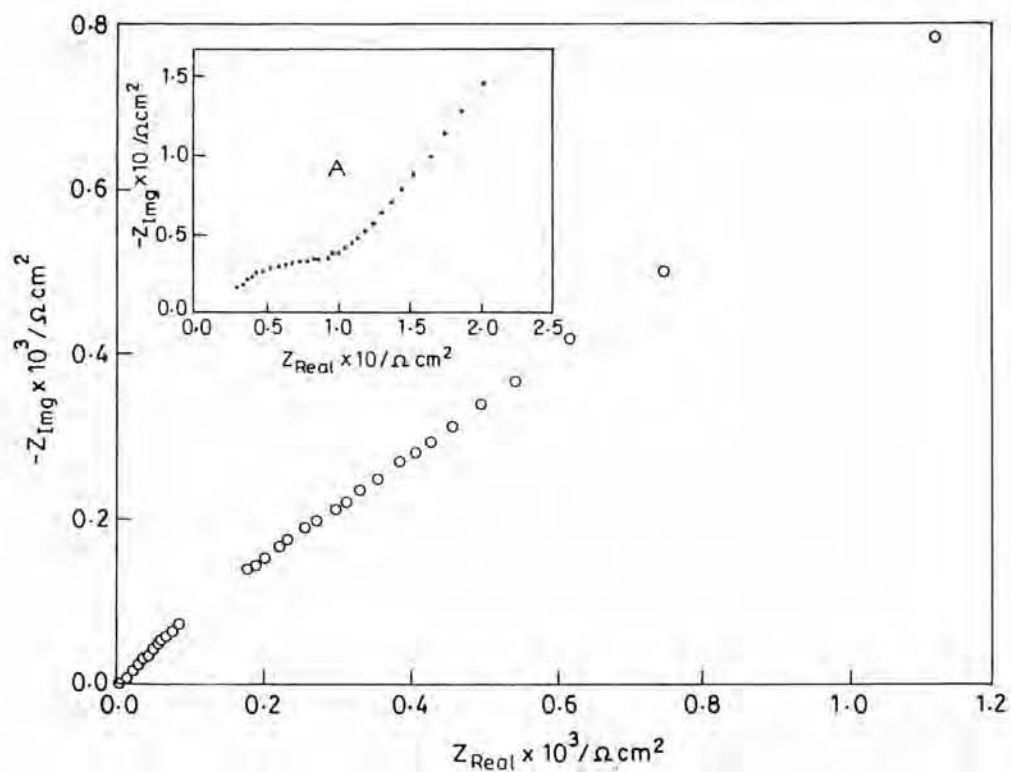


Fig. 3—Complex impedance plots for the LaMnO_3 electrode over the frequency range: $0.02\text{--}10^5$ Hz in 1M KOH at $E = 0.05$ V (25°C). A: $10^2\text{--}10^5$ Hz.

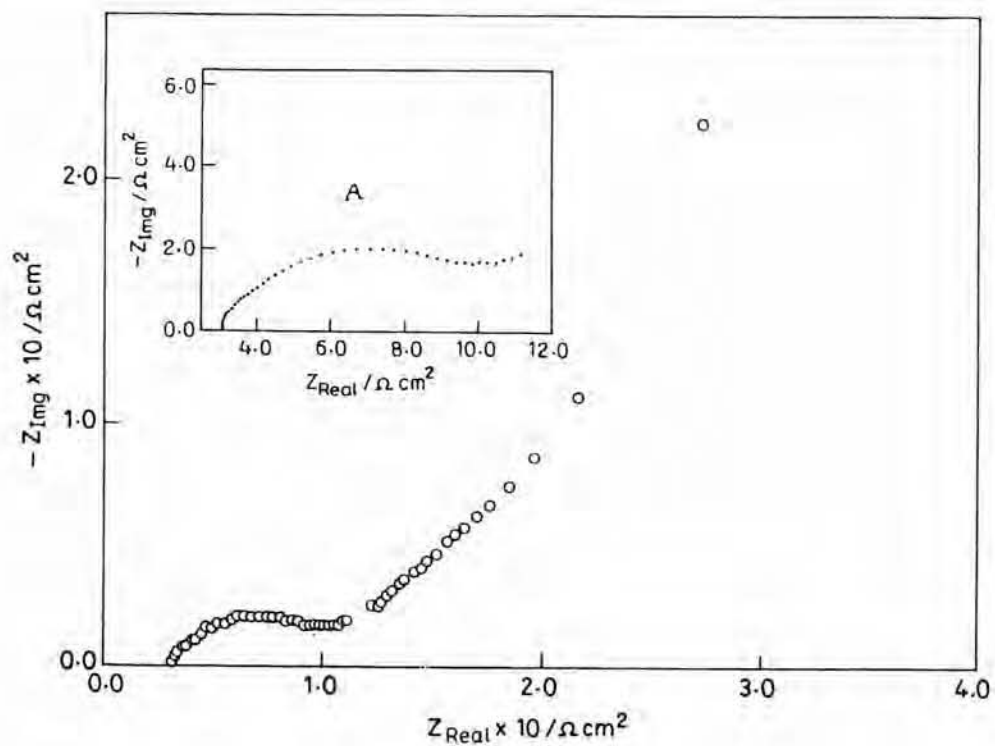


Fig. 4—Complex impedance plots for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ electrode over the frequency range: $0.02\text{--}10^5$ Hz in 1M KOH at $E = 0.05$ V (25°C). A: $20\text{--}10^5$ Hz.

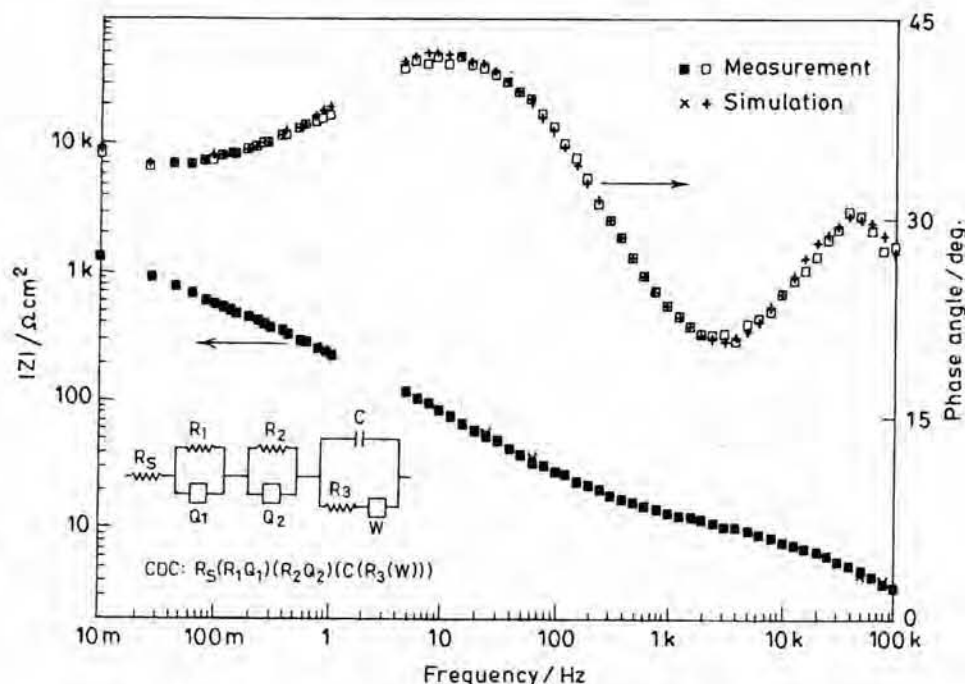


Fig. 5—Bode's plot for the LaMnO_3 electrode in 1M KOH at $E=0.05$ V (25°C).

Cyclic voltammetry (CV)

Cyclic voltammograms of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.5$) film on Ni in 1M KOH were almost similar. The two representative CV curves, one for the base and the other for 0.5 mol Sr-substituted oxide are shown in Fig 2. Each curve exhibited an anodic ($E_{pa}=0.492 \pm 0.017$ V) and a corresponding cathodic ($E_{pc}=0.418 \pm 0.009$ V) peak. However, cyclic voltammetry of similar films on Pt under identical experimental conditions did not indicate any redox peak between 0 V and a potential (~ 0.6 V) corresponding to the oxygen evolution peak. This shows that the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films do not undergo any electrochemical oxidation/reduction reaction before the onset of O_2 evolution reaction. Similar results were also found for the same oxide prepared by malic acid¹³ and citric acid¹⁵ sol-gel routes. The observed redox peaks in the case of film on Ni have been originated from the Ni-support, details of which have already been given elsewhere^{13,22}.

Electrochemical impedance spectroscopy (EIS)/roughness factor (R_F)

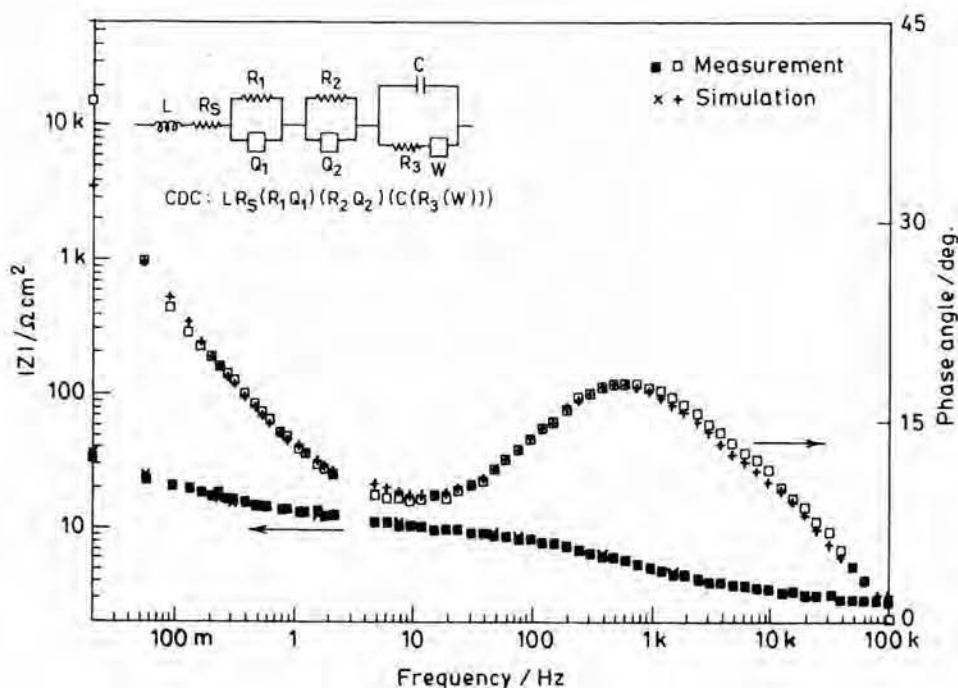
The feature of the complex impedance plane plots for the oxide with $0 \leq x \leq 0.5$ was almost similar. Two representative complex plane diagrams, one for the base oxide (LaMnO_3) and the other for $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$,

at 0.05 V in 1M KOH are shown in Figs 3 and 4. These figures show the solution resistance (R_s) in a serial connection with three time constants. The first constant at high frequencies results from dielectric relaxation in the oxide material. The second time constant at intermediate frequencies can be caused due to the charge (possibly H^+/OH^-) transfer processes at the surface of the oxide film. However, the third time constant observed at low frequencies indicates the establishment of the charge (OH/H^+) transport process into the oxide film through defects and pores.

EI spectra were analyzed with the equivalent circuit shown in Fig 5. This equivalent circuit model with circuit description code (CDC): $R_s(R_1Q_1)(R_2Q_2)(C(R_3(W)))$ gave reasonably good fit to the experimental impedance spectra obtained for the oxide with $0 \leq x \leq 0.3$ only. A set of the experimental and the simulated impedance spectra obtained in the case of LaMnO_3 is shown in Fig. 5, where R_1 , R_2 , R_3 , Q_1 , Q_2 , W , and C are resistance of the bulk oxide, charge transfer resistance, pore's resistance, constant phase element (CPE) at high frequencies, CPE at intermediate frequencies, Warburg impedance, and the double layer capacitance of the anode films respectively. EI spectra for the oxide with $x=0.4$ and 0.5 can be best explained by considering the equivalent circuit (C.D: $\text{LR}_s(R_1Q_1)(R_2Q_2)(C(R_3(W)))$) shown in Fig.6. A set of

Table 2—Value of the circuit parameters estimated by using $R_S(R_1Q_1)(R_2Q_2)(C(R(W)))$ and $LR_S(R_1Q_1)(R_2Q_2)(C(R(W)))$ equivalent circuit models to approximate experimental impedance diagrams for oxide electrode in 1M KOH at 25°C

Electrode	Oxide loading (mg cm ⁻²)	R _S (Ohm)	R ₁ (Ohm)	Q ₁ ×10 ⁵ (mho)	n ₁ (Hrtz)	R ₂ ×10 ⁻² (Ohm)	Q ₂ ×10 ³ (mho)	n ₂ (Hrtz)	C×10 ³ (Farad)	R ₃ ×10 ⁻² (Ohm)	W×10 ³ (mho)	R _F
LaMnO ₃	12.5 ± 0.6	~2	6.1 ± 0.4	2.44±0.28	~0.7	5.9 ± 0.1	1.32±0.04	~0.6	7.47 ± 1.13	4.47 ± 0.32	6.50 ± 1.39	~125
La _{0.9} Sr _{0.1} MnO ₃	13.5 ± 0.5	~3	5.0 ± 1.0	0.79±0.19	~0.9	4.8 ± 0.4	1.0±0.1	~0.7	3.27 ± 0.52	7.01 ± 0.56	4.03 ± 0.57	~55
La _{0.8} Sr _{0.2} MnO ₃	14.0 ± 0.5	~2	4.4 ± 0.2	12.69±0.3	~0.6	3.2 ± 0.1	1.09±0.2	~0.7	4.36 ± 0.2	2.67 ± 0.4	6.47 ± 0.35	~73
La _{0.7} Sr _{0.3} MnO ₃	16 ± 0.2	~2	4.7 ± 0.3	1.66±0.25	~0.8	7.1 ± 0.3	1.69±0.05	~0.6	10.81 ± 0.15	5.39 ± 0.35	9.05 ± 0.3	~180
La _{0.6} Sr _{0.4} MnO ₃	15.8 ± 0.3	~3	0.6 ± 0.3	5.17±0.38	~0.9	4.0 ± 0.2	1.11±0.12	~0.7	4.8 ± 0.14	4.50 ± 0.06	6.60 ± 0.23	~80
La _{0.5} Sr _{0.5} MnO ₃	16.5 ± 0.2	~3	7.6 ± 0.1	163.75±7.25	~0.6	0.3 ± 0.02	0.06±0	~1	11.85 ± 1.1	0.02 ± 0.01	0.01 ± 0	~198

Fig. 6—Bode's plot for the La_{0.5}Sr_{0.5}MnO₃ electrode in 1M KOH at E = 0.05V (25°C).

experimental and the simulated spectra for La_{0.5}Sr_{0.5}MnO₃ at 0.05 V in 1M KOH is shown in Fig. 6. The value of L (inductance, Henri) was in the order of 10⁻⁷ H. The source of this inductive element is unclear²³.

Estimates of C_{dl} and other circuit parameters are given in Table 2. The relative oxide roughness (R_F) values were estimated from the ratio of the estimated C_{dl} of the oxide and the C_{dl} of the smooth oxide surface. The value of 60 μF cm⁻² is usually taken for the capacitance of the smooth oxide surface^{24,25}. Table 2 shows that the effect of the Sr-substitution on the oxide roughness is complex one. With the increase in Sr-concentration, the R_F value initially decreases by approximately 50% and then increases and becomes higher than that of the base oxide at x ≥ 0.3 mol. The

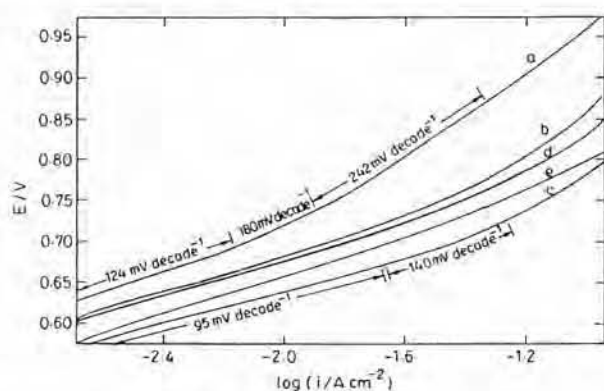
R_F value obtained for La_{1-x}Sr_xMnO₃ *in situ* were similar to those for the same oxide (R_F = 72–106) prepared by malic acid aided route¹³. However, they were considerably low compared to those obtained for the same oxides (R_F = 483–1767) prepared by citric acid precursor route¹⁵. It is noteworthy that in previous papers^{13,15}, the approximate C_{dl} of the oxide/1M KOH solution interface was estimated from the intercept of log |Z| vs log w curve on the log |Z| axis (i.e. y-axis) at w = 1, which is true only when the curve is linear with the slope -1.

Electrocatalytic activity

Electrocatalytic activities of the oxide catalysts towards the OER were determined by recording the E vs log i curve (Fig. 7) in 1M KOH (25°C) at 0.0002 V s⁻¹

Table 3—Electrode kinetic parameters for OER on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ in 1M KOH at 25°C

Electrode	b (V decade ⁻¹)	Order(p)	$I/\text{mA cm}^{-2}$ at E/V			
			0.75		0.80	
			i_{app}	$i_{\text{r}} \times 10^2$	i_{app}	i_{r}
LaMnO_3	0.135 ± 0.008	0.8	13.8 ± 1.8	10.40	21.4 ± 2.6	0.17
$\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$	0.108	1.0	32.6	59.27	59.9	1.09
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	0.107 ± 0.003	0.8	32.3 ± 2.8	44.25	59 ± 7.5	0.81
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	0.092 ± 0.002	1.0	67.7 ± 4.1	37.61	106.1 ± 8.9	0.59
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	0.101	0.8	36.4 ± 2.2	47.89	66.8 ± 5.1	0.88
$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	0.106 ± 0.001	0.8	55.9 ± 4.4	28.23	104 ± 3.2	0.53

Fig. 7—iR-free Tafel plots on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films on Ni in 1M KOH at 25°C: (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.3$, (d) $x=0.4$, and (e) $x=0.5$.

under the anodic condition. Values of the Tafel slope (b) observed at low overpotentials and of the current density (i_a) at two potentials, 0.75 and 0.8 V are given in Table 3. To determine the order for the OER, the E vs $\log i$ curves were also determined on each oxide electrode at varying KOH concentrations keeping the ionic strength constant ($\mu = 1.5$). With the aid of these polarization curves $\log i$ vs $\log C_{\text{OH}^-}$ linear plot was constructed at a constant potential (Fig. 8) and the order was then estimated by measuring the slope of this linear curve (Table 3). μ was maintained using KNO_3 (AR BDH) as an inert electrolyte.

The nature of the anodic polarization curves shown in Fig. 7, the value of initial Tafel slope (b), and the reaction order (p) shown in Table 3, indicate that the OER follows more or less similar mechanistic paths on each catalyst regardless of its nature. The order of OE with respect to OH^- concentration was approximately unity with each oxide catalyst. With the exception of 0.3 mol Sr-substituted lanthanum manganite ($b=3 RT/2F$), all other electrodes had b -values close to $2RT/F$, Sr-substitution for lanthanum in the

perovskite lattice increased the apparent electrocatalytic activity (i_a) of the oxide. However, increase was greatest with 0.3 mol Sr-substituted oxide. The improvement in the electrocatalytic activity of the oxide due to introduction of Sr in the oxide matrix may be caused due to the reduction in the Tafel slopes (Fig. 7).

It was observed that the apparent catalytic activities of oxides prepared *in situ*, were not significantly different from those of corresponding oxides prepared by sol-gel routes involving malic acid¹³ and citric acid-ethylene glycol¹⁵ precursors. As for example, at $i_{\text{app}} = 100 \text{ mA cm}^{-2}$ in 1M KOH at 25°C, the observed oxygen overpotential (η_{O_2}) values were ~ 0.539 , ~ 0.519 , and ~ 0.516 V on $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ prepared by citric acid (the present), citric acid-ethylene glycol¹⁵ and malic acid¹³ precursor methods. However, the apparent electrocatalytic activities of manganites synthesized by these sol-gel routes were significantly higher than those obtained by conventional ceramic methods^{26,27}. Bockris and Otagawa²⁶ found the oxygen evolution current densities 4.3, 1.0 and 10 mA cm^{-2} respectively for massive LaMnO_3 ($R_F=670$), $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ ($R_F=140$) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ($R_F=1200$) electrodes at $\eta_{\text{O}_2} \sim 0.597$ V in 1M NaOH at 25°C. At the same overpotential and for similar electrodes i.e. $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in 1M KOH at 25°C Matsumoto and Sato²⁷ observed the current densities 0.67, 3.5 and 4.0 mA cm^{-2} , respectively. Thus, the result demonstrates that the sol-gel routes impart greater activity to lanthanum manganites compared to conventional methods.

The influence of the temperature on OER has been investigated in the range 25–65°C; results followed the Arrhenius law satisfactorily. Values of the apparent electrochemical activation energy ($\Delta H_{\text{el}}^{\#0}$) esti-

Table 4—Values of activation parameters for OE on manganites in 1M KOH

Electrode	α	$\Delta H_{cl}^{\#0}/\text{kJ mol}^{-1}$ at $E=0.64\text{ V}$	$\Delta H_c^{\#0}/\text{kJ mol}^{-1}$	$-\Delta S^{\#0}/\text{J deg}^{-1}\text{mol}^{-1}$
LaMnO ₃	0.476	50.1	76.4	212.1
La _{0.9} Sr _{0.1} MnO ₃	0.486	46.8	73.2	216.6
La _{0.8} Sr _{0.2} MnO ₃	0.543	54.6	89.4	186.6
La _{0.7} Sr _{0.3} MnO ₃	0.531	45.2	79.1	211.5
La _{0.6} Sr _{0.4} MnO ₃	0.548	48.3	85.8	192.5
La _{0.5} Sr _{0.5} MnO ₃	0.521	47.1	79.0	213.4

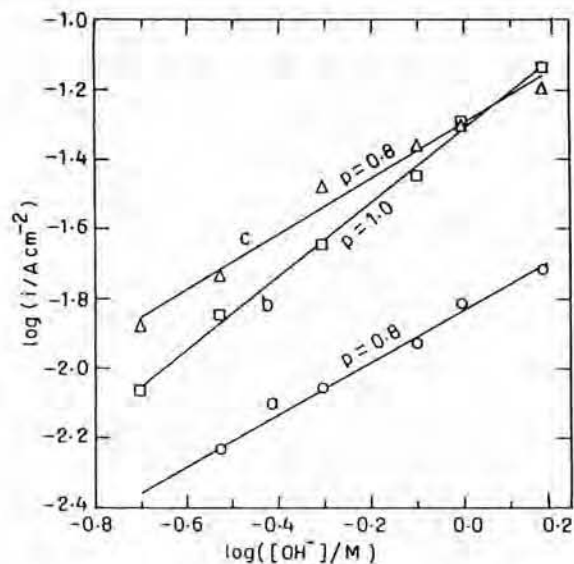


Fig. 8—Plots of $\log i$ vs $\log [\text{OH}^-]$ at a constant potential ($E=0.64\text{ V}$) across the oxide/KOH solution interface at 25°C : (a) LaMnO₃, (b) La_{0.7}Sr_{0.3}MnO₃, and (c) La_{0.5}Sr_{0.5}MnO₃.

mated from the slope of the linear $\log i$ vs $1/T$ plots were observed to decrease linearly with increasing potential or overpotential across the oxide/1M KOH. It was found that with the increase in temperature the b -value increased, while that of the charge transfer coefficient ($\alpha=2.3RT/bF$) slightly decreased. These results are in fact in accordance with the principle of the electrode kinetics. A careful perusal of results shown in Table 4 shows that Sr-substitution slightly increased the α value for the OER, however, its average value for each catalyst was close to 0.5. Sr-substitution slightly decreased the $\Delta H_{cl}^{\#0}$ value, the decrease being maximum with 0.3 mol Sr. The decrease in the $\Delta H_{cl}^{\#0}$ value indicates some modification in the electronic properties of the materials in favour of electrocatalysis. The $\Delta H_{cl}^{\#0}$ values for OE on different electrocatalysts ranged between ~ 45 and $\sim 54\text{ kJ mol}^{-1}$ and that the apparent electrochemical activa-

tion energy at the reversible potential (or at $\eta_{\text{O}_2}=0.0\text{ V}$) ($\Delta H_c^{\#0}$), as estimated using the relation ($\Delta H_c^{\#0}=\Delta H_{cl}^{\#0}+\alpha FE$), ranged between ~ 73 and $\sim 89\text{ kJ mol}^{-1}$. The entropy of activation ($\Delta S^{\#0}$) for OE on each catalyst was found to be highly negative. This suggests the role of adsorption phenomenon in the electrochemical formation of oxygen. The $\Delta S^{\#0}$ values were estimated using the relation²⁸,

$$\Delta S^{\#0} = 2.3 R [\log i + \Delta H_{cl}^{\#0} / 2.3 RT - \log (nF\omega C_{\text{OH}^-})] \quad \dots (1)$$

where, $\omega (=k_B T/h)$ is the frequency term and $n=2$. All the other terms appeared in equation (1) have their usual meanings. The $\Delta S^{\#0}$ values estimated at different temperatures and at three constant potentials chosen in the potential region, 0.62 – 0.65 V, were approximately constant and that their average values are given in Table 4.

As the observed electrode kinetic parameters, namely the Tafel slope and the reaction order for electrocatalysis of O₂ evolution on manganites prepared by us did not show any controversy against their values already reported for similar oxides obtained by other methods, they could be explained by considering a mechanism similar to that already proposed in the literature^{13,26,27}.

It can be concluded that the method used in the oxide preparation influences the oxide roughness greatly. The Sr-substitution (0.1–0.5 mol) in the manganite matrix enhanced both the apparent as well as intrinsic electrocatalytic activity of oxide significantly. Based on the apparent electrocatalytic scale, La_{0.7}Sr_{0.3}MnO₃ has been found to be the best electrocatalyst among the manganites prepared for the investigation.

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References

- 1 Shiao-Tzong shen & Hung-shan Weng, *Ind Eng Res*, 37 (1998) 2654.
- 2 Hee V Lee, Woos Cho, Seung M Oh, H-D Wiemhofer & W Gopel, *J electrochem Soc*, Vol 142 (8) (1995) 2669.
- 3 Tejuca L G, Fierr J LG & Tacson J M D, *Adv catal*, 36 (1989) 237.
- 4 Wendt H & Imarisio G, *J appl Electrochem*, 18 (1988) 1.
- 5 O'Sullivan E J M & Calvo E J, *electrode kinetic reactions*, edited by R G Compton (Elsevier, Amsterdam) 1987, 274.
- 6 Libby W F, *Science*, 171 (1971) 499.
- 7 Tascon J M D, Mediroz S & Tejuca G L, *Phys Chem*, (Munich), 124 (1981) 109.
- 8 Vidyasagar K, Gopalkrishnan J & Rao C N R, *J Solid State Chem*, 58 (1985) 29.
- 9 Sharibba S P, Pomonis P J & Sdonkos A J, *J Mater Chem*, 1 (1991) 637.
- 10 Teraoka V, Kakebayashi B, Moriguchi I & Kagawa S, *Chem Lett*, (1991) 637.
- 11 Teguchi H, Matsuda D & Nagao M, *J Am ceram Soc*, 76 (1992) 201.
- 12 Chang C C & Weng H S, *Ind Eng Chem Res*, 31 (1992) 1615.
- 13 Singh N K, Tiwari S K & Singh R N, *Int J Hydrogen Energy*, 23 (1998) 775.
- 14 Jain A N, Tiwari S K & Singh R N, *Indian J Chem*, 37A (1998) 125.
- 15 Sharma T, Singh N K & Singh R N, *Indian J eng & mat Science*, 5 (1998) 38.
- 16 Verelsto M, Rangaqittal N, Rao C N R & Rousset A, *J Solid State Chem*, 104 (1993) 74.
- 17 Tiwari S K, Chartier P & Singh R N, *J electrochem Soc*, 142(1995)108.
- 18 Singh R N, Koenig J F, Poillera G and Chartier P, *J Electrochem Soc*, 137 (1990)1408.
- 19 Boukamp B A, *Solid State Ionics*, 20 (1986) 31.
- 20 Xiong G, Zheng-Liong zhi, Yang X, Lude Lu & Wang X, *J Mat Sci Letters*, 16(1997) 1064.
- 21 Fradette N & Marsan B, *J electrochem Soc*, 145 (1998) 2320.
- 22 Singh R N, Tiwari S K, Singh S P, Singh N K, Poillera G & Chartier P, *J Chem Soc Faraday Trans*, 92 (1996) 2593.
- 23 Da Silva L A, Alves V S, da Silva M A P, Trassati S and Boodts J F C, *Electrochim Acta*, 42 (1997) 271.
- 24 Levine S & Smith A L, *Faraday Discuss Chem Soc*, 52 (1971) 290.
- 25 Bockris J O'M & Otagawa T, *J Electrochem Soc*, 131 (1984) 290.
- 26 Bockris J O M & Otagawa T, *J phys Chem*, 87 (1983) 2960.
- 27 Matsumoto Y & Sato E, *Electrochim Acta*, 24 (1979) 421.
- 28 Gileadi E, in *Electrode kinetics* (VCH Publishers Inc., New York) 1993, p. 151.