Electrocatalytic properties of Sr-doped LaMn$_3^\text{O}_3$ obtained by a new sol-gel route in doped LaCo$_3^\text{O}_4$ and LaMn$_3^\text{O}_3$ are expected to be used in concert. Efforts have recently been made to develop perovskite-type structures, particularly Ca-containing systems. Suitable preparative methods have been developed to obtain oxides with enhanced roughness and hence the catalytic efficiencies.

Electronically conducting mixed oxides of these perovskites have been obtained by different novel synthetic routes. Very recently, we have carried out investigations of electrocatalysis of La$_{1-x}$Sr$_x$Mn$_3^\text{O}_3$ ($0.05 \leq x \leq 0.5$) obtained by a sol-gel route similar to those recently reported by Lee et al. and Yerelsto. In view of these, the study of electrolytic oxygen evolution on products prepared by malic acid and citric acid-ethylene glycol precursor solutions has been performed. Oxygen evolution on Sr-substituted nickel has been studied to transform into a gel. The latter product was crushed and the final volume of the mixture was maintained by continuous addition of methylene diamine. This solution was evaporated at $-70^\circ\text{C}$ and then dried under vacuum for 5 hours in the presence of water.

Calcination of the oxide film was performed at $700^\circ\text{C}$ for 5 hours in order to produce a viscous sol and then dried under vacuum. The oxide films have been reproducible in the film form on contact with oxide films. The pretreatment of the support and electrical contacts were made as previously described. The pretreatment of the support and electrical contacts were made as previously described. All electrochemical experiments, namely, AC impedance, cyclic voltammetry (CV), and Tafel polarization were performed in a conventional single electrode cell.

La$_{1-x}$Sr$_x$Mn$_3^\text{O}_3$ obtained by the sol-gel technique has been studied for its electrocatalytic properties in water electrolysis and fuel cells. The activation energy of the reaction has been calculated using the Arrhenius equation. The apparent electrochemical activation energy has been found to increase with increasing Sr substitution, while it has no effect on the true electrochemical activation energy. The Tafel slope and the reaction order with respect to the entropy of activation has been found to increase with increasing Sr substitution, while it has no effect on the oxide roughness. The Tafel slope and the reaction order with respect to the entropy of activation has been found to increase with increasing Sr substitution, while it has no effect on the oxide roughness.
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 Hg/HgO/1M KOH (E° = 0.098 V vs NHE) and pure Pt-foil (∼8 cm²), 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 1M KOH were determined over the frequency range 0.02 - 10⁵ Hz at a given DC potential. The double layer capacitance (C₀) and other circuit parameters were analysed using the Equivalent circuit program due to Bernard A. Boukamp. The procedure adopted in other electrochemical measurements, namely, CV and anodic Tafel polarization, were similar to those given elsewhere. 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 cm².

Results and Discussion

XRD

The XRD powder patterns of LaₓSrₓMnO₃ with x = 0, 0.3, 0.5 sintered at 700°C for 5h were recorded between 2θ = 0 and 2θ = 80°. 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 LaMnO₃. However, Sr-substituted manganites showed two weak additional reflections one at 2θ = 36.11 and d = 2.4853 and the other at 2θ = 44.615 and d = 2.0293. These weak reflections can be ascribed to the formation of small amounts of La(OH)₃ (d = 2.4915; JCPDS file No. 38-1481) and La₂O₃ (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 α = β = 90° and γ = 120° and a = b ≠ c. Values of a and c, thus calculated (Table 1) agree well with those reported for LaMnO₃ (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.

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

<table>
<thead>
<tr>
<th>Oxide</th>
<th>a/Å</th>
<th>c/Å</th>
<th>S/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO₃</td>
<td>5.505</td>
<td>13.310</td>
<td>−575</td>
</tr>
<tr>
<td>La₀.₃Sr₀.₇MnO₃</td>
<td>5.450</td>
<td>13.300</td>
<td>−579</td>
</tr>
<tr>
<td>La₀.₅Sr₀.₅MnO₃</td>
<td>5.47</td>
<td>13.310</td>
<td>−744</td>
</tr>
</tbody>
</table>
Fig. 3 — Complex impedance plots for the LaMnO$_3$ electrode over the frequency range: 0.02-10$^5$ Hz in 1M KOH at E = 0.05 V (25°C). A: 10$^5$-10$^7$ Hz.

Fig. 4 — Complex impedance plots for the La$_0.5$Sr$_0.5$MnO$_3$ electrode over the frequency range: 0.02-10$^5$ Hz in 1M KOH at E = 0.05 V (25°C). A: 20-10$^5$ Hz.
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 $1\text{M KOH}$ 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 ($\sim 0.6$ 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 acid$^{13}$ and citric acid$^{15}$ 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 ($\text{LaMnO}_3$) and the other for $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, at 0.05 V in $1\text{M KOH}$ 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 $\text{H}^+$/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 $\text{LaMnO}_3$ 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: $LR_s(R_1Q_1)(R_2Q_2)(C(R_3(W)))$) shown in Fig.6. A set of
Table 2 — Value of the circuit parameters estimated by using $R_s(Q_1)(Q_2)(C(R(W)))$ and $LR_s(Q_1)(Q_2)(C(R(W)))$ equivalent circuit models to approximate experimental impedance diagrams for oxide electrode in 1M KOH at 25°C.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Oxide loading (mg cm$^{-2}$)</th>
<th>$R_s$ (Ohm)</th>
<th>$R_1$ (mho)</th>
<th>$Q_1 \times 10^3$ (mho)</th>
<th>$R_2 \times 10^2$ (mho)</th>
<th>$Q_2 \times 10^3$ (mho)</th>
<th>$n_1$ (Hart)</th>
<th>$n_2$ (Hart)</th>
<th>$C_x \times 10^3$ (Farad)</th>
<th>$R_{f}$ (Ohm)</th>
<th>$R_{c}$ (mho)</th>
<th>$W_x \times 10^3$ (Hertz)</th>
<th>$R_{f}$ (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_3$</td>
<td>12.5 ± 0.6</td>
<td>6.1 ± 0.4</td>
<td>2.44 ± 0.28</td>
<td>0.7</td>
<td>5.9 ± 0.1</td>
<td>1.32 ± 0.04</td>
<td>0.6</td>
<td>7.47 ± 1.13</td>
<td>4.47 ± 0.32</td>
<td>6.50 ± 1.39</td>
<td>-125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>13.5 ± 0.5</td>
<td>5.0 ± 1.0</td>
<td>0.79 ± 0.19</td>
<td>0.9</td>
<td>4.8 ± 0.4</td>
<td>1.01 ± 0.1</td>
<td>0.7</td>
<td>3.27 ± 0.52</td>
<td>7.01 ± 0.56</td>
<td>4.03 ± 0.57</td>
<td>-55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>14.0 ± 0.5</td>
<td>4.4 ± 0.2</td>
<td>1.26 ± 0.3</td>
<td>0.6</td>
<td>3.2 ± 0.1</td>
<td>1.09 ± 0.2</td>
<td>0.7</td>
<td>4.36 ± 0.2</td>
<td>2.67 ± 0.4</td>
<td>6.47 ± 0.35</td>
<td>-73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>16.5 ± 0.2</td>
<td>0.7 ± 0.1</td>
<td>163.57 ± 0.25</td>
<td>0.6</td>
<td>0.3 ± 0.02</td>
<td>0.62 ± 0.1</td>
<td>-1</td>
<td>11.85 ± 1.1</td>
<td>0.02 ± 0.01</td>
<td>0.01 ± 0</td>
<td>-198</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6 — Bode’s plot for the La$_{0.5}$Sr$_{0.5}$MnO$_3$ electrode in 1M KOH at $E = 0.05V$ ($25^\circ$C).

The experimental and the simulated spectra for La$_{0.5}$Sr$_{0.5}$MnO$_3$ 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 unclear.

Estimates of $C_{ad}$ and other circuit parameters are given in Table 2. The relative oxide roughness ($R_f$) values were estimated from the ratio of the estimated $C_{ad}$ of the oxide and the $C_{ad}$ of the smooth oxide surface. The value of 60 µF cm$^{-2}$ is usually taken for the capacitance of the smooth oxide surface. 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 $x \geq 0.3$ mol. The $R_f$ value obtained for La$_{1-x}$Sr$_x$MnO$_3$ in situ were similar to those for the same oxide ($R_f = 72-106$) prepared by malic acid aided route. However, they were considerably low compared to those obtained for the same oxides ($R_f = 483-1767$) prepared by citric acid precursor route. It is noteworthy that in previous papers, the approximate $C_{ad}$ 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 ($25^\circ$C) at 0.0002 V s$^{-1}$
under the anodic condition. Values of the Tafel slope (b) observed at low overpotentials and of the current density (i) 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 (μ = 1.5). With the aid of these polarization curves log i vs log C_{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 KNO₃ (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/2F, Sr-substitution for lanthanum in the perovskite lattice increased the apparent electrocatalytic activity (iₐ) 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 iₐ = 100 mA cm⁻² in 1M KOH at 25°C, the observed oxygen overpotential (ηₒₑ) values were −0.519, −0.516, and −0.516 V on La₀.₆Sr₀.₄MnO₃ 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.²⁶²⁷ Bockris and Otagawa²⁶ found the oxygen evolution current densities 4.3, 1.0 and 10 mA cm⁻² respectively for massive LaMnO₃ (Rᵢ = 670), La₀.₃Sr₀.₇MnO₃ (Rᵢ = 140) and La₀.₅Sr₀.₅MnO₃ (Rᵢ = 1200) electrodes at ηₒₑ = 0.597 V in 1M NaOH at 25°C. At the same overpotential and for similar electrodes i.e. La₀.₃Sr₀.₇MnO₃, La₀.₅Sr₀.₅MnO₃ and La₀.₅Sr₀.₅MnO₃ 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 (ΔHₑ) esti-

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### Table 3—Electrode kinetic parameters for OER on La₁₋ₓSrₓMnO₃ in 1M KOH at 25°C

<table>
<thead>
<tr>
<th>Electrode</th>
<th>b (V decade⁻¹)</th>
<th>Order(p)</th>
<th>l mA cm⁻² at ηₒₑ</th>
<th>l mA cm⁻² at ηₒₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO₃</td>
<td>0.135 ± 0.008</td>
<td>0.8</td>
<td>13.8 ± 1.8</td>
<td>21.4 ± 2.6</td>
</tr>
<tr>
<td>La₀.₃Sr₀.₇MnO₃</td>
<td>0.108</td>
<td>1.0</td>
<td>32.6</td>
<td>59.9</td>
</tr>
<tr>
<td>La₀.₅Sr₀.₅MnO₃</td>
<td>0.107 ± 0.003</td>
<td>0.8</td>
<td>32.3 ± 2.8</td>
<td>59.7 ± 7.5</td>
</tr>
<tr>
<td>La₀.₆Sr₀.₄MnO₃</td>
<td>0.092 ± 0.002</td>
<td>1.0</td>
<td>67.7 ± 4.1</td>
<td>106.1 ± 8.9</td>
</tr>
<tr>
<td>La₀.₇Sr₀.₃MnO₃</td>
<td>0.101</td>
<td>0.8</td>
<td>36.4 ± 2.2</td>
<td>66.8 ± 5.1</td>
</tr>
<tr>
<td>La₀.₈Sr₀.₂MnO₃</td>
<td>0.106 ± 0.001</td>
<td>0.8</td>
<td>55.9 ± 4.4</td>
<td>104 ± 3.2</td>
</tr>
</tbody>
</table>

---

Fig. 7—iR-free Tafel plots on La₁₋ₓSrₓMnO₃ 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.
LAL et al.: ELECTROCATALYTIC PROPERTIES OF Sr-DOPED LaMnO$_3$

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

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\Delta H_e^{0\theta}$ /kJ mol$^{-1}$ at $E=0.64$ V</th>
<th>$\Delta H_c^{0\theta}$ /kJ mol$^{-1}$</th>
<th>$-\Delta S^{0\theta}$/J deg$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LaMnO}_3$</td>
<td>0.476</td>
<td>50.1</td>
<td>76.4</td>
</tr>
<tr>
<td>$\text{La}<em>{0.9}\text{Sr}</em>{0.1}\text{MnO}_3$</td>
<td>0.486</td>
<td>46.8</td>
<td>73.2</td>
</tr>
<tr>
<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{MnO}_3$</td>
<td>0.543</td>
<td>54.6</td>
<td>89.4</td>
</tr>
<tr>
<td>$\text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{MnO}_3$</td>
<td>0.531</td>
<td>45.2</td>
<td>79.1</td>
</tr>
<tr>
<td>$\text{La}<em>{0.6}\text{Sr}</em>{0.4}\text{MnO}_3$</td>
<td>0.548</td>
<td>48.3</td>
<td>85.8</td>
</tr>
<tr>
<td>$\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{MnO}_3$</td>
<td>0.521</td>
<td>47.1</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Fig. 8 — Plots of log i vs log [OH$^-$/M$^+$] at a constant potential (E = 0.64 V) across the oxide/KOH solution interface at 25°C: (a) $\text{LaMnO}_3$, (b) $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

estimated 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 $\alpha$ value for the OER, however, its average value for each catalyst was close to 0.5. Sr-substitution slightly decreased the $\Delta H_e^{0\theta}$ value, the decrease being maximum with 0.3 mol Sr. The decrease in the $\Delta H_e^{0\theta}$ value indicates some modification in the electronic properties of the materials in favour of electrocatalysis. The $\Delta H_e^{0\theta}$ values for OE on different electrocatalysts ranged between -45 and -54 kJ mol$^{-1}$ and that the apparent electrochemical activation energy at the reversible potential (or at $\eta_{O_2} = 0.0$ V) ($\Delta H_e^{0\theta}$), as estimated using the relation ($\Delta H_e^{0\theta} = \Delta H_e^{0\theta} + \alpha FE$), ranged between -73 and -89 kJ mol$^{-1}$.

The entropy of activation ($\Delta S^{0\theta}$) 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 $\Delta S^{0\theta}$ values were estimated using the relation$^{58}$,

$$\Delta S^{0\theta} = 2.3 R \left[ \log i + \Delta H_e^{0\theta} / 2.3 RT - \log (nF\rho C_{O_2}) \right]$$

where, $\omega (=k_BT/h)$ is the frequency term and $n=2$. All the other terms appeared in equation (1) have their usual meanings. The $\Delta S^{0\theta}$ 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 $O_2$ 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$^{13,20,27}$.

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, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has been found to be the best electrocatalyst among the manganites prepared for the investigation.

Acknowledgement

Authors are grateful to the Department of Science and Technology (DST), New Delhi for providing financial support through project SP/S1/H-36/96.
References