

## Electrocatalytic characterization of new $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ films on Pt for use as oxygen anode in alkaline solutions

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Pure and Sr-substituted lanthanum cobaltate films have been prepared on Pt by a sol-gel derived route and their physicochemical and electrochemical properties investigated using XRD, IR, cyclic voltammetry (CV), Tafel-polarization and impedance techniques. The films have been obtained by coating a thick colloidal solution formed by peptization of freshly prepared metal carbonate precipitate in glacial acetic acid and subsequent drying and sintering at  $650^\circ\text{C}$  for 2 h. The substitution of La by Sr in the perovskite lattice does not indicate any significant influence on the rate of  $\text{O}_2$  evolution reaction (OER) in 1M KOH. Values of the Tafel slope and the order for the reaction have been observed to be  $\sim 2.303RT/F$  and  $\sim 1$ , respectively, regardless of the nature of the oxide catalyst. The apparent electrochemical activation energy ( $\Delta H_{\text{el}}^\ddagger$ ) decreases linearly with increasing potential across the oxide/1M KOH interface. Values of the entropy of activation ( $\Delta S^\ddagger$ ) for the OER are highly negative. Based on electrode kinetic results, the OER is considered to proceed with the formation of adsorbed OH radical as the intermediate in a fast step followed by its electrochemical interaction to yield physisorbed  $\text{H}_2\text{O}_2$  in the slow step.

Cobalt perovskites, particularly lanthanum cobaltates with general formula,  $\text{La}_{1-x}\text{A}'_x\text{Co}_{1-y}\text{B}'_y\text{O}_3$  (where  $\text{A}' = \text{Sr, Ca}$ , and  $\text{B}' = \text{Fe, Ni, Cu, Mn}$  etc.,) have been considered as low cost substitutes for noble metals in electrocatalysis<sup>1-6</sup> and automotive exhaust treatment systems<sup>7</sup>. To improve their electrocatalytic properties different chemical methods such as hydroxide, cyanide and nitrate solid solution<sup>8</sup> and carbonate<sup>9</sup> and sol-gel routes involving citric acid<sup>10</sup>, polyacrylic acid<sup>11</sup>, and malic acid<sup>12</sup> precursors were recently employed to synthesize them. These studies have shown<sup>11-13</sup> that the method, conditions and starting materials for the oxide preparation and also metal ion dopings greatly affect textural and catalytic properties of oxides. It is, therefore, of interest to carry out a detailed investigation on physicochemical and electrocatalytic properties of these potential catalytic materials prepared by new methods. We have obtained pure and Sr-substituted lanthanum cobaltate films on Pt by a sol-gel derived route and studied their physico-chemical and electrocatalytic properties using XRD, IR, CV, Tafel polarization and impedance techniques with the objective to find their application as anodes in alkaline water electrolysis cells. Details of results of the investigation are presented in this paper.

### Materials and Methods

Perovskite-type  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $0 \leq x \leq 0.5$ ) samples were prepared by using freshly prepared metal carbonates as precursors. To obtain the oxide of a particular composition, the nitrate of metals, namely,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (CDH, 99%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, 99%), and  $\text{Sr}(\text{NO}_3)_2$  (CDH, 99.5%) as per stoichiometry were dissolved in a fixed volume of distilled water and to this required amount of  $\text{K}_2\text{CO}_3$  (BDH, 99%) in the form of solution was added dropwise with stirring. The precipitated metal carbonate was filtered, washed thoroughly and finally dried in air. The dried carbonate was then dispersed in glacial acetic acid and the resulting thick colloidal solution was coated onto a pretreated Pt-substrate ( $1 \times 1.5 \text{ cm}^2$ ), thermally heated at  $300^\circ\text{C}$  and finally decomposed at  $650^\circ\text{C}$  for 2h to obtain an adherent oxide film on Pt. The pretreatment of the substrate was carried out as previously described<sup>14</sup>.

Oxide materials, so synthesized, were characterized by recording IR spectra ( $4000\text{--}400 \text{ cm}^{-1}$ ) (JASCO FT/IR-5300) and XRD powder pattern ( $0^\circ < 2\theta < 70^\circ$ ) (Philips diffractometer: PW 1710). The  $\text{Cu-K}_\alpha$  radiation ( $d = 1.54056 \text{ \AA}$ ) was used as a radiation source and the scan rate was  $2.4^\circ \text{ min}^{-1}$  (step size =  $0.02^\circ 2\theta$  and time per step = 0.5 s).

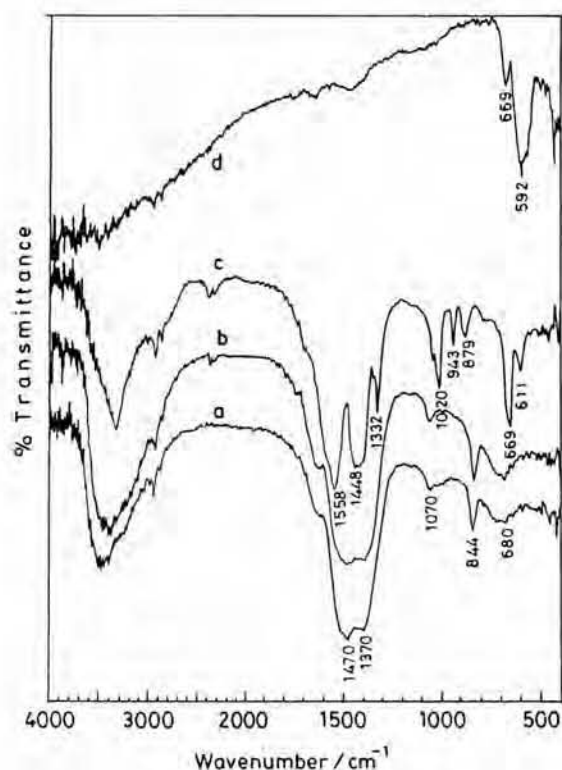


Fig. 1—IR spectra of some compounds on KBr pellets: (a) La-Co-CO<sub>3</sub> precipitate (air-dried), (b) La-Sr-Co-CO<sub>3</sub> precipitate (air-dried), (c) La-Co-CO<sub>3</sub> precipitate dispersed in glacial CH<sub>3</sub>COOH (air-dried gel), (d) after thermal decomposition of (c) at 700°C (6h) (i.e. LaCoO<sub>3</sub>).

For electrochemical measurements, an electrical connection to the oxide films was taken from the platinum surface as mentioned earlier<sup>12,15,16</sup>. All electrochemical experiments, namely, impedance, cyclic voltammetry (CV) and Tafel polarization were performed in a conventional single compartment Pyrex glass cell using electrochemical impedance system (model 273 A, EG & G Princeton Applied Research, U.S.A.); softwares used in the corresponding studies were electrochemical impedance Model 388, Research Electrochemistry Model 270/250, and Corrosion analysis Model 352. The reference and auxiliary electrodes used were Hg/HgO/1 M KOH ( $E^0 = 0.098$  V vs NHE) and pure Pt-foil ( $\sim 8$  cm<sup>2</sup>), respectively. All potential values in the text are given with respect to Hg/HgO only.

Impedance measurements of the oxide film electrodes in 1M KOH were performed with the AC voltage amplitude of  $\pm 5$  mV in the frequency range 0.02 to 10<sup>5</sup> Hz at three DC potentials 0.0, 50, and 100 mV. The  $C_{dl}$  at each DC potential was analysed by using the "Equivalent Circuit" program written by Bernard A. Foukamp<sup>17</sup> considering a series "LRQC"

model for the oxide electrodes. The circuit elements L, R, Q and C are inductance(Henri), resistance(ohm), constant phase element(mho) and capacitance (Faraday), respectively. The proposed series model fits well with the experimental data. The procedure followed in CV and anodic polarization measurements were similar to those whose details are given elsewhere<sup>16</sup>. The  $iR$ -free (where  $R$  is the resistance of the electrolyte between the reference and the oxide film including the resistance of the latter) anodic polarization curves were recorded at a slow scan rate (0.2 mV s<sup>-1</sup>). The  $iR$  compensation was made by interrupting current at every 10s during the polarization.

## Results and Discussion

### IR

The IR spectra of two metal carbonate precursors, La-Co-CO<sub>3</sub> (a) and La-Sr-Co-CO<sub>3</sub> (b) and of a complex gel of 'a' (c) and its thermally decomposed product (d: LaCoO<sub>3</sub>) at 750°C for 6h are shown in Fig. 1. As spectra of compounds 'a' and 'b' were similar, only IR of the complex gel formed with 'a' compound was recorded. A strong broad peak observed in the region,  $\sim 1500$ - $1400$  cm<sup>-1</sup> due to  $\nu(\text{CO})$  vibration in the case of 'a' and 'b' precursors is clearly resolved as three sharp peaks at  $\sim 1560$ ,  $\sim 1450$  and  $\sim 1330$  cm<sup>-1</sup> in the polymer based material 'c'. The latter peaks disappeared almost completely after the thermal treatment of the polymeric compound 'c'. However, the weak broad peak near  $700$  cm<sup>-1</sup> observed in 'a' and 'b' compounds due to  $\delta(\text{O-C-O})$  and  $\nu(\text{CoO})$  vibrations<sup>18</sup> gives rise to two peaks at  $\sim 669$  and  $\sim 600$  cm<sup>-1</sup> in the polymer compound 'c' (Fig. 1d), while a strong peak near  $\sim 590$  cm<sup>-1</sup> (Co-O stretching) in the case of compound 'd'. Thus, the latter compound indicates the formation of a single entity, i.e., LaCoO<sub>3</sub> (ref. 19).

### XRD

The powder X-ray diffraction patterns of the base oxide (i.e. LaCoO<sub>3</sub>) prepared at 700°C in presence of air and at 700°C and 800°C respectively in presence of O<sub>2</sub> shown in Fig.2 indicate the formation of more or less pure perovskite phase regardless of the nature of the carrier gas used. The figure shows very weak diffraction peaks for Co<sub>3</sub>O<sub>4</sub> ( $d = 1.43$  and  $2.45$ - $2.42$  Å) as impurity. The unit cell parameters ' $a$ ' ( $= 5.450$  Å), ' $c$ ' ( $= 13.152$  Å) and  $V$  ( $= 338.31$  (Å)<sup>3</sup>) were estimated assuming the rhombohedral hexagonal crystal geometry ( $a = b \neq c$  and  $\alpha = \beta = 90^\circ$  and  $\gamma =$

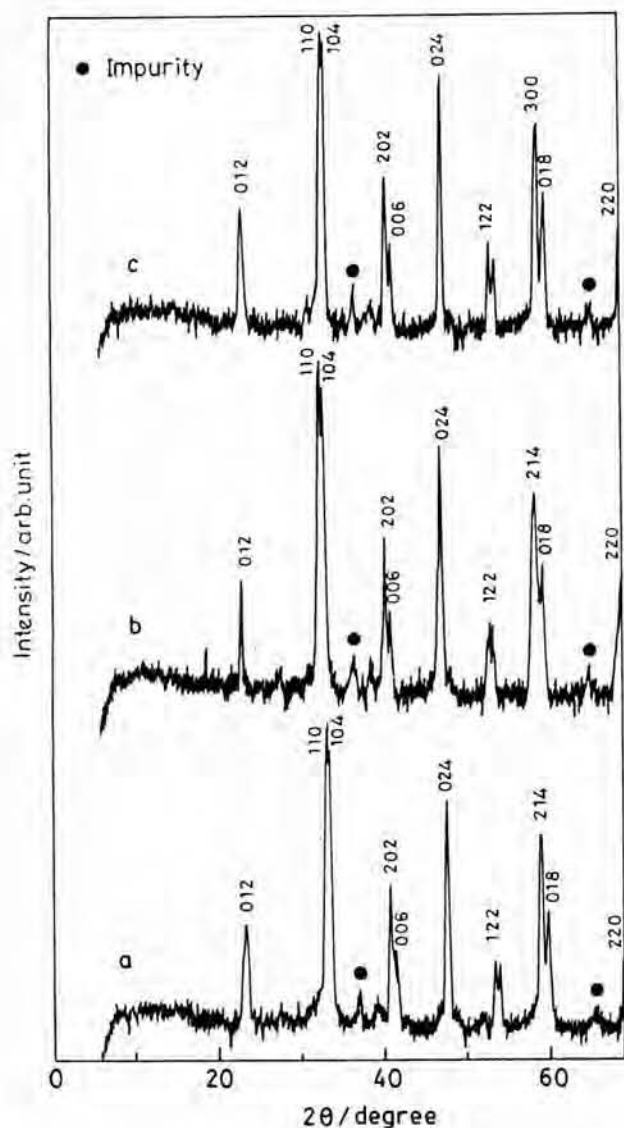


Fig. 2—XRD powder patterns of  $\text{LaCoO}_3$  prepared at different temperatures; (a)  $700^\circ\text{C}$  + air (6h), (b)  $700^\circ\text{C}$  +  $\text{O}_2$  (6h), and (c)  $800^\circ\text{C}$  +  $\text{O}_2$  (6h).

$120^\circ$ ) for lanthanum cobaltate. Values of 'a' and 'c', thus calculated, agree very well with those reported for a similar oxide (i.e.  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ ) in the JCPDS ASTM file No. 28-1229 [ $a = 5.45 \text{ \AA}$ ,  $c = 13.153 \text{ \AA}$  and  $V = 338.31 (\text{\AA})^3$ ]. Values of the crystallite size (S) were also estimated using the Scherrer formula<sup>19,20</sup>,

$$S = 0.9\lambda / B \cos\theta,$$

where  $\lambda$  is the wavelength of the radiation source and B is the full width at half maximum of the most intense perovskite peak in radians and  $\theta$  is the corresponding angle in deg. The S values were  $\sim 133$  at  $700^\circ\text{C}$  in presence of air, and  $\sim 118$  and  $\sim 133 \text{ \AA}$

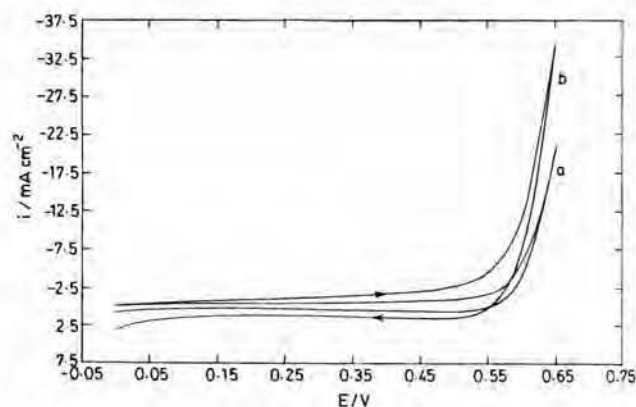


Fig. 3—Cyclic voltammograms of lanthanum cobaltate films on Pt at  $20 \text{ mV s}^{-1}$  in  $1\text{M KOH}$  ( $25^\circ\text{C}$ ); (a)  $\text{LaCoO}_3$ , (b)  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ .

respectively at  $700^\circ$  and  $800^\circ\text{C}$  in presence of  $\text{O}_2$ . Thus, the crystallite size of the oxide appears to be slightly reduced in presence of  $\text{O}_2$  and enhanced with the increase in the preparation temperature from  $700$  to  $800^\circ\text{C}$ . The increase in the grain size of the oxide may be ascribed to the improvement in process of crystallization at higher temperature.

#### Cyclic voltammetry (CV)

The CV curves for the lanthanum cobaltate films on Pt were similar regardless of the nature of the catalytic films. Two representative curves, one for the base and the other for  $0.5 \text{ mol Sr}$ -substituted  $\text{LaCoO}_3$  in  $1\text{M KOH}$  at  $25^\circ\text{C}$  are shown in Fig. 3. This figure demonstrates that the catalytic films are quite stable and that they do not undergo any electrochemical oxidation/reduction reaction before the onset of the OER. Similar CV curves were also found with the same oxides recently prepared by the hydroxide solid solution<sup>13</sup> and sol-gel routes<sup>11,12</sup>.

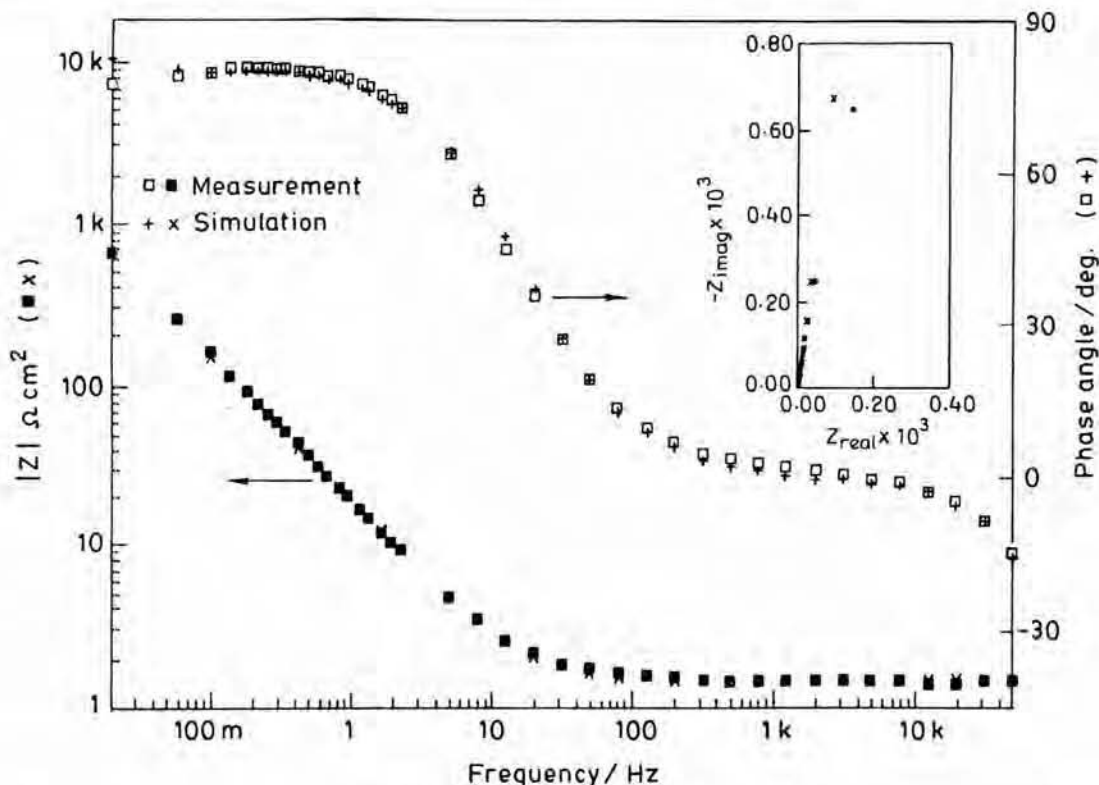
#### Roughness factor ( $R_F$ )

The  $C_{dl}$  of the oxide catalyst/ $1\text{M KOH}$  interface was determined by analysing impedance data using the series LRQC electrical circuit model. Values of the circuit elements are given in Table 1. This series equivalent circuit fairly reproduces the feature of the experimental curve. A representative impedance spectrum both in Nyquist and Bode formats at  $E = 50 \text{ mV}$  for the  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  electrode in  $1\text{M KOH}$  is shown in Fig. 4.

The values of the  $C_{dl}$  of three electrodes, namely,  $\text{LaCoO}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  were also estimated by determining the CV curves in a small potential region ( $0$ – $50 \text{ mV}$ ) at varying potential scan

Table 1—Values of the circuit parameters obtained by using the LRQC equivalent circuit model to approximate experimental a.c. impedance diagrams for oxide electrode in 1 M KOH at 25°C

| Oxide-film electrode                                 | Loading (mg cm <sup>-2</sup> ) | $L \times 10^6 / H$ | $R / \text{ohm}$ | $Q \times 10^2 / \text{mho}$ | $n / \text{Hz}$ | $C / \text{mF cm}^{-2}$ | $R_F$    | $R_{F(\text{CV})}$ |
|------------------------------------------------------|--------------------------------|---------------------|------------------|------------------------------|-----------------|-------------------------|----------|--------------------|
| LaCoO <sub>3</sub>                                   | 6.8 ± 1.4                      | 0.86 ± 0.35         | 2.1 ± 1.2        | 1.73 ± 1.1                   | 0.75 ± 0.1      | 14.69 ± 1.34            | 245 ± 22 | 298                |
| La <sub>0.9</sub> Sr <sub>0.1</sub> CoO <sub>3</sub> | 5 ± 0.1                        | 0.97 ± 0.06         | 1.7 ± 0.1        | 1.31                         | 0.79            | 21.65 ± 0.23            | 361 ± 4  |                    |
| La <sub>0.8</sub> Sr <sub>0.2</sub> CoO <sub>3</sub> | 6.2 ± 0.4                      | 1.20 ± 0.06         | 1.1 ± 0.2        | 1.7                          | 0.79 ± 0.1      | 20.19 ± 0.23            | 336 ± 29 | 336                |
| La <sub>0.7</sub> Sr <sub>0.3</sub> CoO <sub>3</sub> | 4.2 ± 0.5                      | 1.15 ± 0.01         | 1.6 ± 0.1        | 1.52 ± 0.1                   | 0.88            | 36.11 ± 0.14            | 602 ± 2  |                    |
| La <sub>0.6</sub> Sr <sub>0.4</sub> CoO <sub>3</sub> | 5.5 ± 2.5                      | 1.22 ± 0.12         | 1.7 ± 0.4        | 3.17 ± 1.5                   | 0.60 ± 0.1      | 18.17 ± 0.3             | 303 ± 5  |                    |
| La <sub>0.5</sub> Sr <sub>0.5</sub> CoO <sub>3</sub> | 5.1 ± 0.1                      | 0.86 ± 0.01         | 1.9 ± 0.1        | 5.97 ± 2.1                   | 0.64 ± 0.6      | 27.51 ± 5.1             | 459 ± 85 | 438                |

Fig. 4—Nyquist and Bode plots for the La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> electrode in 1M KOH at 25°C. The simulation was made with the equivalent circuit LRQC (series model), using the partial and total NLLS-fits.

rates and then constructing the linear plot, the current density ( $i_{\text{cap}}$ ) vs scan rate, as shown in Fig. 5. The charging current density corresponding to each scan rate was estimated at the middle of the scan range, details of which are described elsewhere<sup>12,13</sup>. The double layer capacitance was estimated from the slope of Fig. 5.

Values of the roughness factor ( $R_F$ ) for oxide catalysts shown in Table 1 are relative ones and have been computed using the following relation,

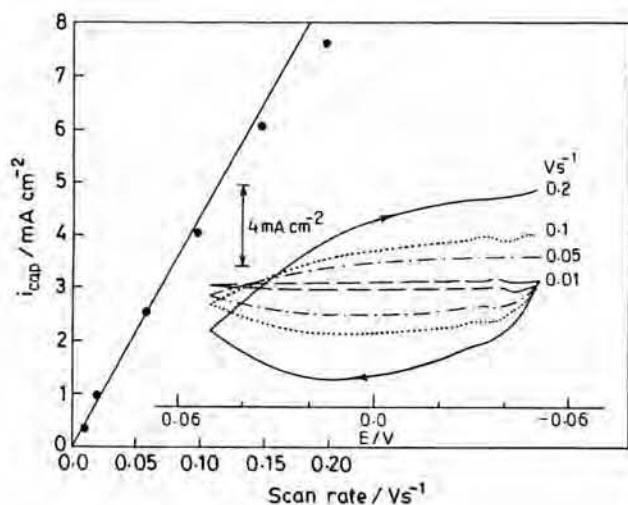
$$R_F = \frac{\text{The } C_{\text{dl}} \text{ of the oxide electrode}}{\text{The } C_{\text{dl}} \text{ of the smooth oxide (60 } \mu\text{F cm}^{-2}\text{)}}$$

In similar estimations,  $C_{\text{dl}}$  value of 60  $\mu\text{F cm}^{-2}$  for a smooth oxide surface has already been considered by several workers<sup>12,21,22</sup>.

Table 1 shows that the  $R_F$  values for oxides determined by both the methods are close to each other. This justifies the application of both impedance as well as cyclic voltammetry in estimation of the real (or true) surface area of the perovskite electrodes. Further, the partial replacement of La by Sr in the perovskite matrix improves the oxide roughness, the improvement being greatest with 0.3 mol Sr. The increase in the  $R_F$  value with Sr-substitution has also been reported in literature<sup>11–13,22</sup>. The  $R_F$  value for the

Table 2—Electrode kinetic parameters for  $\text{O}_2$  evolution on  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  electrodes in 1M KOH at 25°C

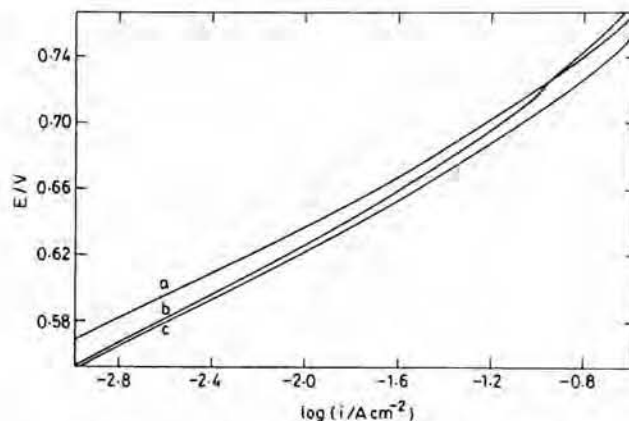
| Oxide-film electrode                         | Loading ( $\text{mg cm}^{-2}$ ) | Tafel slope (b) ( $\text{mV decade}^{-1}$ ) | $i/\text{mA cm}^{-2}$ at $E/\text{mV}$ |                            |                  |                            |
|----------------------------------------------|---------------------------------|---------------------------------------------|----------------------------------------|----------------------------|------------------|----------------------------|
|                                              |                                 |                                             | 600                                    | 700                        | 700              | 700                        |
|                                              |                                 |                                             | $i_{\text{app}}$                       | $i_{\text{r}} \times 10^3$ | $i_{\text{app}}$ | $i_{\text{r}} \times 10^3$ |
| $\text{LaCoO}_3$                             | $6.8 \pm 1.4$                   | $68 \pm 3$                                  | $3.7 \pm 1.5$                          | 15.1                       | $65.5 \pm 6.6$   | 157.5                      |
| $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ | $5 \pm 0.1$                     | $71 \pm 1$                                  | $2.05 \pm 0.2$                         | 5.7                        | $40.5 \pm 4.7$   | 110.9                      |
| $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ | $6.2 \pm 0.4$                   | $72 \pm 3$                                  | $4.9 \pm 0.3$                          | 14.6                       | $70.1 \pm 1.9$   | 208.4                      |
| $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ | $4.2 \pm 0.5$                   | $70 \pm 1$                                  | $3.55 \pm 0.2$                         | 5.9                        | $64.6 \pm 3.2$   | 107.3                      |
| $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ | $5.5 \pm 2.5$                   | $72 \pm 3$                                  | $4.0 \pm 0.9$                          | 13.2                       | $74.9 \pm 11.7$  | 247.1                      |
| $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ | $5.1 \pm 0.1$                   | $69 \pm 1$                                  | $3.6 \pm 0.4$                          | 7.85                       | $52.9 \pm 2.4$   | 115.3                      |

Fig. 5—Typical cyclic voltammograms and linear  $i_{\text{cap}}$  vs scan rate plots on  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  (geometrical area =  $0.5 \text{ cm}^2$ ) in the potential region ( $-0.06$ – $0.06 \text{ V}$ ) in 1M KOH at 25°C.

base oxide obtained in this study was similar to that found for the same oxide recently prepared by malic acid ( $R_F = 265$ )<sup>12</sup>, polyacrylic acid ( $R_F = 265$ )<sup>11</sup> and hydroxide solid solution ( $R_F = 320$ )<sup>13</sup> methods.

#### Electrocatalytic activity

The catalytic activity of oxide film electrodes towards the  $\text{O}_2$  evolution reaction (OER) was determined by recording the anodic Tafel polarization curves at a slow scan rate ( $0.2 \text{ mV s}^{-1}$ ) in 1M KOH at 25°C; results are shown in Fig. 6 and Table 2. The nature and the slope ( $b = 70 \pm 2 \text{ mV decade}^{-1}$ ) of the Tafel polarization curves found for the base and Sr-substituted  $\text{LaCoO}_3$  were almost similar indicating thereby that the OER follows similar mechanistic paths on each electrocatalyst. The order for OE was also found to be approximately the same ( $p = 0.98 \pm 0.05$ ) regardless of the nature of the oxide catalyst. To determine the order,  $E$  vs  $\log i$  curves were determined at varying KOH concentrations

Fig. 6— $iR$ -free Tafel plots on lanthanum cobaltate films on Pt in 1M KOH at 25°C; (a)  $\text{LaCoO}_3$ , (b)  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ , and (c)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ .

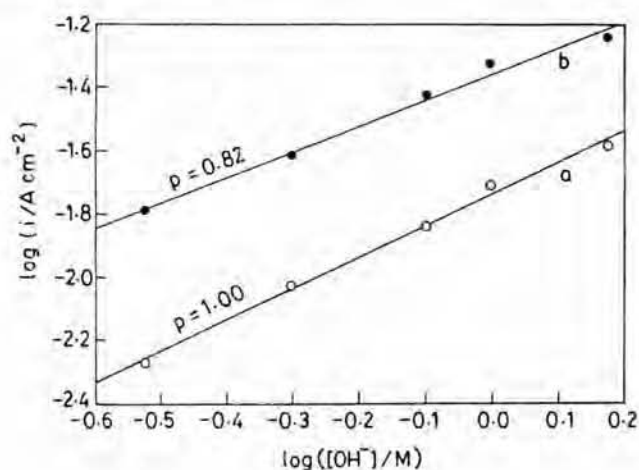
keeping the ionic strength of the medium constant ( $\mu = 1.5$ ) and then the  $\log i$  vs  $\log [\text{OH}^-]$  plots were constructed at a constant potential across the oxide/KOH solution interface as shown in Fig. 7. Potassium nitrate (Merck, 98%) was used as an inert electrolyte to maintain the ionic strength of the solution.

It is evident from Table 2 that the apparent catalytic activity ( $i_{\text{app}}$ ) of the base oxide is not influenced significantly by Sr-substitution. However, similar catalytic layers prepared by other methods<sup>11,13,23</sup> were observed to enhance the apparent catalytic activity greatly. The true catalytic activity ( $i_{\text{r}} = i_{\text{app}}/R_F$ ) of the oxide anode did not show a definite trend; however, its value was the highest with 0.4 mol Sr-substitution.

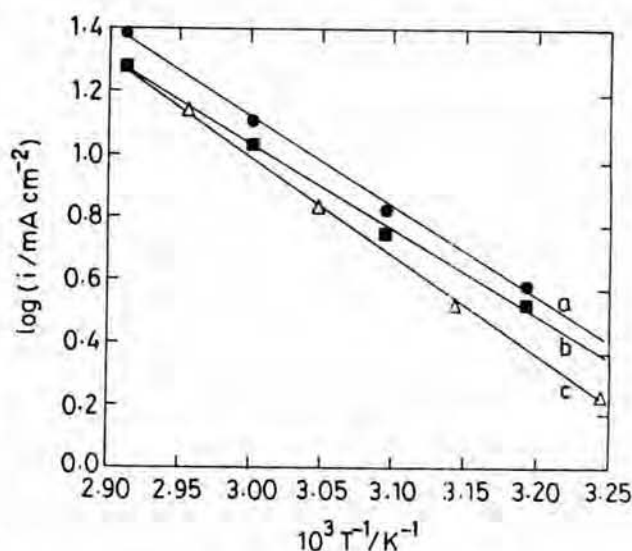
The kinetics of OER at three representative oxide electrodes,  $\text{LaCoO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  in 1 M KOH has been investigated at temperatures 25, 35, 45, 55 and 65°C; results are shown in the form of the Arrhenius plot in Fig. 8. Values of the apparent electrochemical activation energy ( $\Delta H_{\text{el}}^\ddagger$ ) estimated from the slope of the linear plot,  $\log i$  vs

Table 3—Values of activation parameters for OE on cobaltates in 1M KOH

| Electrode                                    | $\Delta H_{cl}^\# / \text{kJ mol}^{-1}$ at $E = 600 \text{ mV}$ | $\Delta H_c^\# / \text{kJ mol}^{-1}$ |                          | $-\Delta S^\# / \text{J deg}^{-1} \text{mol}^{-1}$ |
|----------------------------------------------|-----------------------------------------------------------------|--------------------------------------|--------------------------|----------------------------------------------------|
|                                              |                                                                 | Graphical                            | Calculated from b values |                                                    |
| $\text{LaCoO}_3$                             | 52.1                                                            | 98                                   | 105                      | $166 \pm 1$                                        |
| $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ | 50.6                                                            | 123                                  | 100                      | $175 \pm 6$                                        |
| $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ | 59.8                                                            | 147                                  | 105                      | $154 \pm 5$                                        |

Fig. 7—Plots of  $\log i$  vs  $\log [\text{OH}^-]$  at a constant potential ( $E = 0.6 \text{ V}$ ) across the oxide /KOH solution interface at  $25^\circ\text{C}$ ; (a)  $\text{LaCoO}_3$ , and (b)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ .

$1/T$ , at  $E = 0.6 \text{ V}$  were  $52.1$ ,  $50.6$ , and  $59.8 \text{ kJ mol}^{-1}$  for  $\text{LaCoO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ , respectively. It was observed that the  $\Delta H_{cl}^\#$  value for OE on each oxide electrode decreased linearly with increasing potential across the oxide/1M KOH interface as shown in Fig. 9. Similar results were also obtained by Damjanoic *et al.*<sup>24</sup> for OE on Pt in alkaline solution. The activation energies ( $\Delta H_c^\#$ ) for three different catalysts obtained by the extrapolation of the  $\Delta H_{cl}^\#$  vs  $E$  curve to the reversible potential of OE (i.e.  $303 \text{ mV}$  vs Hg/HgO in 1M KOH) are given in Table 3. This Table also contains the  $\Delta H_c^\#$  value determined from the average value of the Tafel slope (b) obtained at temperatures  $25, 35, 45, 55$  and  $65^\circ\text{C}$ , using the relation,  $\Delta H_c^\# = \Delta H_{cl}^\# - 2.303 RT/b$ . Thus, results show that  $0.4 \text{ mol}$  Sr-substitution reduces the activation energy and hence increases the rate for the OER, while its higher substitution ( $0.5 \text{ mol}$ ) has the adverse effect. Similar conclusion was also drawn from the observed values of the current density at a given potential (Table 2). It is noteworthy that the observed values of  $\Delta H_{cl}^\#$  determined at  $E = 0.6 \text{ V}$  for the oxides prepared *in situ* were considerably lower than those obtained for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  ( $76.4 \text{ kJ mol}^{-1}$ ,  $E = 0.6 \text{ V}$ ) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  ( $74.3 \text{ kJ mol}^{-1}$ ,  $E =$

Fig. 8—Arrhenius plots for oxide film electrodes on Pt in 1M KOH at the constant potential,  $E = 0.6 \text{ V}$ ; (a)  $\text{LaCoO}_3$ , (b)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  and (c)  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ .

$0.6 \text{ V}$ ) prepared by a ceramic method<sup>23</sup>. Average values of the entropy of activation ( $\Delta S^\#$ ) for the OER were  $\sim -166$ ,  $\sim -175$ ,  $\sim -154 \text{ J deg}^{-1} \text{mol}^{-1}$ , respectively for  $\text{LaCoO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ; the values were estimated using the relation<sup>25</sup>,

$$\Delta S^\# = 2.303R[\Delta H_{cl}^\# / 2.303RT + \log i - \log n F w C_{\text{OH}^-}],$$

where,  $w = kT/h$  and  $n = 2$ . Highly negative  $\Delta S^\#$  values are characteristics of the surface catalyzed reactions. The  $\Delta S^\#$  values for OE, to our knowledge, at the oxide electrode have not been reported in the literature.

The observed values of the Tafel slope ( $\sim 2.3RT/F$ ) and the order ( $\sim 1$ ) for the OER on lanthanum cobaltates in the present investigation were similar to those found for similar oxides prepared by other methods<sup>11-13, 22</sup>. There is only one report, in our knowledge, in the literature<sup>23</sup> wherein the order  $\sim 2$  for the OER on  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  with  $x = 0.2$  and  $0.4$  has been quoted. Based on values of the Tafel parameters the following mechanism for the OER can tentatively be given:

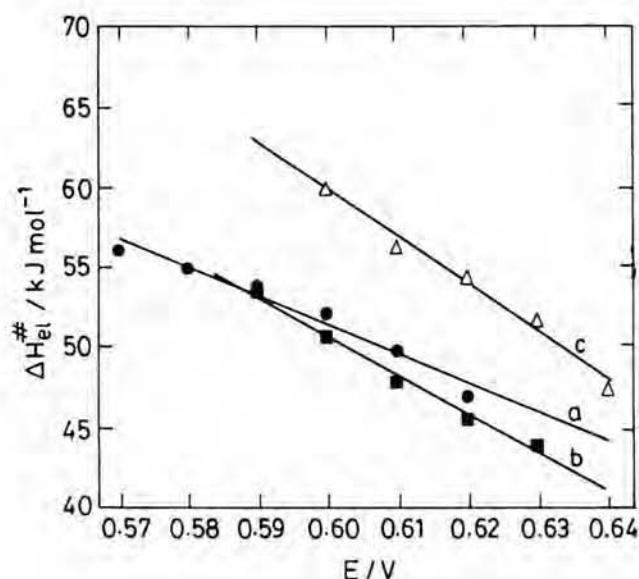
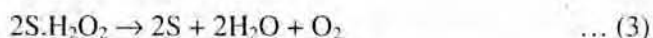
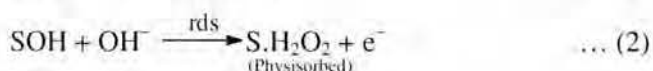


Fig. 9—Plots of  $\Delta H_{el}^{\#}$  vs  $E$  across the oxide/1M KOH interface; (a)  $\text{LaCoO}_3$ , (b)  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  and (c)  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ .



This mechanism is similar to that already given by Bockris and Otagawa<sup>26</sup>. The possibility of other mechanisms as proposed by Krasilschikov<sup>26</sup> and Kretajic and Trasatti *et al.*<sup>27</sup> cannot be ruled out. In the proposed mechanism, 'S' ( $=\text{Co}^{3+}$ ) is an active site on the oxide surface and OH radical and  $\text{H}_2\text{O}_2$  molecule are the surface adsorbed intermediates. Assuming step (2) as the rate determining step (rds) and the total coverage ( $\theta_r = \theta_{\text{OH}} + \theta_{\text{H}_2\text{O}_2}$ ) under Temkin adsorption condition ( $0.2 < \theta_r < 0.8$ ), the observed values of  $b$  ( $\approx 2.3 RT/F$ ) and the order ( $p=1$ ) can be explained, details of which are given elsewhere<sup>14,26</sup>.

## Conclusion

The study has shown that the lanthanum cobaltate films on Pt produced by a sol-gel derived route were adherent and active. Sr-substitution (0.1–0.5 mol) in the oxide matrix did not influence the electrocatalytic activity of the base oxide significantly. The OER seemed to follow similar mechanisms on each oxide electrode regardless of its nature.

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