Strontium Substituted SmNiO₃: Novel Electrode Materials for Alkaline Water Electrolysis

Reena Parihar, Priya Sharma, Amritpal Singh Chaddha, Narendra Kumar Singh*

Department of Chemistry, Faculty of Science, University of Lucknow, Lucknow-226007 (INDIA)

*Corresponding Author Email: nksbhu@yahoo.com, singh_narendra@lkouniv.ac.in, ORCID: 0000-0002-9108-6545

Mob: +91-9451949105

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ABSTRACT

Sr-substituted SmNiO₃ perovskite-type oxides have been investigated for their electrocatalytic properties towards oxygen evolution reaction (OER) in alkaline medium. Materials were obtained by using low temperature malic acid sol-gel route. To know the redox behaviour, electrocatalytic activity and thermodynamic parameters of oxides, cyclic voltammetry (CV) and anodic polarization curve (Tafel plot) were recorded in 1 M KOH at 25 ºC. X-ray diffraction (XRD) study indicates the formation of almost pure perovskite phase of the material. A pair of redox peaks was observed (anodic; Eₚₐ = 494±12 mV and corresponding cathodic; Eₚₐ = 360±4 mV) in the potential region 0.0-0.7 V prior to onset of OER. As observed in the case of La-based perovskite oxides, Sr-substitutions in the SmNiO₃ also enhance the electrocatalytic properties of the material. However, Sm-based oxides showed least electrocatalytic activity as compared to La-based oxides. The estimated values of Tafel slope and reaction order indicate that each oxide electrode, except SmNiO₃, follows similar mechanistic path towards OER. Standard entropy of activation (ΔS°%), standard enthalpy of activation (ΔH°%) and standard electrochemical energy of activation (ΔHf°) was determined by recording the anodic polarization curve in 1M KOH at different temperatures.

1. INTRODUCTION

Perovskite-type mixed oxides of lanthanum having composition LaₓMₓM′O₃ (where, M = Sr, Pb, Cu, Cr; M’ = Co, Mn, Ni and 0.0 ≤ x ≤ 0.8) are considered as very promising materials and have been extensively studied for oxygen evolution/reduction reaction [1-30]. These materials have several technological applications [1,31,32]. There are several methods employed to synthesize these oxides. These include, high temperature solid state reaction and thermal decomposition methods [33-38], which generally produced oxides with low specific surface area and reduced homogeneity and low temperature methods [39-43] in which amorphous organic acids, like malic acid (MA), citric acid (CA), polyacrylic acid (PAA), citric acid-ethylenediamine (CA-EDA), polyvinylpyrrolidone (PVP) etc are used as precursors. These low temperature methods facilitate to provide homogeneity in the metal ions and produced oxides with high specific surface area and therefore improved electrochemical properties.

Recently, Azad et al. [44] reported oxygen evolution electrocatalytic properties of some perovskite mixed oxides as bifunctional electrocatalysts with current density 10 mA cm⁻² at E = 1.65 V vs RHE. Szczancoski et al. [45] developed Fedoped LaNiO₃ electrocatalysts for OER studies at deposited pyrolytic graphite sheets and found highest activity with LaNi₀.₄Fe₀.₆O₃ having Tafel slope value of 52 mV decade⁻¹. Findings of these literatures revealed that the metal ions have vital role in the enhancement of physical and electrocatalytic properties of materials. Further, it has been observed that most of the OER studies have been carried out with La-based perovskite oxides. Sm-based perovskites are very little investigated with regards to oxygen evolution/reduction reaction.

Shao-Horn et al. [46] used elements of lanthanide series instead of lanthanum and prepared double perovskites (Ln₀.₅Ba₀.₅)CoO₃₋ₓ (Ln = Pr, Sm, Gd and Ho) by adopting thermal decomposition method. They observed better electrocatalytic activity towards oxygen evolution reaction in alkaline solution. Very recently [27], we found better results towards OER with partial substitution of Sm for Sr in La₀.₄Sr₀.₆CoO₃.

In view of the above, we extended our research and used Sm-element instead of La to obtain perovskite-type oxides and further studied their electrocatalytic properties for OER in alkaline medium. Results, so obtained, are described in this paper.

2. EXPERIMENTAL

Strontium substituted SmNiO₃ having compositions Sm₁₋ₓSrₓNiO₃ (0 ≤ x ≤ 0.8) were prepared by adopting the method reported by Teraoka et al. [41]. In each preparation, all the reagents and chemicals were taken in purified form. The stoichiometric amount of metal nitrates and excess amount of malic acid were dissolved in 500 ml double distilled. 35%
ammonia solution was used to maintain the pH of mixture 3.5, which then concentrated over a water bath at 60-70°C. A gel like mass was obtained which decomposed and sintered at 600°C for 5h to get the desired oxide material. Techniques like, X-ray diffractometer (Philips and Pananalytical Powder X-Ray Diffractometer) provided with radiation source Cu-Kα (λ = 1.54056 Å) and Scanning Electron Microscope (JEOL, JSM 6490) were used to determine the phase and morphology of the materials. The crystallite size of the material was calculated by using Scherer’s formula.

The electrocatalytic property of the material was determined in the form of oxide film electrode on pre-treated Ni-support. The procedure adopted for the treatment of Ni-support, preparation of oxide film and electrical contact was same as described elsewhere [9,15]. During experiment, the oxide film electrode was used as working electrode. Hg/HgO /1M KOH and Pt-foil were used as reference and auxiliary electrode, respectively. A three-electrode single compartment glass cell, which is connected to the potentiostat/galvanostat (Gamry Reference 600 ZRA) and corrosion and physical electrochemical software compiled personal computer, was used for the electrochemical studies. In order to minimise the additional potential drop, the reference electrode was connected electrically to the electrolyte (1M KOH) via a Luggin capillary (KCl/Agar-Agar salt bridge).

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns of oxide powders, Sm0.2Sr0.8NiO3 and Sm0.6Sr0.4NiO3, sintered at 600°C for 5h and recorded between 20 = 20° to 100° are shown in Fig. 1. The observed patterns indicates the formation of almost perovskite phase of the material and found to be very similar to those with Sm-substituted La(Sr)CoO3 [27] obtained by PVP method, which followed hexagonal crystal geometry of respective JCPDS ASTM file 25-1060. The crystallite size was calculated by using Scherer’s formula [47] and found to be ~30 and ~40 nm for Sm0.2Sr0.8NiO3 and Sm0.6Sr0.4NiO3, respectively.

3.2 Scanning Electron Micrograph (SEM)

Figure 2 represents the SE-micrograph of sintered (600°C for 5 hrs) SmNiO3 and Sm0.2Sr0.8NiO3 oxide powder at the magnification x200. Morphological appearance of both oxides are seemed to be similar and showed nebulous structure. Some small pores has also been observed in the oxide matrix.
It is found that both anodic and cathodic peak currents increased linearly with increase in the scan rates. The variation is represented in the plot of $\frac{|j_p|}{\sqrt{\text{scan rate}}}$ vs square root of scan rate (Fig. 5) for Sm$_{0.2}$Sr$_{0.8}$NiO$_3$ oxide electrode. The voltammetric charge ($q$) was also plotted against (scan rate)$^{-1/2}$ and shown in Fig. 6. The straight line obtained indicates that the surface redox behaviour is diffusion controlled [15].

**Figure 3:** Cyclic voltammograms of Ni/ Sm$_1$-xSr$_x$CoO$_3$ (0 $\leq x \leq 0.8$) in 1 M KOH at 25°C; (scan rate = 20 mV sec$^{-1}$); a: SmNiO$_3$, b: Sm$_{0.8}$Sr$_{0.2}$NiO$_3$, c: Sm$_{0.6}$Sr$_{0.4}$NiO$_3$, d: Sm$_{0.2}$Sr$_{0.8}$NiO$_3$

Other voltammetric constituents, such as peak separation potential ($\Delta E_p = E_{p_a} - E_{p_c}$), formal redox potential [$E^f = (E_{p_a} - E_{p_c})/2$], anodic and cathodic peak current, voltammetric charge ($q$), etc were estimated from the voltammetric curve and listed in Table 1. With exception to Sm$_{0.2}$Sr$_{0.8}$NiO$_3$, the value of $\Delta E_p$ was almost same with each oxide electrode. A negligible change in the formal redox potential has been observed with the substitution of Sr for Sm in the base oxide (SmNiO$_3$). Anodic peak current, cathodic peak current and voltammetric charge ($q$) are increased with increase in concentration of Sr in the oxide. The value of $q$ is estimated by integrating the CV curve from zero to the potential just prior the OER. The ratio of anodic and cathodic peak current is more than unity, indicating the irreversibility [50-52] of the redox process.

**Table 1:** Values of the cyclic voltammetric parameters of Ni/ Sm$_{1-x}$Sr$_x$NiO$_3$ (0 $\leq x \leq 0.8$) in 1 M KOH at 25 °C (scan rate = 20 mV sec$^{-1}$)

| Electrode         | $E_{p_a}$/mV | $E_{p_c}$/mV | $\Delta E_p$/mV | $E^f$/mV | $|j_{p_a}|$ mA cm$^{-2}$ | $|j_{p_c}|$ mA cm$^{-2}$ | $|j_{p_a}|/|j_{p_c}|$ | $q$/mC cm$^{-2}$ |
|-------------------|--------------|--------------|-----------------|---------|------------------------|------------------------|----------------------|----------------|
| SmNiO$_3$         | 483          | 360          | 123             | 422     | 0.78                   | 0.35                   | 2.2                  | 1.7             |
| Sm$_{0.8}$Sr$_{0.2}$NiO$_3$ | 482        | 362          | 120             | 422     | 1.14                   | 0.52                   | 2.2                  | 2.6             |
| Sm$_{0.6}$Sr$_{0.4}$NiO$_3$ | 486        | 364          | 122             | 425     | 1.94                   | 0.84                   | 2.3                  | 3.7             |
| Sm$_{0.2}$Sr$_{0.8}$NiO$_3$ | 506        | 356          | 150             | 431     | 4.69                   | 2.77                   | 1.7                  | 16.0            |

The effect of scan rate on the redox process has also been studied in 1 M KOH at 25°C and shown in Fig. 4 for the Ni/Sm$_{0.2}$Sr$_{0.8}$NiO$_3$. The nature of CV curve as shown figure 4 is almost similar to that observed at scan rate of 20 mV sec$^{-1}$. But, a shift in anodic and cathodic peak potential was observed with the increase of scan rates from 20 to 120 mV sec$^{-1}$.

**Figure 4:** Cyclic voltammogram of Ni/Sm$_{0.2}$Sr$_{0.8}$NiO$_3$ film electrode at different scan rates in 1 M KOH (25°C)

**Figure 5:** Plot of $|j_p|$ vs (scan rate)$^{-1/2}$ for the oxide film electrode on Ni in 1 M KOH (25 °C)

**Figure 6:** Plot of voltammetric charge ($q$) vs (scan rate)$^{-1/2}$ for the oxide film electrode on Ni in 1 M KOH (25 °C)

### 3.4 Electrocatalytic Activity

To know the electrocatalytic activity of the oxide electrocatalyst, iR-compensated anodic polarization curves (E vs.\log j) was recorded in 1 M KOH at 25 °C. The polarization curve, so obtained is shown in Fig. 7. The Tafel slope values as well as the electrocatalytic activity in terms of potential and current density were estimated from the polarization curve and listed in Table 2. The Tafel slope value were ranged between 111-118 mVdecade$^{-1}$. On the comparison of electrocatalytic activity in terms of current density at fixed potential of 800 mV, it is observed that a slight increase in the electrocatalytic activity has been found with Sr-substitution. The activity being maximum with 0.8 mol Sr-substitution.
As per Table 2, oxide electrodes show the following order of electrocatalytic activity at constant potential (E = 800 mV):

$$Sm_{0.2}Sr_{0.8}NiO_3 (j = 4.1 \text{ mA cm}^{-2}) > Sm_{0.8}Sr_{0.2}NiO_3 (j = 1.5 \text{ mA cm}^{-2}) > Sm_{0.6}Sr_{0.4}NiO_3 (j = 1.3 \text{ mA cm}^{-2}) > SmNiO_3 (j = 1.1 \text{ mA cm}^{-2})$$

The anodic polarization curve was recorded to determine the reaction order of OER with each oxide electrode in different KOH concentration at 25°C. During the process, the electrical intensity of the each electrolytic solution was kept uniform. An inert electrolyte KNO₃ was used to maintain the ionic strength (μ = 1.5) of each solution constant. A representative polarization curve for Ni/SmₓSr₁₋ₓNiO₃ is shown in the Fig. 8. From figure, values of current density (log j/A cm²) were estimated at a certain potential and plotted against log [OH⁻], which is shown in the Fig. 9 at a constant potential of E= 700 mV. The order of reaction was calculated by measuring the slope of straight line and values are listed in Table 2. The observed values of Tafel slope and reaction order as given in Table 2 suggest that the OER taking place at the electrocatalysts follows similar mechanistic path except SmNiO₃, which has reaction order 1.9 with Tafel slope 118 mV decade⁻¹.

### Table 2: Electrode kinetic parameters for oxygen evolution reaction on Ni/SmₓSr₁₋ₓNiO₃ (0 ≤ x ≤ 0.8) electrodes in 1 M KOH at 25°C

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Tafel slope (b)</th>
<th>Order (p)</th>
<th>E/ mV at 10 mA cm⁻²</th>
<th>j/ mA cm² at 1000 mV</th>
<th>j/ mA cm² at 700 mV</th>
<th>j/ mA cm² at 800 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmNiO₃</td>
<td>118</td>
<td>1.9</td>
<td>921</td>
<td>1134</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Sm₀.₈Sr₀.₂NiO₃</td>
<td>113</td>
<td>1.2</td>
<td>849</td>
<td>1068</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Sm₀.₆Sr₀.₄NiO₃</td>
<td>114</td>
<td>0.9</td>
<td>888</td>
<td>1116</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Sm₀.₂Sr₀.₈NiO₃</td>
<td>111</td>
<td>1.0</td>
<td>815</td>
<td>1045</td>
<td>1.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>

### 3.5 Thermodynamic Parameters

Thermodynamic parameters of two oxide electrocatalysts towards OER have also been determined by recording the anodic polarization curve in 1 M KOH at 20, 30, 40, and 50°C. A set of polarization curve for SmNiO₃ is shown in Figure 10. During the experiment, the temperature of the reference electrode was kept constant. From figure, values of log j (in mA cm⁻²) were estimated at a constant applied potential and plotted against 1/T. The standard apparent enthalpy of activation (∆H°) was calculated at a certain potential (E = 650 mV) by measuring the slope of Arrhenius plot, log j vs 1/T (Fig. 11).

Further, following two relations (1) and (2) [53] are used to determine the values of standard enthalpy of activation (∆H°) and standard entropy of activation (∆S°), respectively.

$$\Delta H° = \Delta H°_0 - \alpha \eta \quad ...... \text{(1)}$$

$$\Delta S° = 2.3 R \left[ \log j + \frac{\Delta H°}{2.3 R T} \right] \quad ...... \text{(2)}$$

In equation (1), α (= 2.303RT/bF) is the transfer coefficient. η is the overpotential equal to E - E₀₂/OH⁻, where E is the potential applied and E₀₂/OH⁻ (= 0.303 V vs. Hg/HgO) [54] is the theoretical equilibrium Nernst potential in 1 M KOH at 25°C. The Tafel slope (b) is determined from the polarization curves obtained at different temperatures. R, F are the universal constants and T is the absolute temperature.
In equation (2), the value of frequency term \((\omega)\) is equal to \(k_b T h / k_b h\). \(k_b\) and \(h\) are the Boltzmann constant and Planck’s constant, respectively. Here, the value of ‘n’ was taken 2 in every calculation. The calculated values of thermodynamic parameters are listed in the Table 3. Values of electrochemical activation energy were found to be 47.5 and 54.9 kJ mol\(^{-1}\) for SmNiO\(_3\) and Sm\(_{0.8}\)Sr\(_{0.2}\)NiO\(_3\), respectively.

![Image 10](https://example.com/image10.png)

**Figure 10**: Anodic polarization curve for the SmNiO\(_3\) film electrode on Ni at different temperatures in 1 M KOH

![Image 11](https://example.com/image11.png)

**Figure 11**: The Arrhenius plot at a constant applied potential (650 mV) for La\(_{1-x}\)Sr\(_x\)CoO\(_3\) (x = 0 and 0.2) in 1 M KOH

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(\Delta H^#) (kJ mol(^{-1}))</th>
<th>(-\Delta S^#) (J deg(^{-1}) mol(^{-1}))</th>
<th>(\alpha)</th>
<th>(\Delta H^*) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmNiO(_3)</td>
<td>47.5</td>
<td>195.1</td>
<td>0.5</td>
<td>64.4</td>
</tr>
<tr>
<td>Sm(<em>{0.8})Sr(</em>{0.2})NiO(_3)</td>
<td>54.9</td>
<td>171.9</td>
<td>0.5</td>
<td>71.5</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The present work has been undertaken to study the electrocatalytic properties of Sm-based perovskite over La-based. Sr-substitution in the base oxide increased the electrocatalytic properties of the material. But, this increase is not so significant as observed in the case of La-based perovskites. As per present study, Sm-based perovskites are not prolific electrocatalysts for the electrolysis point of view.

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**REFERENCES**

5. Kobussen A.G.C., Willems H., Broers G.H.J. (1982). The oxygen evolution on La\(_{0.8}\)Ba\(_{0.2}\)CoO\(_3\): Passivation parameters, J. Electroanalitical Chemistry and Interfacial Electrochemistry 142:85-94. [https://doi.org/10/S0022-0728(82)80007-7](https://doi.org/10/S0022-0728(82)80007-7).


