Impact of Strontium-Substitution on Oxygen Evolution Reaction of Lanthanum Nickelates in Alkaline Solution

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In the present study, activity for anodic oxygen evolution reaction (OER) has been evaluated by varying the degree of Sr2+-substitution in La1−xSrxNiO3 from x = 0.0 to 1.0. EDS was utilized to measure the elemental composition. XRD and Rietveld refinement were employed for the phase and crystal structure analysis. It was observed that the crystal structure of LaNiO3 was distorted after Sr2+-substitution and formed tetragonal lanthanum-strontium nickelates (LSN) for x ≤ 0.8, and rhombohedral strontium nickelate for x = 1.0. For all the samples, secondary phases (NiO for 0.2 ≤ x ≤ 1.0 and SrCO3 for 0.8 ≤ x ≤ 1.0) were also observed. Rietveld analysis suggests that Sr2+-substitution caused the cell volume to contract. The oxidation state of Ni in the samples was investigated by XPS for the elusive NiIII. An increase in the mass specific activity for OER was observed as the degree of Sr2+-substitution increase until x = 0.6, however, the activity decreased for higher values of x. The LSN samples were significantly more active than that of LaNiO3, and the state-of-the-art electrocatalyst Ba0.6Sr0.4CoO3−δ for OER with the state-of-the-art electrocatalysts in alkaline solution.

Dedicated effort has been made to tune the electrocatalytic properties of perovskite oxides by systematic substitution of lanthanides or alkaline earth elements at A-site, and/or transition elements at B-site of the ABO3 structure. The enhancement in the activity for OER is attributed to the increase in the oxidation state of transition metals at B-site of perovskites, the formation of molecular level oxygen vacancies, broadening of the angle between B-site transition element (M) and lattice oxygen (O), and improvement in the electrical conductivity.

Metallic nickel (Ni) has been the most extensively investigated active electrocatalyst for alkaline water electrolysis with its superior stability and electrochemical activity than any other transition elements. However, oxides of nickel have shown better activity than nickel metal itself. Among other oxides, lanthanum nickelate (LaNiO3) belonging to the perovskite family has been of considerable interest due to its better corrosion resistance in alkaline solution, economically feasible, and high electrical conductivity. In pursuit of enhancing the activity for OER of perovskites, the substitution of divalent strontium (Sr2+) cation at A-site has been shown to enhance the OER activity for lanthanum cobaltates and ferrites. This has been attributed to the increase in the oxidation state of the transition elements present at the B-site, which increase with the degree of Sr2+ substitution. Further, the bond strength between Ni and OH− ion is weaker as compared to the other transition metals (Co, Fe, Mn, and Cr), which can have a positive effect on activity for OER. Thus, it is desirable to have Ni at B-site and some amount of Sr-substitution at A-site of ABO3 perovskite. In this paper, we synthesized lanthanum-strontium nickelate samples by substituting Sr2+ for La3+ at A-site of LaNiO3 to adopt the aforementioned characteristics of Sr and Ni. Material and electrochemical characterizations were carried out to find the efficient electrocatalyst and compare its activity for OER with the state-of-the-art electrocatalysts in alkaline solution.

Materials and Methods

Synthesis of strontium-substituted lanthanum nickelates.— Strontium substituted lanthanum nickelate (La1−xSrxNiO3, x = 0.0 to 1.0) samples were synthesized using a citrate-nitrate solution
combustion method. Initially, stock solutions of 1 M La\textsuperscript{3+} and Ni\textsuperscript{2+} cations were prepared by dissolving La(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (AR, SDFCFL) and Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (AR, LOBA Chemie), respectively, in deionized water. Whereas, the stock solution of 0.5 M Sr\textsuperscript{2+} cation was prepared by initially dissolving 37.6607 g of SrCO\textsubscript{3} (LR, SDFCFL) in 75 mL of 69% nitric acid (EMPLURA, Merck) solution, and then it was diluted to 500 mL using deionized water. Stoichiometric amounts of metal nitrate solutions (0–10 mL of 1 M La\textsuperscript{3+}, 0–20 mL of 0.5 M Sr\textsuperscript{2+}, and 10 mL of 1 M Ni\textsuperscript{2+}) were mixed together and then 14.8655 g of citric acid monohydrate (EMPARTA, Merck) was added to it. The molar ratio of fuel/oxidant (F/O) was maintained at 0.3 and 1.3–6.53

The total volume of the solution was adjusted to 30 mL using a n d 10 mLo f1MN i2

and stirring, the gel was ignited, producing voluminous solid powders. These were initially dried at 80 °C in a hot-air oven for around 12 h and then ground into fine powders using an agate mortar and pestle. These powders were heated again at 400 °C for 10 min on a hot plate for complete ignition of any unreacted precursors in the powders. Subsequently, these powder samples were calcined at 800 °C for 6 h using a muffle furnace in the air with a ramp-up rate of 300 °C h\textsuperscript{−1}. The same procedure was used to synthesize the state-of-the-art Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.3}Fe\textsubscript{0.7}O\textsubscript{3−δ} (BSCF) oxygen electrolyte, but it was calcined at 1000 °C for 3 h. Also commercially available noble metal oxygen electrocatalysts such as Ir\textsubscript{0.8}(Alfa Aesar) and Pt black (Sigma-Aldrich) were used. Henceforth, these samples were referred as electrocatalysts and these were used for further study.

Material characterization.—The elemental composition of strontium-stabilized lanthanum nickelate samples were measured by the energy dispersive spectroscopy (EDS) using a field emission gun scanning electron microscope (JEOL JSM-7600F, Japan). The Brunauer-Emmett-Teller (BET) surface area was measured with a 3Flex surface characterization analyzer (Micromeritics Instrument Corporation, U.S.A.). The powder X-ray diffraction (XRD) spectrum were recorded on an EMPIREAN, PANalytical diffractometer with Cu K\textalpha radiation. The tube current was 40 mA and a generator voltage of 45 kV was applied. The XRD spectrum were done in the scan range of 20 = 10–100°. The phase formation in the samples was identified using X’pert HighScore Plus (version 2.1.0) software by comparing them with the International Centre for Diffraction Data (ICDD). Further, the FullProf Suite program (3.00)\textsuperscript{13} was used for the Rietveld analysis, which permits the refinement of lattice parameters and quantification of phases.

X-ray photoelectron spectroscopy (XPS) measurements were recorded in a Kratos AXIS-supa analytical system. The XPS was obtained with Al K\textalpha monochromatic radiations. The pass energy and resolution were kept at 160 and 2 eV, respectively for survey scans; whereas a pass energy of 20 eV with 0.5 eV resolution were used for the high resolution scans. Surface charge correction of the binding energies was performed using the C 1s spectral line (C-C) of adventitious carbon at the binding energy of 284.8 eV.\textsuperscript{32} The collected XPS survey and high resolution scans of all samples were analyzed using the ESCApe software (version-1.1). In addition, the XPS spectra of Ni 3p and Ni 2p\textsubscript{3,2} (for x = 1.0) were deconvoluted into separate peaks by specifying spin-orbital splitting (SOS), full width at half-maximum (FWHM) and the ratio of peak areas for doublets after Shirley background subtraction and employing a mixed Gaussian-Lorentzian line shape function with 30% mixing.

Electrochemical characterization.—Electrocatalyst ink and thin film preparation.—Electrocatalyst ink (80 wt%) was prepared by adding 5 mL of deionized water and 50 μL of basic Nafion (pH 14) to a mixture of 4 mg of electrocatalyst and 1 mg of Vulcan carbon (XC-72R). The basic Nafion solution was prepared by mixing deionized water and 5 wt% Nafion solution (Sigma Aldrich, U.S.A.) in the volume ratio of 1:1, and then adding few drops of NaOH solution (5 M) to raise its pH to 14. Here, the carbon was used as a conductive additive, as most commonly used for the metal oxide electrocatalysts.\textsuperscript{9,10} Experiments done in similar condition (see Oxygen evolution reaction activity measurement section) suggest that the contribution of carbon to the activity for OER of the metal oxide electrocatalysts is minuscule (~0.39–2.52%). This electrocatalyst-carbon suspension was sonicated for around 30 min prior to drop-casting onto a glassy carbon electrode (GCE, Pine Instruments) with a geometrical surface area of A = 0.196 cm\textsuperscript{2}. After sonication, 20 μL of this ink was drop-casted immediately onto a GCE and was dried under an infrared lamp for around 15 min. The loading density of the electrocatalysts on the GCE was 80.82 μg cm\textsuperscript{−2}. Prior to drop-casting, the GCE was polished successively with 0.3, 0.1, and 0.05 μm alumina suspension and rinsed thoroughly with deionized water while transferring between each particle size of alumina. The polishing was continued till a mirror-finished surface was obtained.

Oxygen evolution reaction activity measurement.—The activity for OER was measured using a thin-film rotating disk electrode (RDE) setup as described elsewhere,\textsuperscript{33} which was similar to the measurement of activity for oxygen reduction reaction.\textsuperscript{34} In brief, electrochemical measurements were carried out with a three-electrode system in 0.5 M NaOH electrolyte. A thin film electrocatalyst coated GCE as described in the previous Electro catalyst ink and thin film preparation subsection, platinum mesh, and Hg/HgO (0.5 M KOH) were used as working, counter, and reference electrodes, respectively. However, the potential recorded using a Hg/HgO reference electrode was converted to the reversible hydrogen electrode (RHE) as described elsewhere\textsuperscript{35} and henceforth, the potential values reported in this paper are versus (vs.) RHE unless otherwise stated. The electrochemical measurements were carried out using a Gamry potentiostat (Interface 1000, U.S.A.) and controlled using Gamry Echem Analyst software. Prior to the measurements of activities for OER, the electrocatalyst surface was cleaned by performing cyclic voltammetry (CV) in argon (Ar, 99.99%, Mars Gas Company, Mumbai)-saturated and continuously purged 0.5 M NaOH solution (50 mL) between the potential window of −0.30 to 1.65 V vs. RHE at a scan rate of 50 mV s\textsuperscript{−1} for five cycles. Thereafter, the cleaned electrocatalyst thin film coated GCE was fixed into the RDE assembly, which was controlled by MSR rotator (AFM/MSRC, Pine Research Instrumentation, U.S.A.). The RDE was immersed in a similar but separate three electrode configuration cell having 0.5 M NaOH solution as electrolyte (500 mL), but saturated and continuously purged with O\textsubscript{2}-gas (99.999%, Mars Gas Company, Mumbai). The open circuit voltage (OCV) of the electrocatalyst in O\textsubscript{2}-saturated electrolyte and the ohmic resistance for iR compensation were measured in the same setup at a rotation rate of 1600 rpm prior to the measurement of activity for OER. Subsequently, CVs were performed between the applied potential (E\textsubscript{applied}) of 1.0 and 1.8 V at a scan rate of 10 mV s\textsuperscript{−1} for 10 cycles. For iR compensation (E\textsubscript{iR,compensated} = E\textsubscript{applied} − iR), an inbuilt script “Get Ru” available in the Gamry Framework software was employed, which utilizes electrochemical impedance spectroscopy to determine the uncompensated resistance, R. The overpotentials (η) were calculated using η = E\textsubscript{iR,compensated} − E\textsubscript{OCV}, where E\textsubscript{iR,compensated} and E\textsubscript{OCV} are iR compensated potential (V) and the open circuit voltage (V) at equilibrium, respectively as discussed earlier.

Results and Discussion

Analysis of elemental composition by EDS.—The EDS analysis results for calcined La\textsubscript{x}Sr\textsubscript{1−x}NiO\textsubscript{3} electrocatalysts are presented in Table I. The atomic ratios of (La + Sr)/Ni were found to vary from 0.8 to 1.1, which are close to the nominal atomic ratio of 1.0. While, the atomic composition of most of the samples as determined from
the EDS analysis were in good agreement with the nominal values, a slight deviation was observed for the samples with \( x = 0.4 \) and 0.6.

**Phase identification by X-ray diffraction.**—The XRD patterns of calcined \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 \) \( (x = 0.0 \) to 1.0) and the BSCF electrocatalyst samples are presented in Figure 1. For \( x = 0.0 \), a single phase \( \text{LaNiO}_3 \) perovskite with a rhombohedral crystal system of \( R3c \) (167) space group was obtained, which is in agreement with the ICCD reference card number 01-088-0633. When \( \text{Sr}_2 \) was substituted for \( \text{La}^{3+} \) in the A-site of \( \text{ABO}_3 \) perovskite with \( x = 0.2, 0.4 \) and 0.6, a secondary phase of \( \text{NiO} \) was also observed along with the primary phase of lanthanum-strontium nickelate \( (\text{La}_{1-x}\text{Sr}_x\text{NiO}_3) \). This primary phase for \( 0.2 \leq x \leq 0.6 \) belongs to the \( A_2\text{BO}_4 \)-type tetragonal crystal structure \( (I4/mmm) \), which consists of p-type doped \( \text{NiO}_2 \) layers. These \( A_2\text{BO}_4 \) mixed oxides are built up by alternate layers of \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 \) perovskite type and \( \text{LaO} \) rock salt (AO) type structures. When \( x \) is further increased to 0.8, along with the secondary phase of \( \text{NiO} \), \( \text{SrCO}_3 \) was also observed as an impurity, while the primary phase consisted of \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 \), retaining the same crystal structure and space group of lanthanum-strontium nickelate. We believe that the \( \text{SrCO}_3 \) is formed via the reaction of strontium oxide with the carbon dioxide formed on combustion of citric acid. This is also consistent with secondary phases of \( \text{NiO} \) and \( \text{SrCO}_3 \). Moreover, the intensity of \( \text{SrCO}_3 \) during the synthesis of strontium substituted lanthanum perovskite \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 \) was formed instead of the \( \text{SrNiO}_3 \) along with their crystallographic information.

A substitution of divalent cation \( \text{Sr}^{2+} \) for the trivalent \( \text{La}^{3+} \) cation will increase the oxidation state of \( \text{Ni} \) from 3+ toward 4+ if no oxygen vacancies are created. Although, \( \text{Ni}^{4+} \) is the highest oxidation state usually attainable, formation of \( \text{Ni}^{4+} \) cannot be completely ruled out and the presence of quadrivalent \( \text{Ni} (\text{Ni}^{4+}) \) has been reported in the past for similar perovskites and \( \text{NiO} \). The limited ability of \( \text{Ni} \) to form \( \text{Ni}^{4+} \) might explain the possible distortion in the crystal structure for \( 0.2 \leq x \leq 0.8 \) (tetragonal lanthanum-strontium nickelates with secondary \( \text{NiO} \) phases) instead of the \( \text{Sr} \) substituted rhombohedral lanthanum nickelate. Summarily, the analysis of XRD patterns show that the \( x=1 \)-substitution for \( \text{La}^{3+} \) in the \( \text{ABO}_3 \) perovskite structure has distorted it, leading to a \( A_2\text{BO}_4 \) layered perovskite structure. The XRD pattern of synthesized state-of-the-art electrocatalyst BSCF (Figure 1) was compared with XRD patterns available in the literature and it is in good agreement with them.

**Structure analysis and phase quantification by Rietveld refinement.**—In addition to the phase identification by XRD patterns, Rietveld refinement was employed in this study for refinement of lattice parameters \( (a, b \) and \( c) \), quantification of phase, and the calculation of cell volume \( (V) \). Rietveld refinement profiles are presented in Figure 2 and their corresponding parameters in Table III for the calcined electrocatalysts. The refinement results suggest that the weight fraction of lanthanum-strontium nickelate decreased with an increase in the value of \( x \) from 0.2 to 0.8, which was compensated by an increase in the amount of secondary phase \( (\text{NiO}) \). For \( x = 0.8 \), \( \text{SrCO}_3 \) in a substantial amount was also observed in addition to \( \text{NiO} \). Further increase in the value of \( x \) to 1.0, the weight fraction of \( \text{SrCO}_3 \) increased to 62.44% and became dominant while the weight fraction of strontium nickelate and \( \text{NiO} \) were in almost equal amount. Moreover, with an increase in the value of \( x \) from 0.2 to 0.8, the cell volume of the lanthanum-strontium nickelate phases decreased. This decrease in the cell volume can be attributed to either the substitution of smaller ionic radius cation at A-site and/or formation of smaller ionic radius cation at B-site. However, in the present study ionic radius of substituted \( \text{Sr}^{2+} (1.26 \text{ Å}) \) is larger than that of the \( \text{La}^{3+} (1.16 \text{ Å}) \), hence this substitution is expected to increase the cell volume, which is contrary to the observations. Hence, we suspect the possible oxidation of larger ionic radius \( \text{Ni}^{3+} (0.63 \text{ Å}) \) to smaller ionic radius \( \text{Ni}^{4+} (0.56 \text{ Å}) \) and/or \( \text{Ni}^{4+} \) to the still smaller ionic radius \( \text{Ni}^{4+} (0.48 \text{ Å}) \) might be responsible for the decrease in the cell volume of lanthanum-strontium nickelate samples for \( x = 0.2 \) to 0.8. The decrease in the lattice parameters particularly “c” (Table III), also supports the contraction in the lattice structure. It has been also reported that the presence of any oxygen vacancies in the perovskite structure can also contribute to the contraction in the cell volume. Thus, the net contraction in the cell volume of the samples can be a combined result of an increase in the oxidation state of \( \text{Ni} \) and creation of oxygen vacancies. The ionic radii referred in this paper are adopted from the work of Shannon.

**Table I. The elemental composition of perovskite samples \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 (x = 0.0 \) to 1.0) analyzed by the energy dispersive X-ray spectroscopy (EDS). The values represent the average of two spots on the same sample.**

| \( x \) \((\text{Sr}^{2+})\) | \( \text{La} \) | \( \text{Sr} \) | \( \text{Ni} \) | \( \text{O} \) | Measured atomic % by EDS |
|---|---|---|---|---|---|
| 0.0 | 20 | 0 | 20 | 60 | 21.9 | 0.0 | 20.3 | 57.8 |
| 0.2 | 16 | 4 | 20 | 60 | 17.7 | 3.9 | 20.7 | 57.7 |
| 0.4 | 12 | 8 | 20 | 60 | 15.2 | 6.6 | 24.2 | 54.0 |
| 0.6 | 8 | 12 | 20 | 60 | 10.1 | 9.8 | 24.8 | 55.2 |
| 0.8 | 4 | 16 | 20 | 60 | 4.0 | 14.2 | 19.0 | 62.9 |
| 1.0 | 0 | 20 | 20 | 60 | 0.0 | 18.4 | 22.1 | 59.5 |

**Table II. The XRD pattern of synthesized state-of-the-art electrocatalyst BSCF (Figure 1) was compared with XRD patterns available in the literature and it is in good agreement with them.**

| \( x \) \((\text{Sr}^{2+})\) | \( \text{La} \) | \( \text{Sr} \) | \( \text{Ni} \) | \( \text{O} \) | Measured atomic % by EDS |
|---|---|---|---|---|---|
| 0.0 | 20 | 0 | 20 | 60 | 21.9 | 0.0 | 20.3 | 57.8 |
| 0.2 | 16 | 4 | 20 | 60 | 17.7 | 3.9 | 20.7 | 57.7 |
| 0.4 | 12 | 8 | 20 | 60 | 15.2 | 6.6 | 24.2 | 54.0 |
| 0.6 | 8 | 12 | 20 | 60 | 10.1 | 9.8 | 24.8 | 55.2 |
| 0.8 | 4 | 16 | 20 | 60 | 4.0 | 14.2 | 19.0 | 62.9 |
| 1.0 | 0 | 20 | 20 | 60 | 0.0 | 18.4 | 22.1 | 59.5 |

**Figure 1.** X-ray diffraction patterns of synthesized \( \text{La}_{1-x}\text{Sr}_x\text{NiO}_3 \) \( (x = 0.0 \) to 1.0) electrocatalysts after calcination at 800 °C and the state-of-the-art electrocatalyst \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (BSCF), which was calcined at 1000 °C.
Table II. Phases identified by the X-ray diffraction technique with their crystal structure information.

| x (Sr<sup>2+</sup>) | Phase identified | Crystal system | Space group (number) | PDF number | Reference |
|-------------------|------------------|----------------|----------------------|------------|-----------|
| 0.0               | LaNiO<sub>3</sub> | Rhombohedral   | R<sub>3</sub>c (167) | 01-088-0633 | 35        |
| 0.2–0.6           | La<sub>1</sub>–xSr<sub>x</sub>NiO<sub>4</sub> | Tetragonal | I<sub>4</sub>mm (139) | 01-089-8310 | 36        |
| 0.8               | La<sub>1</sub>–xSr<sub>x</sub>NiO<sub>3.8</sub> | Tetragonal | I<sub>4</sub>mm (139) | 01-089-0425 | 45        |
| 1.0               | Sr<sub>2</sub>NiO<sub>4</sub>O<sub>2</sub> | Rhombohedral | R<sub>3</sub>c (167) | 01-086-1217 | 43        |
|                  | NiO              | Cubic          | Fm<sub>3</sub>m (225) | 01-089-5881 | 44        |
|                  | SrCO<sub>3</sub> | Orthorhombic   | Pmcn (62)         | 01-071-2393 | 46        |
|                  | BSCF             | Orthorhombic   | Pnnm (62)         | -          | 16, 47    |

X-ray photoelectron spectroscopy analysis.—Further, the XPS surface technique was employed in this study to examine the change in the oxidation state of Ni at B-site of oxide and a possible change in the binding energies of other elements. The XPS survey scans for all the samples (x = 0.0–1.0) are presented in Figure 3. Before identifying the peaks, all the binding energy values were adjusted with reference to the C 1s peak of adventitious carbon (C–C) at 284.8 eV (peak 4). A sharp peak (peak 5) at around 528.5 eV, which corresponds to O 1s peak is due to the lattice oxygen in the perovskites. The binding energy at 134.0 eV corresponds to the Sr 3d (peak 2) and those at 269.0 and 278.5 eV correspond to the Sr 3p<sub>3/2</sub> (peak 3(a)) and Sr 3p<sub>1/2</sub> (peak 3(b)), respectively. The peaks 2 and 3 are absent

Figure 2. Rietveld refinement plots of the X-ray diffraction profiles of La<sub>1</sub>–xSr<sub>x</sub>NiO<sub>3</sub> (x = 0.0 to 1.0) electrocatalyst samples calcined at 800°C.
for \( x = 0.0 \) and their intensities increased with an increase in the value of \( x \) as seen in Figure 3. The binding energies at 849.7 and 853.4 eV correspond to La 3d \(_{5/2}\) (peak 6(a)) and La 3d \(_{3/2}\) (peak 6(b)), respectively, which are absent for \( x = 1.0 \). The peaks 7(a) and 7(b) at 853.4 and 871.0 eV binding energies correspond to the Ni 2p \(_{3/2}\) and Ni 2p \(_{1/2}\), respectively. However, Ni 2p \(_{3/2}\) (peak 7(a)) strongly overlap with the La 3d \(_{5/2}\) (peak 6(b)) and its satellite peak, which complicates distinguishing the possible presence of Ni\(^{3+}\) and/or Ni\(^{4+}\) species in the lanthanum nickelate samples. Hence, Ni 3p (peak 1) at the binding energy of around 67.0 eV is considered for further detailed analysis of Ni\(^{3+}\) and Ni\(^{4+}\) species as it is not obstructed by other peaks even though its relative intensity is weak. A slight increase in binding energy values for all the peaks are observed with an increase in the value of \( x \). These binding energies are compared with the NIST XPS database.\(^{3,2}\)

As mentioned earlier, due to the overlapping La 3d \(_{5/2}\) (peak 6(b)) and Ni 2p \(_{3/2}\) (peak 7(a)) peaks at around 853.4 eV binding energy, it is less reliable for identifying the presence of Ni\(^{3+}\) and Ni\(^{4+}\) even though a method was developed to separate both the peaks.\(^{3,2}\) Hence, XPS spectra of Ni 3p between binding energy of 80 and 62 eV is considered to distinguish Ni\(^{2+}\) and Ni\(^{3+}\) as reported by Qiao and Br.\(^{52}\) The deconvoluted peaks (A, B, C, and D) of high resolution scans for all the samples are presented in Figure 4 and their results are given in Table IV. Binding energies of peaks (A and B) corresponding to Ni\(^{2+}\) increased with an increase in the value of \( x \) from 0.0 to 1.0. However, values of binding energies corresponding to peaks C (Ni \(_{3p/2}\)) and D (Ni \(_{3p/2}\)), which are attributed to the Ni\(^{3+}\) also moved to higher binding energies with an increase in the value of \( x \) from 0.0 to 0.6. But further increase in the value of \( x \) to 0.8, a slight decrease in the binding energy values for peaks C and D was observed which may be due to decrease in the average oxidation state of Ni present in the lanthanum-strontium nickelate. However, when \( x \) value was further increased to 1.0, a large shift in the binding energy (1.51 eV) to higher values are distinguishable for all the peaks. The atomic ratio of Ni\(^{3+}/\)Ni\(^{4+}\) also decreased with an increase in the value of \( x \) from 0.0 to 0.4, which is likely due to the formation of secondary phase containing Ni\(^{2+}\) species. This also corresponds to the XRD results discussed in the Structure analysis and phase quantification by Rietveld refinement subsection where the formation of NiO phase increased with an increase in the \( x \) value from 0.2 to 0.6 resulting in a decrease in the Ni\(^{3+}/\)Ni\(^{4+}\) ratio. Interestingly, the Ni\(^{3+}/\)Ni\(^{4+}\) atomic ratio increased as the value of \( x \) increased to 0.8 and 1.0. This increase in the ratio of Ni\(^{3+}/\)Ni\(^{4+}\) and shift in the binding energy values to higher values suggest the possible presence of the elusive Ni\(^{4+}\). To the best of our knowledge, literature binding energy value of Ni 3p for Ni\(^{4+}\) is unavailable. However, Gottschall and co-workers assumed that binding energy of Ni 2p \(_{3/2}\) for Ni\(^{4+}\) will be ca. 4.5 eV more than that of Ni\(^{3+}\) in oxides.\(^{53}\) If similar assumption holds for Ni 3p \(_{1/2}\) line, peaks (C) between 71.18 and 74.16 probably correspond to Ni\(^{4+}\), therefore samples with the value of 0.2 \( \leq x \leq 1.0 \) may contain this elusive Ni\(^{4+}\).

Further, an effort was made to identify the elusive Ni\(^{4+}\) using a high resolution spectra of Ni 2p \(_{1/2}\) for \( x = 1.0 \) sample as this sample did not have lanthanum, and its deconvoluted spectra is presented in Figure 5. It can be seen from the deconvoluted spectra that the net intensity can be decomposed into four separate peaks at binding energies of 854.1, 857.9, and 859.9, and 864.2 eV. Evidently, each peak should correspond to the different oxidation states of Ni, nickel hydroxide, and/or satellite peak of Ni. The peak at binding energy of 854.1 eV can be assigned to the oxide having Ni\(^{3+}\). Moreover, according to the NIST database, the peaks associated with nickel hydroxide are between binding energies of 855.3 and 856.6 eV, however, no such peak was observed in this range of binding energy. Thus, the peak present at a higher binding energy of 857.9 eV can be assigned to the Ni\(^{4+}\) of nickel oxide (Ni\(_2\)O\(_3\)),\(^{39}\) although it is slightly higher than 856.0 eV.\(^{53}\) There is an additional peak at higher binding energy of \( \approx 859.9 \) eV to the Ni\(^{3+}\) peak, which is lower than that of the satellite peak (864.2 eV). Interestingly, it has been reported that binding energy of 859.0 eV\(^{35}\) or 861.2 eV\(^{49}\) corresponds to Ni\(^{4+}\). Thus, the peak at binding energy of \( \approx 859.9 \) eV may be assigned to the Ni\(^{4+}\). However, further characterization such as X-ray absorption spectroscopy (XAS) or X-ray absorption near edge structure (XANES)\(^{35,36}\) may be required to confirm the presence of Ni\(^{4+}\) ions in the lanthanum-strontium nickelate samples.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** XPS survey scans of La\(_{1-x}\)Sr\(_x\)NiO\(_3\) (\( x = 0.0 \) to 1.0) electrocatalysts. Here numbers 1 to 7 represent the elements Ni 3p, Sr 3d, Sr 3p, C 1s, O 1s, La 3d, and Ni 2p, respectively, and (a) and (b) are spin-orbital-splits of corresponding elements.
Figure 4. High resolution and deconvoluted XPS spectra of Ni 3p for La$_{1-x}$Sr$_x$NiO$_3$ ($x = 0.0$ to $1.0$) electrocatalyst samples.

**Oxygen evolution reaction activity.**—The current density vs. $iR$ compensated potential curves for OER on the La$_{1-x}$Sr$_x$NiO$_3$ samples are presented in Figure 6a along with the state-of-the-art electrocatalyst BSCF, and the most commonly used precious metal electrocatalysts IrO$_2$ and Pt black. It may be mentioned here that the 10th cycle of the CVs performed at 10 mV s$^{-1}$ in O$_2$-saturated 0.5 M NaOH electrolyte on a RDE setup with 1600 rpm was extracted and the obtained current-potential data were corrected for the ohmic resistance before analysis. The corresponding specific activities normalized by the geometric area of the GCE (disk) or $j_{\text{oxide}}$ (mA cm$^{-2}$) for OER at $iR$ compensated potential of 1.70 V are also presented in the inset of Figure 6a. It is evident that the current densities ($j_{\text{disk}}$) corresponding to OER activities for La$_{1-x}$Sr$_x$NiO$_3$ increased as the value of $x$ increased from 0.0 to 0.6. However, any further increase in the value of $x$ (0.8 and 1.0) decreased the current densities. The decrease in the specific current density ($j_{\text{disk}}$) of samples for $x = 0.8$ and 1.0 is likely due to (i) the possible change in the surface area of samples, (ii) decrease in the weight fraction of lanthanum-strontium nickelate for $x = 0.8$ and strontium nickelate for $x = 1.0$, and/or (iii) the presence of impurity phase SrCO$_3$. To evaluate the effects of surface area and weight fraction, the surface area specific activities, $j_{\text{oxide}}$ (mA cm$^{-2}$) and weight fraction specific activities, $j_{Wf}$ (A g$^{-1}$ Wf) were calculated by normalizing with the BET surface area of electrocatalysts and the weight fraction of lanthanum and strontium nickelates calculated by Rietveld analysis (Table III), respectively, as presented in Figure 6b. The measured BET surface areas of electrocatalysts were found to be 4.08, 5.95, 4.28, 2.59, 1.56, and 0.47 m$^2$ g$^{-1}$ for $x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0, respectively. After normalization of the current density with respect to the BET surface area and the weight fraction, no change is expected upon increasing the Sr content in the samples for all values of $x$ if the changes in specific activities are due to (i) the BET surface area and (ii) weight fraction. However, from Figure 6b, it can be deduced that the specific activities ($j_{\text{oxide}}$ and $j_{Wf}$) increase with increase in the degree of Sr$^{2+}$ substitution. Thus, it clearly demonstrates that the change in the activity for OER is intrinsic and...
not due to the changes in the surface area or the weight fraction of lanthanum-strontium nickelates. Juxtaposing the Rietveld refinement results (Table III) with the OER activities (Figure 6a) also indicate that the activity for OER of perovskite-type electrocatalysts in Table V. The mass based specific activities, \(i_{\text{mas}} \ (\text{A g}^{-1})\) were considered for the comparison at an \(iR\) compensated potential of 1.70 V. It is observed that substitution of \(\text{Sr}^{2+}, x = 0.6\) achieved the highest mass based specific activity (816 A g\(^{-1}\)) among \(\text{La}_{1-x}\text{Sr}_x\text{NiO}_3\) electrocatalysts and also the lanthanum-strontium nickelate electrocatalysts surpassed the state-of-the-art and precious metal electrocatalysts. The electrocatalyst with \(x = 0.6\) has around four times higher mass specific activity than that of BSCF and \(\text{IrO}_2\), and six times that of Pt black at 1.70 V. Amongst the tabulated values of mass specific activity for OER of perovskite-type electrocatalysts in Table V, \(\text{La}_{0.6}\text{Sr}_{0.4}\text{NiO}_3\), i.e., for the value of \(x = 0.6\) in \(\text{La}_{1-x}\text{Sr}_x\text{NiO}_3\) shows higher activity than that of the state-of-the-art electrocatalyst BSCF but lower than that of hybrid \(\text{NiO-(La}_{0.625}\text{Ca}_{0.375})_2\text{NiO}_3\) and precious metal electrocatalyst \(\text{IrO}_2\) reported in the literature.

It has been reported that oxides having mixed oxidation state and/or higher oxidation state of transition metal present at B-site, \(\text{La}_{1-x}\text{Sr}_x\text{NiO}_3\), \(\text{Ni}_{3/2}^3+\text{Ni}_{1/2}^{2+}\) have shown better electrocatalytic activity for OER. In the present case, both these effects might be operative. While the \(\text{Sr}^{2+}\)-substitution induces mixed oxidation states of \(\text{Ni} (\text{Ni}^{2+}, \text{Ni}^{3+}, \text{and possibly Ni}^{4+}), \) the secondary phase of \(\text{NiO}\) along with lanthanum-strontium nickelate possibly provides a synergistic effect. Although, the contribution of the synergistic effect to the overall OER activity might be small considering the weight fraction of \(\text{NiO}\) in the samples. In essence, the higher activity for OER for the synthesized lanthanum-strontium nickelates may be attributed to the combined effect of the existence of mixed oxidation state of \(\text{Ni}\) and presence of hybrid \(\text{NiO}-\text{lanthanum-strontium nickelate electrocatalyst}.

### Table IV. X-ray photoelectron spectroscopy deconvolution results of peaks (A, B, C and D), binding energy (B.E.), relative area (R.A.), and full width at half-maximum (FWHM) from \(\text{Ni 3p}\) spectra for strontium-substituted lanthanum nickelate \((\text{La}_{1-x}\text{Sr}_x\text{NiO}_3; x = 0.0 \text{ to } 1.0)\) samples.

| \(x\) (Sr\(^{2+}\)) | Peak | B.E. (eV) | R.A. (%) | FWHM (eV) | Species identification | \(\text{Ni}^{3+}/\text{Ni}^{2+}\) ratio |
|-----------------|------|-----------|---------|-----------|-----------------------|-------------------|
| 0.0             | A    | 66.68     | 53.73   | 2.59      | \(\text{NiO}\) 3p\(_{3/2}\) | 0.241             |
|                 | B    | 68.88     | 26.87   | 2.59      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 70.46     | 12.94   | 2.82      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) | 0.183             |
|                 | D    | 72.66     | 6.47    | 2.82      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
| 0.2             | A    | 66.96     | 56.37   | 3.00      | \(\text{NiO}\) 3p\(_{3/2}\) | 0.158             |
|                 | B    | 69.16     | 28.17   | 3.00      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 71.62     | 10.30   | 2.65      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
|                 | D    | 73.82     | 5.16    | 2.65      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
| 0.4             | A    | 67.13     | 57.58   | 2.69      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | B    | 69.33     | 28.79   | 2.69      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 71.94     | 9.09    | 2.49      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
|                 | D    | 74.14     | 4.54    | 2.49      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
| 0.6             | A    | 67.24     | 55.18   | 2.95      | \(\text{NiO}\) 3p\(_{3/2}\) | 0.208             |
|                 | B    | 69.44     | 27.59   | 2.95      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 72.21     | 11.48   | 2.15      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
|                 | D    | 74.41     | 5.74    | 2.15      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
| 0.8             | A    | 67.28     | 48.39   | 2.94      | \(\text{NiO}\) 3p\(_{3/2}\) | 0.378             |
|                 | B    | 69.48     | 24.19   | 2.94      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 71.92     | 18.28   | 4.64      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
|                 | D    | 74.12     | 9.14    | 4.64      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
| 1.0             | A    | 69.66     | 4.36    | 3.52      | \(\text{NiO}\) 3p\(_{3/2}\) | 14.291            |
|                 | B    | 71.86     | 2.18    | 3.52      | \(\text{NiO}\) 3p\(_{3/2}\) |                |
|                 | C    | 73.48     | 62.31   | 3.58      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |
|                 | D    | 75.64     | 31.15   | 3.58      | \(\text{Ni}_2\text{O}_3\) 3p\(_{3/2}\) |                |

Figure 5. High resolution and deconvoluted XPS spectra of \(\text{Ni 2p3/2}\) for \(x = 1.0\) i.e., \(\text{SrNiO}_3\) electrocatalyst sample.
### Table V. Specific activities, $j_{\text{mass}}$ (A g$^{-1}$) for oxygen evolution reaction of synthesized electrocatalysts and various benchmark electrocatalysts at iR compensated potential of 1.70 V vs. RHE. The values reported here from the literature are extracted from the $i - E$ polarization curves and the mass activities in the present study were using the electrocatalyst loading of 15.84 μg, which included secondary phases NiO and SrCO$_3$.

| Electro catalyst       | Mass specific activity $j_{\text{mass}}$ (A g$^{-1}$) at 1.70 V | Reference |
|------------------------|---------------------------------------------------------------|-----------|
| ABO$_3$                |                                                                |           |
| LaNiO$_3$              | 0.1 M KOH                                                      | ≈ 3       | 38        |
| LaNiO$_3$              | 0.1 M KOH                                                      | 559       | 59        |
| SrNiO$_3$              | 0.5 M NaOH                                                     | 278       | This work |
| SrFeO$_4$              | 0.1 M KOH                                                      | 8         | 60        |
| CaFeO$_3$              | 0.1 M KOH                                                      | 45        | 60        |
| CaCuFeO$_3$$_{12}$     | 0.1 M KOH                                                      | 45        | 60        |
| SrCoO$_3$              | 0.1 M KOH                                                      | 563       | 21        |
| La$_{1-x}$Sr$_x$NiO$_3$| 0.1 M KOH                                                      | 816       | This work |
| BaNiO$_3$              | 0.1 M KOH                                                      | 89        | 61        |
| BSCF                   | 0.1 M KOH                                                      | 753       | 9         |
| BSCF                   | 0.1 M KOH                                                      | 27        | 59        |
| BSCF (950°C)           | 0.1 M KOH                                                      | 15        | 60        |
| BSCF (1100°C)          | 0.1 M KOH                                                      | 8         | 60        |
| BSCF                   | 0.5 M NaOH                                                     | 193       | This work |
| A$_2$BO$_4$            |                                                                |           |
| La$_2$NiO$_4$          | 0.1 M KOH                                                      | ≈ 2       | 38        |
| La$_{1-x}$Sr$_x$NiO$_3$| 0.1 M KOH                                                      | ≈ 5       | 38        |
| (La$_{0.6}$Ca$_0.4$)$_2$NiO$_4$-$x$ | 0.1 M KOH                                    | 764       | 59        |
| NiO-(La$_0$,$Sr$0.1)Ca$_{0.387}$NiO$_3$$\cdot$562 | 0.1 M KOH                                       | 8174      | 59        |
| Noble                  |                                                                |           |
| IrO$_2$                | 0.1 M KOH                                                      | 7569      | 9         |
| IrO$_2$                | 0.1 M KOH                                                      | 563       | 21        |
| IrO$_2$                | 0.5 M NaOH                                                     | 170       | This work |
| Pt black               | 0.5 M NaOH                                                     | 125       | This work |

### Table VI. Kinetic parameters of OER on La$_{1-x}$Sr$_x$NiO$_3$ electrocatalysts in 0.5 M NaOH electrolyte. The open circuit voltage (OCV, V vs. RHE) of the electrocatalysts was measured in O$_2$ saturated 0.5 M NaOH solution prior to the OER measurements. Here, $b$, $\alpha$, and $j_0$ represent Tafel slope (mV dec$^{-1}$), transfer coefficient, and exchange current density (mA cm$^{-2}$), respectively.

| $x$ (Sr$^{2+}$) | OCV (V) | $R^2$ | $b$ (mV dec$^{-1}$) | $\alpha$ | $j_0$ (mA cm$^{-2}$) |
|----------------|---------|-------|---------------------|----------|----------------------|
| 0.0            | 1.15    | 0.9991 | 71.2                | 0.83     | 7.6 × 10$^{-7}$      |
| 0.2            | 1.19    | 0.9991 | 71.0                | 0.83     | 6.8 × 10$^{-6}$      |
| 0.4            | 1.07    | 0.9976 | 67.0                | 0.88     | 1.3 × 10$^{-7}$      |
| 0.6            | 1.13    | 0.9983 | 65.3                | 0.91     | 5.7 × 10$^{-7}$      |
| 0.8            | 1.18    | 0.9987 | 68.3                | 0.87     | 4.2 × 10$^{-6}$      |
| 1.0            | 1.16    | 0.9984 | 61.9                | 0.96     | 2.4 × 10$^{-7}$      |

### Conclusions

Strontium-substituted lanthanum nickelate (La$_{1-x}$Sr$_x$NiO$_3$) perovskite-type oxides were synthesized by the nitrate solution combustion method. The values of the elemental composition of electrocatalysts measured by the EDS are in good agreement with nominal values. Further, structural characterization done with the help of XRD showed that the substitution of Sr$^{2+}$ for La$^{3+}$ at A-site distorted the original crystal structure of lanthanum nickelate to form a tetragonal lanthanum-strontium nickelates with smaller cell volume and also produced a secondary phase of NiO, and impurity SrCO$_3$ for higher values of $x$. Rietveld analysis suggests that contraction in the lattice structure was due to the formation of smaller ionic radii Ni ions at B-site of oxides and/or due to creation of oxygen vacancies. It is also suspected that a still higher oxidation state of Ni than Ni$^{3+}$ is present, however, corroboration with XPS was found to be weak. The substitution of Sr$^{2+}$ in La$_{1-x}$Sr$_x$NiO$_3$ enhanced the activity for OER until $x = 0.6$ and decrease in the OER activities were observed with a further increase in the value of $x$. Irrespective of the decrease in the OER activity at higher values of $x$ (0.8 and 1.0), all synthesized lanthanum-strontium nickel oxide electrocatalysts have higher OER activities than the most commonly used electrocatalysts (IrO$_2$ and Pt) and the state-of-the-art electrocatalyst (BSCF). Therefore, present results suggest that use of single phase strontium substituted lanthanum nickel oxide and/or single phase strontium nickel oxide can be a promising anode oxygen electrocatalyst for the alkaline water electrolysis.

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Figure 6. (a) Cyclic voltammograms for oxygen evolution reaction on 80 wt% synthesized La$_{1-x}$Sr$_x$NiO$_3$ ($x = 0.0$ to $1.0$) and the state-of-the-art electrocatalysts, and specific activities normalized to the disk area, $j_{\text{OER}}$ (mA cm$^{-2}$) are given in inset. (b) OER specific activities normalized to the BET specific area, $j_{\text{OER}}$ (mA cm$^{-2}$), and those normalized to the weight fraction calculated by the Rietveld refinement, $j_{\text{OER}}$ (mA cm$^{-2}$, line+symbol). All the specific activities reported here for OER are at iR compensated potential of 1.70 V vs. RHE at scan rate of 10 mV s$^{-1}$ in O$_2$ saturated 0.5 M NaOH solution with RDE rate of 1600 rpm.

Figure 7. Experimental overpotential ($\eta$) vs. log of current density ($j$) plots (symbols) for La$_{1-x}$Sr$_x$NiO$_3$ ($x = 0.0$ to $1.0$) electrocatalyst samples, which were used for the oxygen evolution reaction. The Tafel plots are shown by solid lines.
56. W.-S. Yoon, M. Balasubramanian, X.-Q. Yang, Z. Fu, D. A. Fischer, and J. McBreen, J. Electrochem. Soc., 161, A246 (2004).
57. M. Ao, G. H. Pham, V. Sage, and V. Pareek, J. Mol. Catal. A Chem., 416, 96 (2016).
58. Y. Ren, Y. Cheng, R. J. Gorte, and K. Huang, J. Electrochem. Soc., 164, F3001 (2017).
59. R. Liu, F. Liang, W. Zhou, Y. Yang, and Z. Zha, Nano Energy, 12, 115 (2015).
60. S. Yagi, I. Yamada, H. Tsukasaki, A. Seno, M. Murakami, H. Fujii, H. Chen, N. Umezawa, H. Abe, N. Nishiyama, and S. Mori, Nat. Commun., 6, 8249 (2015).
61. J. G. Lee, J. Hwang, H. J. Hwang, O. S. Jeon, J. Jang, O. Kwon, Y. Lee, B. Han, and Y.-G. Shul, J. Am. Chem. Soc., 138, 3541 (2016).
62. R. E. Carbonio, C. Fierro, D. Tryk, D. Scherson, and E. Yeager, J. Power Sources, 22, 387 (1988).
63. K. J. May, C. E. Carlton, K. A. Storzezinger, M. Risch, J. Suntivich, Y.-L. Lee, A. Grimaud, and Y. Shao-Horn, J. Phys. Chem. Lett., 3, 3264 (2012).