

SUMMARY

The interfacial physicochemical and electrochemical properties of some transition metal mixed oxides having spinel ($M_xFe_{3-x}O_4$, $M = Co, Ni$ and $0 \leq x \leq 1.5$) and perovskite ($La_{1-x}M'_xCoO_3$, $M' = Sr, Cu$ and $0 \leq X \leq 0.8$) structure have been studied in relation to oxygen evolution reaction in 1M KOH solution. Ferrite spinels were obtained by low temperature egg white sol-gel (EW-SG) and sodium hydroxide co-precipitation (COP) methods. The Sr and Cu-substituted lanthanum cobaltate perovskite oxides were prepared by sol-gel type routes and the precursors used in the synthesis were malic acid and citric acid. In order to know the effect of pH of the precursor solution in the synthesis of the oxide, the Cu-substituted lanthanum cobaltates were obtained at two different pH viza 3.75 and 4.00. Materials, so obtained, were confirmed by powder X-ray diffraction (XRD) pattern and IR spectroscopy. Morphology of oxide in the form of powder and/or film on Ni was determined by scanning electron micrograph (SEM). For electrochemical studies, the oxide powder was transferred in the form of film on pre-treated Ni-substrate ($1.5 \times 1.0 \text{ cm}^2$) by an oxide slurry painting technique. For the purpose, slurry of the oxide was made with Triton X-100 in an agate pastel mortar. This slurry was painted on one side of the pre-treated Ni with fine brush and then heat treated at $380 \text{ }^\circ\text{C}$ for 2 hrs. This procedure was repeated two or three times to get the desired loading of the oxide on Ni-support. In the treatment of Ni plate, the Ni-plate was first polished on a fine emery paper, kept in conc. HCl for 20 minutes, degreased in acetone and cleaned with double distilled water and dried. Electrical contact with the catalytic films was obtained by using copper wire, silver paint and Araldite. Approximately 0.5 cm^2 area of the oxide layer was left for electrochemical studies. Remaining part of the Ni-substrate was covered with Araldite epoxy.

The powder X-Ray diffraction (XRD) pattern of sintered oxides was determined by using Philips and PAN analytical Powder X-Ray Diffractometer using $Cu-K\alpha_1$ as the radiation source ($\lambda = 1.54056 \text{ \AA}$). Morphology of the oxide powder was determined by using scanning electron microscope (SEM; JEOL

JSM 6490) and SEM (LEO 430). Spinel ferrite phase of the material was confirmed by infrared spectra (FT-IR Thermoscientific; Nicole-6700).

All the electrochemical investigations that include cyclic voltammetry (CV) and anodic Tafel polarization were performed in a three electrode single compartment glass cell using potentiostat/galvanostat (Gamry Reference 600 ZRA) provided with corrosion and physical electrochemistry software and a desktop computer (HP). A platinum foil ($\sim 2 \text{ cm}^2$) and Hg/HgO/1M KOH ($E^\circ = 0.098 \text{ V vs NHE at } 25^\circ\text{C}$) were used as an auxiliary and reference electrodes, respectively. The reference electrode was connected electrically to the electrolyte through a Luggin capillary (agar-agar and potassium chloride salt bridge gel) for the minimization of the solution resistance (iR drop) between the working and the reference electrode. The oxide film electrode was used as working electrode. The formal overpotential values mentioned in the data were obtained by the relation, $\eta = E - E_{\text{O}_2/\text{OH}^-}$, where E and ($= 0.303 \text{ V vs. Hg/HgO}$) are the applied potential across the catalyst/ 1 M KOH interface and the theoretical equilibrium Nernst potential in 1 M KOH at 25°C , respectively..

Cyclic voltammogram of each film electrodes was recorded in the 1M KOH at 25°C in the potential region 0.0-0.7 V. Each voltammogram shows a pair of redox peaks, an anodic and a corresponding cathodic just prior to the onset of oxygen evolution reaction. The cyclic voltammetric parameters, such as anodic and cathodic peak potential, peak separation potential and formal redox potential were estimated from curves in each case. The observed peaks were further characterized and found that they were originated from the oxidation of Ni-support and not from the oxidation of the catalytic layer. It was considered that when the film electrode is inserted into the cell solution, the electrolyte might enter into the oxide mass through pores, intercrystalline gaps, grain boundaries, cracks etc. and exhibited a contact with the substrate. The effect of scan rates on the voltammetric curves has also been investigated with each oxide electrode. The electrochemically active surface area of the

perovskite oxides was determined in terms of roughness factor by recording the CV curves in the small potential region 0.0-0.1 V.

Tafel plots (E vs log j curves) were recorded to determine the electrode kinetic parameters of the oxide film electrodes towards oxygen evolution reaction. The value of Tafel slope (b) and electrocatalytic activity in terms of current density as well as in terms of overpotential were estimated from the polarization curves. study shows that the certain degree of substitution of other metal ion in base oxide (in both spinel and perovskite type oxides) improves the electrocatalytic activity of oxide catalysts and maximum achievement was found with, 0.5 mol Co substitution in Fe_3O_4 (EW-SG), 1.5 mol Ni substitution in Fe_3O_4 (COP), 1.0 mol Co substitution in Fe_3O_4 (COP), 0.8 mol Sr substitution in LaCoO_3 (CA-SG), 0.6 mol Cu substitution in LaCoO_3 (MA-SG-A), 0.4 mol Cu substitution in LaCoO_3 (MA-SG-B).

Among all spinel type oxide film electrodes the value of Tafel slope was found to be minimum for $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($b = 44 \text{ mV decade}^{-1}$, COP) and maximum for $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($b = 102 \text{ mV decade}^{-1}$, EW-SG). In case of perovskite-type oxides, the oxides prepared by MA-SG method at pH 4.00 exhibit less Tafel slope value than base oxide, whereas the copper substituted oxides prepared at pH 3.75 have Tafel slope more than that of base. Also, the strontium substituted oxides are found to have less Tafel slope value than base oxide but the value is found very close for all substituted oxides. The order of reaction in case of spinel type of oxide film electrodes vary from 1.0 to 1.9 whereas in the case of perovskite type oxide film electrodes reaction order was found to be ~ 1 .

Electrochemical study of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ (COP) indicates that the substitution of Co with 0.5, 1.0 and 1.5 mol in Fe_3O_4 lattice increases the apparent electrocatalytic activity of the oxide, the activity being more than 2 times with 0.5 mol Co substitution. The order of reaction was found ~ 1 for substituted oxides while ~ 1.5 for base oxide electrode.

In case of Ni substituted oxides prepared by COP method, it has been found that the 1.5 mol Ni substituted oxide exhibit maximum apparent electrocatalytic activity, and found more than 6 times more active than base oxide. The order of reaction was found ~ 1 for both most active substituted oxide and least active base.

The substitution of Co (0.5, 1.0 and 1.5 mol) in Fe_3O_4 (COP) increased the electrocatalytic activity of the oxides and maximum activity was found with 1.0 mol Co substituted oxide electrode and found ~ 13 times more active than least active base oxide. The order of reaction was found ~ 1 for base oxide and ~ 1.5 for most active oxide. Tafel slope was found maximum for Fe_3O_4 (68 mV decade^{-1}) while minimum (44 mV decade^{-1}) for 0.5 mol Co substituted oxide.

Based on the overpotential data (Table 4.7.1) at a fixed current density of 100 mAcm^{-2} (on geometrical scale) the decreasing order of electrocatalytic activity of all spinel type prepared oxides film electrodes are as following:

CoFe_2O_4 ($\eta_{\text{O}_2} = 462 \text{ mV, COP}$) > $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($\eta_{\text{O}_2} = 459 \text{ mV, COP}$) > $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($\eta_{\text{O}_2} = 487 \text{ mV, COP}$) > $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($\eta_{\text{O}_2} = 513 \text{ mV, EW - SG}$) > $\text{Ni}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($\eta_{\text{O}_2} = 516 \text{ mV, COP}$) > NiFe_2O_4 ($\eta_{\text{O}_2} = 538 \text{ mV, COP}$) > CoFe_2O_4 ($\eta_{\text{O}_2} = 557 \text{ mV, EW-SG}$) > $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($\eta_{\text{O}_2} = 580 \text{ mV, COP}$) > $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($\eta_{\text{O}_2} = 585 \text{ mV, EW - SG}$) > Fe_3O_4 ($\eta_{\text{O}_2} = 662 \text{ mV, COP}$) > Fe_3O_4 ($\eta_{\text{O}_2} = 668 \text{ mV, EW - SG}$).

However, based on the apparent current density data at a certain potential ($\eta_{\text{O}_2} = 547 \text{ mV}$), the electrocatalytic activity of spinel type oxides indicated the following order:

CoFe_2O_4 ($j_a = 315.6 \text{ mAcm}^{-2}$, COP) > $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($j_a = 219.2 \text{ mAcm}^{-2}$, COP) > $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($j_a = 183.5 \text{ mAcm}^{-2}$, COP) > $\text{Ni}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($j_a = 158.0 \text{ mAcm}^{-2}$, COP) > $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($j_a = 119.9 \text{ mAcm}^{-2}$, EW-SG) > NiFe_2O_4 ($j_a = 107.0 \text{ mAcm}^{-2}$, COP) > CoFe_2O_4 ($j_a = 96.1 \text{ mAcm}^{-2}$, EW-SG) > $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (j_a

= 89.4 mAcm⁻², COP) > Co_{1.5}Fe_{1.5}O₄ (j_a = 84.7 mAcm⁻², EW-SG) > Fe₃O₄ (j_a = 50.7 mAcm⁻², EW-SG) > Fe₃O₄ (j_a = 23.7 mAcm⁻², COP).

In case of Sr substituted LaCoO₃ oxide, every substituted oxide has been found more active than base oxide and maximum activity was found with 0.8 mol Sr substituted oxide (j_a = 379.0 mAcm⁻² at η_{O₂} = 447 mV) film electrode. The material is found to be more than 5 times more active than least active LaCoO₃ (j_a = 71.7 mAcm⁻² at η_{O₂} = 447 mV). Order of reaction was found ~1 for all film electrodes 0.6 Cu.

Substitution of Cu in LaCoO₃ (MA-SG-A) prepared at pH 4.00 has been found beneficial only for 0.6 mol Cu substitution but other substituted oxides are found less active than base oxide. Among the oxide studied, 0.2 mol Cu substituted product was found to be least active. Tafel slope value was found to be maximum for base oxide (80 mV decade⁻¹), while minimum for most active La_{0.4}Cu_{0.6}CoO₃ oxide (80 mV decade⁻¹). The order of reaction was found ~1 for all oxide film electrodes.

In case of Cu substituted oxide catalysts (MA-SG-B) prepared at pH 3.75 maximum activity was found with 0.4 mol Cu substituted oxide, while base oxide showed minimum electrocatalytic activity. Order of reaction was found ~1 for each oxide film electrode.

Based on the overpotential data at a fixed current density of 100 mA cm⁻² (on geometrical scale) the decreasing order of electrocatalytic activity of all perovskite type prepared oxides are as following:

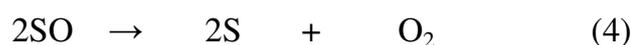
La_{0.2}Sr_{0.8}CoO₃ (η_{O₂} = 383 mV, CA-SG) > La_{0.4}Sr_{0.6}CoO₃ (η_{O₂} = 406 mV, CA-SG) > La_{0.4}Cu_{0.6}CoO₃ (η_{O₂} = 408 mV, MA-SG-A) > La_{0.6}Sr_{0.4}CoO₃ (η_{O₂} = 417 mV, CA-SG) > LaCoO₃ (η_{O₂} = 424 mV, MA-SG-A) > La_{0.6}Cu_{0.4}CoO₃ (η_{O₂} = 431 mV, MA-SG-B) > La_{0.8}Sr_{0.2}CoO₃ (η_{O₂} = 436 mV, CA-SG) ≈ La_{0.2}Cu_{0.8}CoO₃ (η_{O₂} = 438 mV, MA-SG-A) > LaCoO₃ (η_{O₂} = 467 mV, CA-SG) ≈ La_{0.6}Cu_{0.4}CoO₃ (η_{O₂} = 470 mV, MA-SG-A) > La_{0.8}Cu_{0.2}CoO₃ (η_{O₂} = 476 mV, MA-SG-A) ≈ La_{0.2}Cu_{0.8}CoO₃ (η_{O₂} =

477 mV, MA-SG-B) > La_{0.4}Cu_{0.6}CoO₃ (η_{O_2} = 519 mV, MA-SG-B) > La_{0.8}Cu_{0.2}CoO₃ (η_{O_2} = 541 mV, MA-SG-B) > LaCoO₃ (η_{O_2} = 571 mV, MA-SG-B).

However, based on the apparent current density data at a certain potential (η_{O_2} = 447 mV), the electrocatalytic activity of all perovskite type oxides indicated the following order:

La_{0.2}Sr_{0.8}CoO₃ (j_a = 379.0 mAcm⁻², CA-SG) > La_{0.4}Sr_{0.6}CoO₃ (j_a = 230.7 mAcm⁻², CA-SG) > La_{0.6}Sr_{0.4}CoO₃ (j_a = 187.2 mAcm⁻², CA-SG) > La_{0.4}Cu_{0.6}CoO₃ (j_a = 182.4 mAcm⁻², MA-SG-A) > LaCoO₃ (j_a = 138.1 mAcm⁻², MA-SG-A) > La_{0.8}Sr_{0.2}CoO₃ (j_a = 121.7 mAcm⁻², CA-SG) > La_{0.6}Cu_{0.4}CoO₃ (j_a = 111.6 mAcm⁻², MA-SG-B) > La_{0.2}Cu_{0.8}CoO₃ (j_a = 111.4 mAcm⁻², MA-SG-A) > La_{0.6}Cu_{0.4}CoO₃ (j_a = 79.1 mAcm⁻², MA-SG-A) > LaCoO₃ (j_a = 71.7 mAcm⁻², CA-SG) > La_{0.2}Cu_{0.8}CoO₃ (j_a = 70.2 mAcm⁻², MA-SG-B) > La_{0.8}Cu_{0.2}CoO₃ (j_a = 66.3 mAcm⁻², MA-SG-A) > La_{0.4}Cu_{0.6}CoO₃ (j_a = 59.3 mAcm⁻², MA-SG-B) > La_{0.8}Cu_{0.2}CoO₃ (j_a = 49.2 mAcm⁻², MA-SG-B) > LaCoO₃ (j_a = 39.9 mAcm⁻², MA-SG-B).

The electrode kinetic parameters (b and p) observed for oxide film electrodes in present electrochemical study could be explained by assuming the following mechanistic steps for oxygen evolution reaction.



Where the term S and S.OH are the active site and surface adsorbed intermediate, respectively.

Under Langmuir adsorption condition, assuming equation (2) as the rate determining step (rds) and the total coverage, $\theta_T (= \theta_{OH} + \theta_{O^-} + \theta_O)$, the overall current density expression can be obtained as

$$j = nFK_1k_2C_{OH^-}^2 \exp\left[\frac{FE}{RT}\right] \quad (5)$$

(Tafel slope ≈ 120 mV and order 1)

Where, $K_1 = k_1/k_{-1}$, is the adsorption-desorption equilibrium constant for reaction (1) and 'n' is the total no. of electrons.

Similarly under Langmuir adsorption condition Considering reaction (3) as the rds and θ_T , the expression for overall current density may be written as,

$$j = nFk_3K_1k_2C_{OH^-}^2 \exp\left[\frac{3FE}{2RT}\right] \quad (6)$$

Tafel slope ≈ 40 mV and order of reaction = 2

In the above equation, $K_2 = k_2/k_{-2}$, and it is adsorption-desorption equilibrium constant for reaction (2).

If the above reaction (2) and (3) are considered to be indistinguishable; they can then be represented as:



Assuming above equation (2a) as rate determining step and total coverage θ_T under Temkin adsorption condition ($0.2 < \theta_T < 0.8$), the expression for overall current density can be written as,

$$j = nFk_{2a} \theta_{OH} C_{OH^-} \exp\left(\frac{FE}{2RT}\right) \cdot \exp\left\{\ln K_1^0 C_{OH^-} + \frac{FE}{RT}\right\} \quad (7)$$

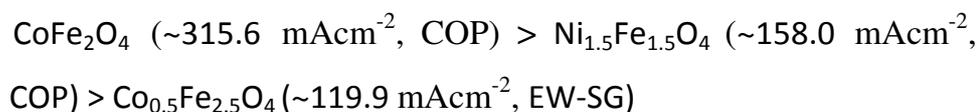
The expressions (5), (6) and (7) deduced under different conditions for overall current density explains fairly well the p and b values similar to those observed experimentally.

In a nutshell, the above results can be concluded as following:

1. IR and Powder X-Ray Diffraction spectra shows that the synthesized oxide catalysts prepared, exhibited characteristic bands of pure

spinel (cubic crystal geometry) or perovskite phase (hexagonal crystal geometry) and it has been found that the substitution of foreign metal ions decreased the crystallize crystallite size (S).

2. Substitution of Co or Ni for Fe in the Fe₃O₄ matrix in COP method greatly increased the electrocatalytic activity of the catalyst, however, the activity being the greatest with 1.5 mol Ni and 1.0 mol Co substitution.
3. Partial substitution of Sr in place of La in LaCoO₃ prepared by CA-SG method enhance the electrocatalytic activity significantly and maximum activity was found for 0.8 mol Sr substituted product.
4. The presence of Cu in the LaCoO₃ lattice synthesized by MA-SG-A method at pH 4.00 increased the electrocatalytic activity only for 0.6 mol Cu substitution while other degree of substitutions are found less active than base oxide
5. Introduction of Cu in the LaCoO₃ matrix prepared by MA-SG-B method at pH 3.75 is found beneficial for all degree of substitutions and maximum activity has been found with 0.4 mol Cu substituted oxide film electrode.
6. Based on the values of the current density at a constant overpotential (547 mV), the active spinel type oxide catalysts of each series of substituted oxides can be placed in the activity order:



7. Based on the values of the current density at a constant overpotential (447 mV), the active perovskite type oxide catalysts of each series of substituted oxides can be placed in the activity order:

