Synthesis of ternary electrocatalysts for exploration of methanol electro-oxidation in alkaline media

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Abstract

In the quest for alternate and efficient electrode materials, ternary metal electrocatalysts (TMEs), part of the perovskite family, were synthesized and tested for methanol electro-oxidation in alkaline media. La₀.₅Ca₀.₅MO₃ (M = Ni, Co, or Mn) was synthesized via sol-gel method. X-ray diffraction analysis revealed that the perovskite crystal structure possesses characteristic sharp and crystalline peaks for all synthesized ternary electrocatalysts. The average particle size calculated using Debye–Scherrer equation was in the order of La₀.₅Ca₀.₅NiO₃ (LCNO) > La₀.₅Ca₀.₅CoO₃ (LCCO) > La₀.₅Ca₀.₅MnO₃ (LCMO). The elemental composition of as prepared sample, LCCO was investigated via x-ray fluorescence spectroscopy. The qualitative and quantitative analysis revealed the presence of La, Ca and Co in parent crystal structure with percentage compositions of 9.0, 3.12 and 87.82% respectively. The particle size distribution was homogenous, as determined by scanning electron and transmission electron microscopes. The electrocatalytic activity of the synthesized ternary electrocatalysts was studied electrochemically by cyclic voltammetry. The calculated diffusion coefficient values showed that electrode surface of LCNO and LCCO have limited efficiency for diffusion related phenomenon. The heterogeneous rate constants inferred better electrode kinetics of LCCO and LCNO which exhibited good electrocatalytic behavior; sharp anodic peaks were observed in the potential range of +0.3 to 0.6 V and +0.6 to 0.8 V, respectively. Methanol electro-oxidation was found minimal in case of LCMO sample. We have observed that Co substitution at B-site of perovskite electrode materials attains better electrochemical properties, thus in relation with reported literature.

1. Introduction

The environmental concern of and ever-increasing dependence on oil has galvanized the research on fuel cells because of their utilization in stationary, portable, and transportation applications. Fuel cells can be operated continuously as long as fuel is supplied and the products/bystreams are removed, which is practically limited by the degradation of some of the precursor components [1, 2]. Fuel cells are primarily classified according to the nature of the ion-conducting medium [3]. Solid-oxide fuel cells (SOFCs) are considered as one of the most promising electrochemical devices for power generation (with low emission and high energy conversion efficiency) [4, 5]. Practically, natural gas is used as the fuel in SOFCs, because of its abundance [6–8], although to achieve high energy density, liquid fuels are preferred because they help in the reduction of size, complexity, and cost of SOFC systems. Methanol, with an energy density of 6 kWh kg⁻¹, can be used as the fuel for portable SOFCs and can be the best alternative to natural gas for SOFCs [9].

Perovskite-type oxides are well known due to their versatile functional properties, especially in catalysis [10–13]. La₁₋ₓSrₓMnO₃ (LSM), La₁₋ₓSrₓCo₁₋ₓFeₓO₃₋ₓ (LSCF), Ba₁₋ₓSrₓCoₓFe₁₋ₓO₃₋ₓ (BSCF), La₁₋ₓSrₓCoO₃₋ₓ (LSC), Sm₁₋ₓSrₓCoO₃₋ₓ (SSC), and SrᵬFe₁₋ₓMoₓOₓ|La₁₋ₓSrₓGaₓMgₓO₆|Ba SrₓCo₦Fe₁₋ₓO₃₋ₓ lanthanum ferrite and cobaltite were found to be suitable candidates as electrode materials for SOFCs possessing good electronic conductivity and thermal expansion [14]. Perovskite materials have been synthesized via
mechanochemical processing [15], Pechini method [16], solid state reaction, microwave route [17], combustion synthesis [18], and the sol-gel method [19] resulting in various properties and microstructures [20].

Among perovskites family, electrocatalysts facilitate catalytic/electrochemical reactions at the electrode surface and have been used for methanol electro-oxidation in alkaline and acidic media due to their thermal and chemical stability along with mechanical, catalytic, and electrical properties [21]. Literature studies revealed that non-noble and noble metals and their complex compounds (NiO, CuO, CeO2) has been used extensively for methanol electro-oxidation [22–26].

Referring above literature related to doping in perovskite family and contribution of Ni and Co for improved electronic/ionic and mixed electronic/electrochemical behavior, a library of electrocatalysts having the general formula La$_{0.5}$Ca$_{0.5}$M$_{3}$O$_{3}$ (M = Ni, Co, Mn) were synthesized by the sol-gel method. Their structural and textural properties were investigated via x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The elemental analysis was carried out using x-ray florescence spectroscopy (XRF). The electrocatalysts were tested for methanol electro-oxidation in alkaline media through cyclic voltammetric (CV) measurements. The CV analysis of methanol electro-oxidation proves that the synthesized perovskite materials with Ni and Co on B-site can be promising candidates for air electrodes of SOFC.

2. Materials and methods

2.1. Chemicals

Lanthanum (III) nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O, Sigma Aldrich), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O, Sigma Aldrich), cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma Aldrich), nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O Sigma Aldrich), manganese (II) nitrate tetrahydrate (Mn(NO$_3$)$_2$·4H$_2$O, Sigma Aldrich) and citric acid (Sigma Aldrich) were used as precursors. Nafion solution (Sigma Aldrich) was used as binder and silver paste for making electrical contacts on pallets for electrical measurement. Solvents used were methanol, ethanol and de-ionized water. Potassium hydroxide (KOH) was used as electrolytes. All analytical grade chemicals were used in this experimental work.

2.1.1. Characterization framework

X-ray diffraction patterns of all samples were observed using an X’Pert PRO diffractometer at room temperature. Resistivity measurement was performed using a homemade four-probe setup. The surface morphology was studied by scanning electron microscopy using a JEOL JSM 5600 scanning electron microscope and transmission electron microscopy using a JEOL JEM 2011 transmission electron microscope. The qualitative and quantitative analysis was performed using JEOL JSX 3202 M x-ray Fluorescence to identify the types and elemental content of the elements present within the sample. Cyclic voltammetry was carried out using the Nova 1.1 CV technique (the current-potential range of the potentiostat was 1 A and +8 V to −2 V). CV measurements of the synthesized electrocatalysts were carried out in both acidic and basic media. The CV profile of the electrocatalysts in basic media showed profound results in contrast to acidic media, and therefore, basic media were chosen for the detailed investigations.

Prior to the modification, a glassy carbon electrode (GC, 0.071 cm$^2$) was polished using alumina and then ultrasonically washed with acetone and distilled water to remove all types of organic and inorganic impurities from the electrode surface. A mass of 0.1 mg of synthesized electrocatalysts in 1 ml of ethanol was homogenously dispersed ultrasonically for 30 lA volume of 10 μl of the suspension was dropped on the polished GC surface and dried in air. Finally, after the evaporation of the solvent, 10 μl of 1% Nafion solution was added on the modified electrode. The modified electrode was left for complete dryness of the Nafion solution before use.

2.2. Experimentation

2.2.1. Synthesis of electrocatalysts

Ternary electrocatalysts La$_{0.5}$Ca$_{0.5}$MO$_3$ (M = Ni, Co, Mn) were synthesized using the sol-gel method [19]. In metal nitrate precursor solution, citric acid was added. The solution was concentrated at 100 °C with stirring which led to gelation. The final dried powder was obtained after thermal treatment at 1150 °C in air for 7 h which were then used for structural, morphological, electrical and electrochemical testing. The synthesized samples were labeled as LCNO for La$_{0.5}$Ca$_{0.5}$NiO$_3$, LCCO for La$_{0.5}$Ca$_{0.5}$CoO$_3$, and LCMO for La$_{0.5}$Ca$_{0.5}$MnO$_3$ respectively.
3. Results and discussion

3.1. Structural analysis via XRD

The XRD patterns as shown in figures 1(a)–(c) indicate the perovskite crystal structure of the synthesized materials. The appearance of sharp peaks can be attributed to the small particle sizes. In the XRD pattern (figure 1(a)), (103), (110), (200), (105), (006), (114), (211), (107), and (008) crystal planes were found at 31.76°, 33.22°, 37.33°, 43.47°, 44.31°, 47.66°, 54.06°, 56.71°, and 58.54°, respectively, on the angular axis for La0.5Ca0.5NiO3. The diffraction peaks at 2θ angles appearing at 32.80°, 40.54°, 47.54°, and 58.96° can be assigned to scattering from the (200), (022), (202), and (123) planes, respectively, in the case of La0.5Ca0.5MnO3 (figure 1(b)). For La0.5Ca0.5CoO3, maximum counts were obtained from planes (103), (104), (202), (024), and (116) at 32.83°, 33.22°, 40.61°, 47.66°, and 58.54°, respectively (figure 1(c)). All peaks were calculated from JCPDS-036-1390 [27].

LCNO and LCCO exhibit a rhombohedral crystal structure, whereas LCMO possesses an orthorhombic crystal structure. The crystallite sizes for LCMO, LCNO, and LCCO were calculated by the Debye Scherrer formula from peaks (200), (103), and (104), and were found to be 33.7, 43.4, and 52.9 nm, respectively.

3.2. Elemental compositional analysis via x-ray fluorescence spectroscopy

In order to determine qualitative and quantitative elemental composition of the samples, XRF analysis of LCCO was performed as displayed in figure 2. The results indicated that LCCO is composed of La, Ca and Co elements, with percentage compositions of 9.0, 3.12 and 87.82% respectively.

3.3. Morphological analysis

Figures 3(a)–(f) shows the scanning electron micrographs of LCNO, LCCO and LCMO samples, showing crystalline nature of all the samples. An excrescent homogenous particle size distribution can be observed in all.
SEM images. A smaller particle size can be perceived along with agglomeration. Although, the Sherrer formula resulted in an average particle size of \( \sim 60 \) nm in almost all the samples, the particles’ average sizes estimated from the SEM appear as \( \sim 160 \) nm, 200 nm and 1 \( \mu \)m for LCNO, LCCO and LCMO, respectively. The comparative difference in the particle size with respect to XRD appears because of the stresses and structural imperfections, resulting in broadening of XRD peaks and full-width-half-maxima extends in the denominator of the Sherrer formula. We cannot rule out the possibility of coalescence that results in larger size distribution. The coalescence/agglomeration can be due to an increase in the surface-to-volume ratio with the reduction in particle size, as well as, due to the magnetic nature of the ions on the \( M \)-sites (\( M = \text{Ni, Co, and Mn} \)) [28, 29].

Transmission electron micrographs for LCNO and LCMO manifest their surface morphology, particle size and particle shape. In TEM images of LCMO and LCNO, fringes/terraces were observed, which indicate the presence of atomic planes in a crystal structure as shown in figure 4 [27]. TEM analysis also supports the XRD and SEM analysis. The agglomeration of particles of an average size of \( \sim 250 \) nm was observed in both cases that form larger particles containing multiple crystallites/domains.

3.4. Electrical properties
The electrical properties of the electrocatalysts were measured on pellets by four-probe method. The pellet formation was performed in a hydraulic press. A mass of 0.8 mg of catalyst was placed in a 13 mm die, and the
powder was pressed under 400 bar pressure. The pellets were then sintered for 48 h at 500 °C to improve adhesion and remove porosity. Conducting silver paste was applied on the sintered pellets. Then, four-probe measurements were performed by regulating the temperature using liquid nitrogen. The resistivity was measured comparatively at low temperatures because the trend at high temperature is akin to our current measuring temperature [27].

The resistivity measurement for La0.5Ca0.5NiO3 is shown in figure 5. Inverse dependence of resistivity on temperature was observed, which reflects the typical trend of semiconductors [30]. Literature reveals the presence of Ni at the B-site in the ABO3 structure leads to comprehensive resistivity as compared to other transition metals [31–33].

3.5. Electrochemical properties
The blank electrochemical response of the GC electrode was measured in 1 M methanol solution containing 3 M KOH prior to every reading of the ternary electrocatalysts, as shown in figure 6. The modified electrode (method of electrode fabrication is discussed in experimental section) was then dipped into 1 M methanol solution with 3 M KOH.

The electrochemical response of LCNO is shown in figure 6(A). An anodic peak signal for methanol electro-oxidation was observed in the forward scan, whereas in the reverse scan no cathodic peak for methanol electro-oxidation was observed. This may correspond to catalytic behavior of Ni in LCNO [23, 25]. The system demonstrates the irreversibility of LCNO for methanol electro-oxidation. The electrode was left in solution for 20 min, and then the scan was re-taken at 1 mV s⁻¹ as shown in figure 6(A), (a). This time-reverse scan was superimposed on the anodic peak in the forward direction, which indicates better electrocatalytic behavior of

![Figure 4. Transmission electron microscopic images of lanthanum calcium nickel oxide and lanthanum calcium manganese oxide.](image)

![Figure 5. Variations in resistivity of lanthanum calcium nickel oxide with temperature.](image)
LCNO for methanol electro-oxidation. The scans were recorded at different scan rates (1 mV s$^{-1}$, 10 mV s$^{-1}$, 50 mV s$^{-1}$, 100 mV s$^{-1}$, and 200 mV s$^{-1}$) as shown in figure 6(A), (B).

The mechanistic approach related to catalytic activity of Ni based composite material (LCNO) in presence of methanol and alkaline media can be proposed as suggested by Fleischmann et al [34], intermediates are formed upon oxidation of methanol in presence of electrocatalysts which further catalyze the methanol electro-oxidation process in alkaline media.

The electrochemical response of LCMO is shown in figure 6(B). In case of LCMO, no significant oxidation peak was observed; however, a current rise beyond 0.5 V could be seen [35]. This system also reflects the irreversible behavior of LCMO in alkaline media.

LCNO shows a well-defined methanol oxidation peak in the anodic sweep within the potential window of +0.6-0.8V; for the reverse scan, no cathodic peak was observed, as shown in figure 6(C). This may infer that upon reduction, Co [Co(II) or C(III)] is captivated by methanol. The proposed mechanism of methanol electrode-oxidation in our case is based on previous findings, intermediates (like CoOOH) are formed upon oxidation of methanol in presence of Co (possibly due to Co$^{3+}$ which is being reduced to Co$^{2+}$) [22, 34] where methanol reacts with these intermediates to catalyze the whole process. The availability of Co active sites for methanol leads to better methanol electro-oxidation. LCCO exhibits irreversible behavior. Scans were recorded at different scan rates and the same behavior was observed.

LCNO and LCCO showed anodic peak current at low scan rates, which indicates the slow kinetics of the system in the potential range of +0.3 to 0.6 V and +0.6 to 0.8 V, respectively. Strong anodic peak signals were observed in both LCNO and LCCO towards methanol electro-oxidation. The research shows that transition metals (i.e., nickel and cobalt) are most favored metals (for air electrodes in SOFC) because of their high activity towards methanol electro-oxidation [22, 23]. By contrast, the absence of an anodic peak in LCMO demonstrates its suitability as a candidate for the opposite electrode (i.e., cathode) [35].

In comparison to three synthesized ternary electrocatalysts, pronounced electro-oxidative behavior of methanol in alkaline media was observed in LCCO, as shown in figure 6(D). This may be due to the electroactivity of cobalt, which enhances the oxidation of methanol. Cobalt exhibits good electroactive behavior noticed for oxygen reduction and oxygen evolution reactions [36]. In all cases, irreversibility was observed.
Anodic peaks for methanol electro-oxidation in all catalysts were found only in forward scans. The difference in peak heights of all the catalysts demonstrates the catalytic activity of the samples.

3.6. Evaluation of diffusion coefficient and rate constant

The diffusion coefficient of ternary electrocatalysts was calculated using the Randles-Sevick equation [37–39]:

$$I_p = (2.99 \times 10^5)n(\alpha n_a)^{1/2}AC_oD^{1/2}V^{1/2},$$  \(1\)

where $$I_p$$ is the peak current, $$n$$ is the number of electrons involved in the charge transfer step (in current calculations, $$n = 1$$), $$A$$ represents the area of the working electrode (GC), $$C_o$$ is the concentration of methanol, $$V$$ is the scan rate, and $$D$$ is the diffusion coefficient. The peak currents ($$A$$) for La0.5Ca0.5NiO3 and La0.5Ca0.5CoO3, was found to be $$7.23 \times 10^{-8}$$ and $$8.26 \times 10^{-8}$$ respectively while La0.5Ca0.5MnO3 showed no electrochemical response. The diffusion co-efficient values for LCNO and LCCO were calculated by solving equation no. 2 and were found to be $$2.35 \times 10^{-5}$$ and $$3.06 \times 10^{-8}$$ respectively. The calculated diffusion constant values indicate that diffusion is limited towards electrode surface.

The Nicholson-Shain equation [40] was used to calculate heterogeneous rate constants for synthesized ternary electrocatalysts:

$$I_p = 0.227nFAC_o k_s \exp\left(\frac{\alpha n_aF}{RT}(E_p - E^0)\right).$$  \(3\)

$$k_s = \frac{I_p}{0.227nFAC_o} \exp\left(-\frac{\alpha n_aF}{RT}(E_p - E^0)\right).$$  \(4\)

where $$I_p$$ is the peak current, $$n$$ represents the number of electrons transferred (in current calculations, $$n = 1$$), $$A$$ is the area of the working electrode (GC), $$C_o$$ is the concentration of methanol, $$E^0$$ is the standard electrode potential (taken as 0.7 here), $$F$$ and $$R$$ represent the Faraday and gas constants, respectively; $$k_s$$ represents the standard heterogeneous rate constant for the electro-oxidation of methanol. The calculated $$k_s$$ (cms$$^{-1}$$) for LCNO and LCCO, was found to be $$1.44 \times 10^{-6}$$ and $$1.36 \times 10^{-6}$$ respectively. From the electrochemical data, it can be inferred that LCNO and LCCO exhibit better electrode kinetics towards methanol electro-oxidation while LCMO shows sluggish kinetics towards methanol oxidation.

4. Conclusion

In our work, ternary electrocatalysts La0.5Ca0.5MO3 (M = Ni, Co and Mn), belonging to the perovskite family, were successfully synthesized using the sol-gel method and investigated as catalysts for methanol electro-oxidation in alkaline environment. All synthesized samples attained excellent crystallinity with a uniform particle size distribution. The electrochemical response of LCCO, LCNO towards methanol electro-oxidation was pronounced. The diffusion related phenomenon at electrode surface is limited in LCNO and LCCO as observed from calculated diffusion coefficient values. The heterogeneous rate constants inferred better electrode kinetics of LCCO and LCNO. Finally, it can be reasonable to conclude that LCCO and LCNO shows good electro-catalytic activity towards methanol electro-oxidation in alkaline media making it suitable candidate for air electrodes in SOFC.

**Future Perspective:** On behalf of our study and literature findings, it can be suggested that conductivity and efficiency of energy storage materials/electrocatalysts can be improved by pondering cost effectiveness on selection of materials, modifying electrode fabrication while studying electrochemical parameters considering the current challenges of alternative energy resources.

In the light of future outlooks, energy storage capability of electrocatalysts should be improved so it can be suggested that materials with strong electrical, mechanical and electrochemical properties can overcome the underline lapses. In the library of these materials, Co based perovskite materials can be proposed as the best candidates for electrode materials.

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Conflict of interest

There is no conflict of interest.

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