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Electrocatalytic activity of $LaCoO_3$ on Ni-electrode for oxygen evolution reaction in 1M KOH at 25°C

Pankaj Chauhan[a] & Basant Lal[b]

[a] Department of Chemistry, Faculty of Basic and Applied Sciences, Madhav University, Pindwara, Sirohi 307 026, Rajasthan, India
[b] Department of Chemistry, Institute of Applied Sciences and Humanities, GLA University, Mathura 281 406, Uttar Pradesh, India
E-mail: pankajc010198@gmail.com, basant.lal@gla.ac.in

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The alginic acid sol-gel (AA) method has been used to synthesize perovskite-type oxide ($LaCoO_3$) for the electrocatalysis of water in alkaline solution. The extra pure nitrate salts of lanthanum, and cobalt and alginic acid have been used in this process. The TGA, FT-IR, and XRD techniques established the formation of perovskite-type oxide. The catalytic performance of fabricated oxide electrode towards the electrochemical formation of oxygen by the splitting of water in an alkaline medium has been explored using the Tafel polarization and cyclic voltammetry techniques. Based on the electrochemical investigation, fabricated $LaCoO_3$/Ni electrode exhibits comparatively better electrocatalytic activity for the oxygen evolution reaction (OER) in 1M KOH solution due to its higher value of oxide roughness factor ($R_F \approx 16$) and with slightly lower Tafel slope ($b \approx 85$ mV dec^{-1}) than those prepared by the conventional routes. The OER follows a first-order reaction mechanism that occur by the adsorption of reaction intermediates.

Keywords: Sol-gel method, Tafel polarization, Oxygen evolution reaction, Cyclic voltammetry, Roughness factor

There are many different ways that humans use energy in their daily lives. Most of it is generated as electrical energy and comes from the combustion of finite fossil fuels. Reduced reliance on fossil fuels is required because burning fossil fuels releases large volumes of carbon dioxide into the environment. Alternative energy sources must be found. The need for sustainable and eco-friendly energy conversion has renewed interest in electrochemical and photo-electrochemical water splitting since it promotes the large-scale storage of wind and solar electricity into fuels[1]. One major challenge in this research is the development of economically viable electrocatalyst materials for the oxygen evolution reaction. Transition metal oxide catalysts, of which perovskite-type lanthanum cobaltate oxide nanoparticles ($LaCoO_3$ NPs) are one example, have garnered a lot of attention due to these criteria. This is because of their unique qualities and potential applications as gas sensors[2], heterogeneous catalysts[3], electrochemical devices[4], lithium batteries[5], magnetic materials[6], and photocatalysts[7]. The properties and applications of $LaCoO_3$ nanoparticles are influenced by particle size and form, which is why there has been a surge in interest in their synthesis in recent years[8]. These materials are easily found on Earth, need little preparation, and have strong catalytic stability in neutral and alkaline electrolytes[9]. Several methods, including thermal salt decomposition[10], autoclave synthesis[11], sol-gel synthesis[12], co-electrodeposition and subsequent oxidation[13], direct oxide electrodeposition[14], and photochemical reactions[15], can be used to create cobalt oxides in either an amorphous or crystalline form. Oxides prepared by conventional methods suffer small surface area and hence low electrocatalytic activity. To improve the electrocatalytic activity for OER or other applications oxides were prepared by using algic acid, lanthanum(III) nitrate hexahydreate, and cobalt(II) nitrate hexahydrate as precursors, an affordable low-temperature sol-gel method. The synthesized $LaCoO_3$ in the study was characterized by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), and electrochemical techniques for oxygen evolution reaction in an alkaline medium.

Experimental Section

Synthesis of $LaCoO_3$

$LaCoO_3$ was prepared by dissolving the stoichiometric ratios of metal nitrates such as $La(NO_3)_2$. $6H_2O$, AR, Sigma Aldrich, 99.99%, and $Co(NO_3)_2$. $6H_2O$, AR, Sigma Aldrich, 98%, in

200 mL of double distilled water maintaining 0.01 M concentration of each nitrate salts and mixed with 200 mL solution of 0.2 M alginic acid keeping solution neutral (*p*H 7) by ammonia solution. The resultant solution was evaporated at 100℃ until it converted into a dark gel, and finally decomposed at 600°C for 5 hours in an electrical muffle furnace to obtain the requisite oxide ($LaCoO_3$) (Ref. 16).

Characterization Techniques

The formation of a perovskite-type oxide was established by thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and powdered X-ray diffraction spectroscopy (PXRD). For TGA, a thrmogram of dried gel samples was recorded between the temperature range 25℃ to 600℃ in an inert atmosphere with the continuous flow of nitrogen using the Thermal Analysis (Model: Mettler Toledo TGA/DSC 3+), IRSPIRIT-T Shimadzu spectrophotometer was used for FT-IR of oxide recorded in KBr between wavenumber of 400 and 4000 cm^{-1} and for the XRD powder pattern, D8 Advance BRUKER, Cu-Kα as the source of radiation with λ = 1.54059 Å was used to record PXRD spectrum between the phase angle 20° and 80°.

The oxide electrodes for the electrochemical investigation were fabricated by repeated coating of oxide paint prepared with glycerol (2 drops/100 mg of oxide powder) onto one side of the pre-treated nickel plate. The treatment of nickel plate was carried out in concentrated HCl and cleaned ultrasonically in acetone. Finally, the coated plate was heated in an electrical furnace at 300℃ for one hour to achieve an oxide loading of about 5 mg cm^{-2}. A copper wire end that had been flattened was used to make an electrical connection with the nickel plate's opposite side using silver paste. The electrode was mounted using an epoxy glue (Araldite), leaving an exposed oxide area (~0.5 cm^{-2}) (Ref. 17). The three-electrode system consists of a working electrode (Ni/oxide electrode), a counter electrode (graphite), and a reference electrode (Hg/HgO/1M KOH) used for electrochemical experiments performed in a single-compartment Pyrex glass cell.

Results and Discussion

TGA

The formation of thermally stable oxide was determined by the TGA analysis recorded from 25℃ to 600℃ in an inert atmosphere of nitrogen gas. The thermogram of the dried gel sample is given in Fig. 1. The weight loss of the sample can be observed up to 500°C owing to the decomposition of salt formed from metal nitrates (such as La, and Co) and alginic acid, and the elimination of water molecules. After 500°C, the thermogram showed very slow weight loss, indicating a stable oxide phase formation.

FT-IR

The FT-IR technique was used to confirm the formation of lanthanum cobaltate ($LaCoO_3$). the recorded IR spectrum in the wavenumber region between 400 and 4000 cm^{-1} shown in Fig. 2, which exhibited characteristic vibration band for lanthanum cobaltate bands at 563 cm^{-1}, which can be attributed to the bending mode of vibration. Additional absorption band 419 cm^{-1} of O–Co–O and La–O–Co,

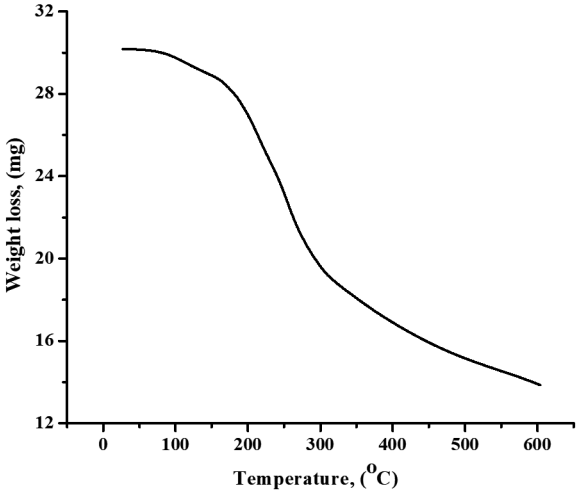

Fig. 1 — TGA of the gel obtained at 100℃ for $LaCoO_3$

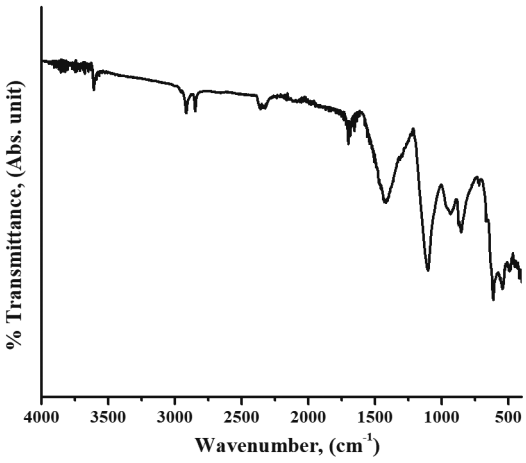

Fig. 2 — FT-IR spectrum of $LaCoO_3$ prepared at 600°C

which represent the generation of $LaCoO_3$ phase structure[18]. Lanthanum cobaltate is also shows a stretching vibration peak at 1458 cm^{-1} (Ref. 19). Due to the presence of the spinel phase Co_3O_4 in addition to the perovskite oxide at 660 cm^{-1} (Ref. 20). The IR spectrum of oxides revealed the presence of several additional peaks at 1375, and 3595 cm^{-1}, which were attributed to the vibration of carbonate group CO_3^{2-} groups of the O–C–O bond, and the stretching vibration from the O–H bond of the moisture moiety[21]. Additionally, an absorption peak at 2350 cm^{-1} was associated with the stretching vibration of O=C=O (Ref. 22). However, an unidentified peak at 1100 has also appeared in the spectrum.

PXRD

The synthesis of oxide was also confirmed by the XRD powder pattern diffraction recorded in the phase angle ranges of 20 to 80°. PXRD of oxide synthesized at 600°C shown in Fig. 3, which has a very close agreement with the JCPDS file no. 48-0121 of lanthanum cobaltate having similar peaks with reflections at (100), (110), (111), (200), (210), (211), (220), (300), and (310) planes. However, other peaks (impurities) that are present in trace amounts were also seen in addition to the perovskite-type oxide peaks. These include cobalt oxide (JCPDS file 43-1004). The crystallite size (S) of oxide was calculated by the Debye Scherrer formula $S = \frac{0.9\,\lambda}{\beta\, cos\,\theta}$ where β is the full width at half maximum (FWHM) of a most intense peak, λ is the wavelength and θ is the Bragg angle. The lanthanum cobaltate is nano-crystalline with ~30 nm dimension which is similar to that reported in the literature for the same oxide by Singh *et al*.[23]

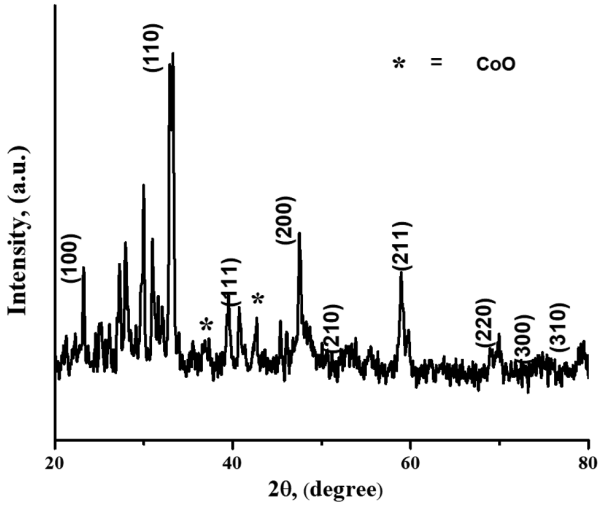

Fig. 3 — PXRD spectrum of $LaCoO_3$ prepared at 600°C

Cyclic Voltammetry

Fig. 4 shows the voltammogram of Ni/$LaCoO_3$ recorded at 20 mV sec^{-1} between potential regions 0 to 0.7 V against Hg/HgO in 1M KOH at 25°C. The voltammogram of the oxide electrode exhibited a pair of redox peaks just before the oxygen evolution reaction. The anodic and cathodic peaks appeared at the potentials $E_{pa} \simeq 419$ mV and $E_{pc} \simeq 309$ mV, respectively, and have potential differences ($\Delta E \simeq 110$ mV) and pseudo-capacitive in nature.

Roughness Factor (R_F)

Oxide roughness factor (R_F) was estimated from the cyclic voltammetry recorded at various scan rates such as 10, 20, 40, 60, 80, and 100 mV s^{-1} in 1 M KOH solution at 25°C between potential regions 0.075 and 0.125 V, where the effect of charge transfer reaction is negligible (Fig. 5a). The double layer capacitances (C_{dl}) of lanthanum cobaltate were determined by calculating the slope of the straight line curve log i *versus* scan rate shown in (Fig. 5b). The measured values of C_{dl} were 948 μF. Assuming that the C_{dl} of a smooth oxide surface is 60 μF the roughness factor for the oxide electrode was computed based on the C_{dl} values. The estimated value of R_F for the oxide electrode was ~16 (Ref. 24).

Electrocatalytic Activity

The Tafel polarization curves in 1M KOH at 25°C, as seen in Fig. 6, were used to study the electrocatalytic activities for oxygen evolution

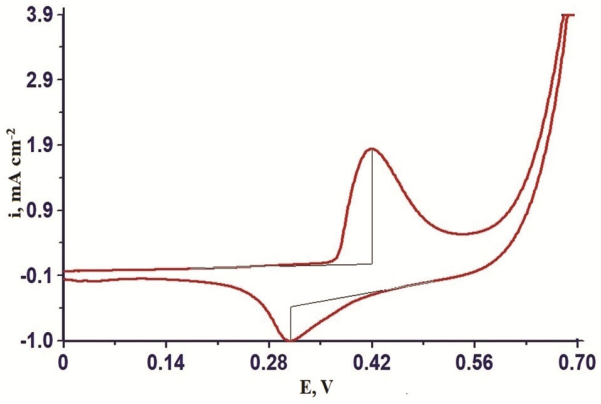

Fig. 4 — Cyclic voltammogram of Ni/ $LaCoO_3$ electrode at 20 mVs^{-1} in 1M KOH at 25°C recorded between 0 to 0.7 V

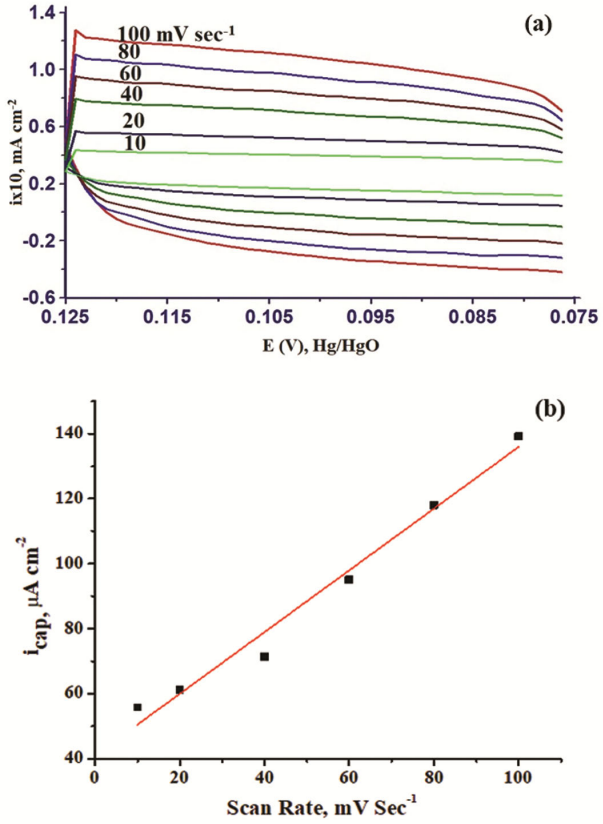

Fig. 5 — (a) CV curve of Ni/ $LaCoO_3$ electrode at different scan rates in 1 M KOH at 25°C recorded between 0.075 to 0.125 V; (b) The plot of charging current density *vs*. scan rate for Ni/$LaCoO_3$ electrodes

on the lanthanum cobaltate electrode. Two Tafel polarization regions were seen in the polarization curve, and the Tafel slopes in the lower and high polarization regions had measured values 85 and 128 mV dec^{-1} and the current density is 4.2 mA cm^{-1} at 0.7 V. The Tafel slope value was observed significantly low as shown in Fig. 6. The current density recorded by the produced similar oxide electrodes was very close to that reported by Maurya *et al*.[24] It was also evident from the polarization curves of the electrode tested for OER electrocatalytic activity that the oxide electrode, $LaCoO_3$, had a high current density value in an alkaline medium at 25°C. The lanthanum cobaltate showed higher apparent current density (i_{app}) as well as true current density (i_{tr}) because more oxygen vacancies were created in the prepared oxide while the valency of the La site was reduced, increasing the number of oxygen vacancies, the $LaCoO_3$ electrode showed the greatest improvement.

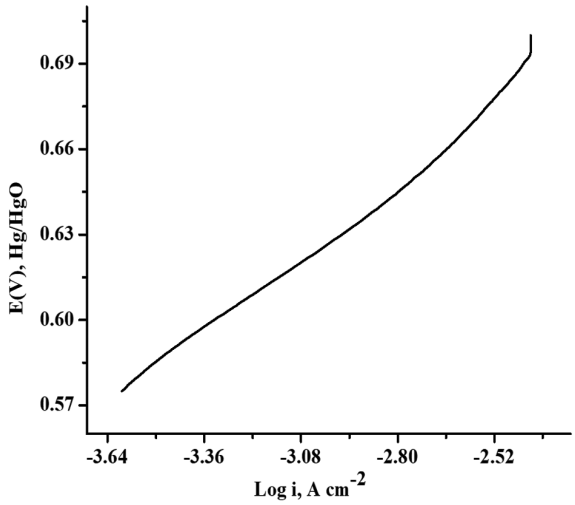

Fig. 6 — Tafel polarization curves on Ni/$LaCoO_3$ electrodes at the potential scan of 0.5 mVs^{-1} in 1 M KOH at 25°C

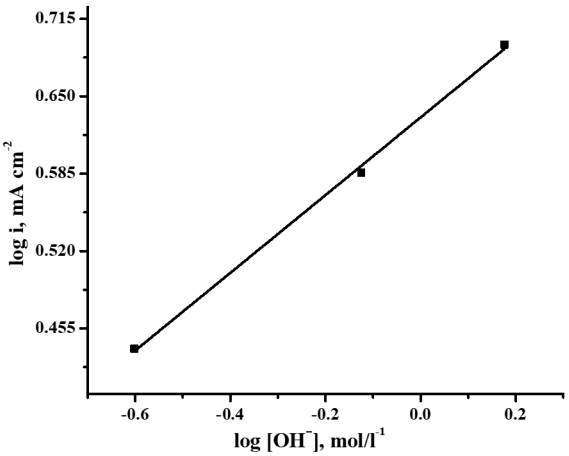

Fig. 7 — Plot of Ni/$LaCoO_3$ log i (at E = 0.7V) *vs*. log OH^- at 25°C

Order of Reaction

The Tafel polarization curves were recorded at various KOH concentrations (0.25, 0.5, 0.75, 1.0, and 1.5 M) to determine the order of the oxygen evolution reaction. The ionic strength of the medium (μ = 1.5) was maintained constant by using KNO_3 as an inert electrolyte at a temperature of 25°C. The slope of the log i *vs*. log [OH^-] plot at constant potential (0.7 V) was used to determine the order of the reaction as shown in Fig. 7 and found to be approximately one for OER in an alkaline medium. A similar kind of mechanism for OER in 1M KOH medium was also reported by Singh and co-workers for $La_{1-x}Sr_xCoO_3$ (Ref. 25) and $La_{1-x}Sr_xMnO_3$ (Ref. 26) electrodes.

Conclusions

The current investigation involves the synthesis and characterization of lanthanum cobaltate by the sol-gel method using alginic acid as a gelling agent. The results of the XRD analysis demonstrated the formation of the nano-sized crystalline perovskite-type oxide as a dominating phase along with trace amounts of other phases that also appeared in the XRD spectrum. The method of preparation for oxide catalyst is cost-effective and eco-friendly and produces electrocatalytic active oxides for the oxygen evolution reaction in an alkaline solution. the sol-gel approach may prove beneficial. It has been discovered that lanthanum cobaltate made using the alginic acid sol-gel method has noticeably better electrocatalytic activity than oxides made using other traditional high-temperature procedures. The current study also demonstrated that lanthanum cobaltate is a promising option for energy storage devices and electrocatalytic applications.

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Conflict of Interest Statement

The authors declare that there is no conflict of interest related to this work.

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