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One Pot Synthesis of Lanthanum Doped Cobalt Selenate Electrocatalyst for Oxygen Evolution Reaction (OER)

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Abstract

There is a continuous demand and burning of limited fossil fuel prompted the urgent need to develop renewable, abundant, and clean energy source. Therefore, for solving the energy crisis, the production of green hydrogen by electrochemical water splitting plays a vital role in achieving this goal. But, this electrochemical energy production process is kinetically sluggish due to multi-electron transfer reactions Therefore, the development of an efficient inexpensive catalyst towards OER have been required to accelerate the rate of oxygen evolution. We effectively designed and synthesized sheet-like morphology of lanthanum doped cobalt selenate through the one-pot hydrothermal route. The synthesized material is confirmed by different techniques. Herein prepared sheet-like La doped $CoSe_2O_5$ *material is employed as an efficient electrocatalyst towards OER in alkaline medium. This electrocatalyst show the low Overpotential and the low the Tafel slop value. Also successfully doped with the rare earth metal it show the large exchange current density and the active sites.*

1. Introduction

Nowadays world facing the energy shortage and rising the global warming lead to the increasing demands of exploit the efficient way energy conversion. In this way hydrogen production via electrochemically water electrolysis consisting of an oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) is the promising route to tackle this energy crisis. Adopting the electrochemical process because it feedstock is water, which is abundant and applied low voltage electricity needed for the highly pure clean hydrogen and oxygen generation. These two half reaction for water splitting has large energy barrier and slow reaction kinetics because it requires the four electron for the one oxygen molecule and two electron for one hydrogen molecule produced (J. Zhu et al.). Theoretically, 1.23V of minimum voltage is required to split the water but practically it operate at the voltage range 1.8-2.0V, which increases the cost and limits its commercial application at worldwide range (He et al.). Therefore, it trigger the much efforts of the researchers to minimize the potential range using the electrocatalyst. However the platinum-based material used for HER process and the iridium and ruthenium based oxide (RuO2/ IrO2) for the OER process provided significantly low Overpotential for both the reaction respectively. But these are very high cost and the scarcity makes most disappointed for industrial application for long run as the renewable energy source. Therefore, exploring the cost effective and earth abundant transition metal based metal composite used as the electrocatalyst. Over a past few decades besides the expensive Iridium and ruthenium based oxides, various other earth abundant transition metal have been extensively explored for the electrocatalyst (Anantharaj, Kundu, and Noda).

Recently not only metal oxide, but metal chalcogenide also demonstrated as the attractive catalyst for the OER process. Using selenide there are more synergistic electronic interactions between with metals, which makes the catalyst more conductive than the simple metal oxide (Jin). Variation of oxidation state of the cobalt from +2 to +3 is also investigated for the OER process (Manjunatha et al.). In recent year, the rare earth transition metal based electrocatalyst have been much explored for the OER activity. The main reason behind that it has the presence of the empty 4f orbital, which can promote the electron, which can promote the electron transfer for the better catalytic activity (Leduc et al.). Domínguez-Crespo and co-workers used the different reaction condition formed the different morphology based rare earth doped catalyst developed for the water splitting. In the presence of the rare earth disordered polycrystalline line of multiphase alloys formed which is responsible for the increases the surface area and the catalytic site for the kinetics of the electron transfer of the OER process. The presence of two non-metal modifies the electronic structure and its conductive property of the electrocatalyst for the catalytic activity towards OER process (Huang and J.-J. Zhu).

Inspired from the above discussion we have synthesized the cobalt selenate, which is successfully doped by Lanthanum. This catalyst is synthesized by one-step ecofriendly hydrothermal process, which show the activity towards the OER process. This electrocatalyst gives the small value of the Tafel slop and low Overpotential for the oxygen evolution process. It has the high active site and high exchange current density compared to the noble metal based electrocatalyst.

2. Experimental section

2.1. Materials

All precursor used for the synthesis electrocatalyst is brought from different source without any further purifications. Lanthanum (III) nitrate hexahydrate ($La(NO_3)_3.6H_2O$), cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), Selenium (Se) Metal Powder, sodium borohydride ($NaBH_4$) potassium hydroxide(KOH) flakes, ethylene diamine $C_2H_4(NH_2)_2$, potassium ferrocynide $K_4[Fe(CN_6)]$, nafion solution, and ethanol (C_2H_5OH) were purchased from SRL, Alfa Aesar and Merck Pvt. Ltd (India).

2.2. Synthesis Procedure

Lanthanum doped cobalt selenate synthesis hydrothermal process as described earlier with slight modification and its scheme shown below Figure 1. (Inta et al.). Initially 4 mmol of selenium powder and 24 mmol of $NaBH_4$ is dissolved in 20 ml of distilled water in 100 ml of beaker. After continuous stirring for 30 minute selenium powder gets completely reduced indicates black colors turns to colorless. Then added 2mmol and 1mmol of cobalt (II) chloride hexahydrate and lanthanum (III) nitrate hexahydrate respectively. After that with keeping stirring 2 ml of ethylene diamine solution added dropwise. In the mixture and finally obtained black colour mixture transferred into the 50 ml Teflon- lined autoclave 24 at 180ºC for 24 h. It was allowed to come at room temperature naturally. Then obtained product was washed several times with distilled water and ethanol and then dried it at 68º C for 12 hours.

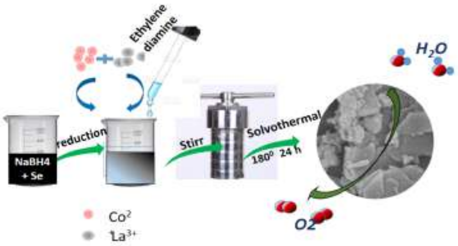

FIGURE 1. Schematic representation of the synthesis procedure of the catalyst

3. Result and discussion

3.1. Characterization of the prepared material

The prepared catalyst is firstly characterized by the XRD and matched with X' pert highscore plus using Rigaku smartlab diffractometer, having the $K\alpha$ source with 2θ range of 15ºto 75º. XRD pattern of the synthesized materials displayed in the Figure 2A. It show that diffraction peak of $CoSe_2O_5$ indexed as the orthorhombic crystalline structure which is confirmed by the JCPDS file No. 01-077-1740, sharp peak located at 17.10º, 26.64º, 46.06º, 51.240º and 63.29ºcorresponds to the plane of (002), (112), (132), (231) and (241) respectively. In the XRD pattern three extra peaks appeared at 29.27º,33.56º and 71.09º can be singed as plane (111), (200) , (400) corresponding to JCPDS file No 01-077-1740, which indicates that lanthanum successfully doped with cubic (space group Fm3m) crystalline phase. Therefore, the assignment of XRD peaks shows that material is successfully synthesized.

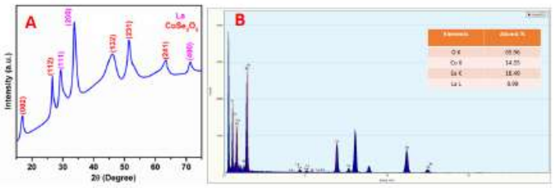

FIGURE 2. **(A) Powder XRD pattern and (B) EDAX spectra of the as prepared sample La doped $CoSe_2O_5$**

Further EDAX (energy dispersive X-ray) study on the same HR- TEM instrument for the elemental analysis. The element content in the nanocomposite clearly display in the EDAX Figure 2B. This study show the atomic weight of Co/Se/O in the ratio of 1: 1.28: 4.53 respectively. In this EDAX pattern we can clearly see that atomic percentage of Lanthanum is very low so it is doped in the $CoSe_2O_5$ uniformly which indicates that XRD data accept the spectra of EDAX. So it stoichiometry nearly close to expected ratio of element.

For the further study, the d-spacing given by SAED and XRD pattern holds very good agreement. In SAED pattern Figure 3A, the large diameter ring represent the plane (132) of $CoSe_2O_5$ and small diameter ring corresponds to the (200) plane of lanthanum supporting the JCPDS NO. 01-077-1740 and 01-077-1740 respectively. This is very strong hold investigated the synthetic protocols. At the same time elemental distribution proved that, the doping of Lanthanum at the Cobalt Selenate is uniformly distributed. Again elemental mapping of Co, Se and O show they are formed evenly shown in Figure 3B-F.

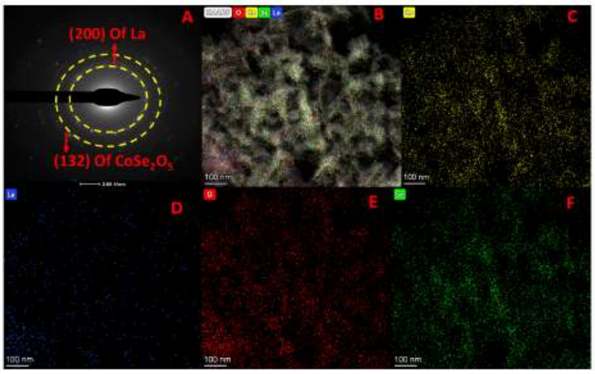

FIGURE 3. **SAED pattern (A), Corresponding elemental mapping of product (B-F)**

To understand the Morphological study of synthesized material done by FESEM (field emission electron microscopy) and HRTEM was performed on Carl Zeiss, supra55 with SDD X MAX50 EDAX and Talos F200X G2 of 200kV instrument respectively. From The FESEM image Figure 4A-B of the material, we can clearly see that it has sheet like morphology at which the Lanthanum is grown as particle like structure on the sheet of Cobalt Selenate . HRTEM images are also studied for the sheet like morphology of the synthesized electrocatalyst, which are shown in Figure 4C-D.

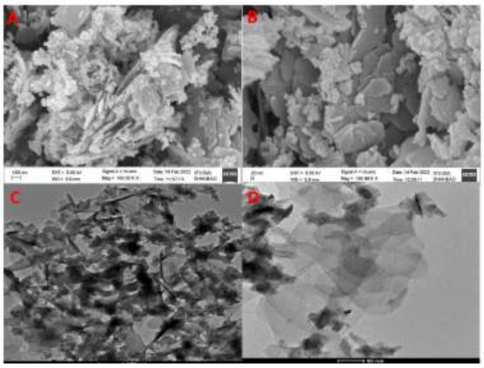

FIGURE 4. **FESEM image of sample (A-B), HRTEM images (C-D).**

In addition, FFT (fast Fourier Transformation) analysis of synthesized crystalline material, shown in Figure 5. also reveal the interplanar spacing is found to be ~0.3030 nm and ~.2654 nm represent the plane of lanthanum (111) and (200) plane. This analysis clearly show the plane of CoSe2O5 having d- spacing of ~0.1787 nm of plane (231) with well-matched with above mentioned JCPDS file.

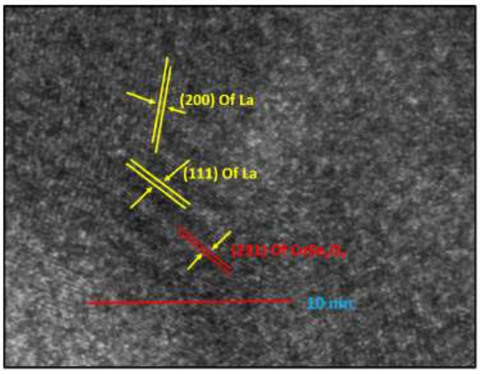

FIGURE 5. HRTEM image for lattice fringe calculation of electrode material.

4. Electrochemical measurement

Electrochemical study done in the three conventional electrode set up in which the saturated Ag/AgCl used as the reference electrode and platinum and glassy carbon electrode (GCE) of (0.07065 cm^2) used as a counter electrode and the working electrode respectively. The electrochemical test was executed on the corrtest CS Studio 5 workstation and carried out at the room temperature. For the coating of the working electrode 10 mg of sample is well dispersed in the 400 μL and 100 μL of 5% Nafion solution was added. After 2h of ultrasonication of the sample to make the homogeneous solution, taken the 10 μL (0.2 mg) of dispersed solution coated on the working electrode and dried it for the 12h at the room temperature.

The electrochemical test were conducted in the pursing of O_2 gas containing 1.0 M KOH electrolyte. Electrochemical impedance measurement (EIS), linear cyclic voltammetry (LSV), cyclic measurement (CV) and the bulk analysis with coulometry done for the OER measurement. Using the Nernst equation the measured potential of Ag/AgCl ($E_{Ag/AgCl}$) was converted to reversible hydrogen electrode potential (E_{RHE}), as following the equation (1) below,

$$E_{RHE} = E^{0}_{Ag/AgCl} + 0.059pH + 0.197 \qquad ....1$$

For the estimation of the OER we recorded CV and LSV at potential range 0.9 -1.6 V vs. RHE at the scan rate is 5 mV/s using the 1.0 M KOH (~pH= 14) of electrolyte. So the optimized parameter used for all further the electrochemical study for the oxygen evolution process. The obtained Overpotential is corrected by the EIS study measuring the solution resistance at the particular frequency range.

4.1. Oxygen Evolution Reaction (OER performance

After the mass loading, glassy carbon electrode (GCE) electrode we performed CV and LSV at the specific potential range 0.9 -1.6 V vs. RHE. After the optimized some crucial parameter such as scan rate (5 mV/sec), potential and the electrolyte concentration (1M KOH). We have found that catalyst has appreciable OER activity shown in Figure 6A. So we conclude that the prepared electrocatalyst efficient for the activity with small onset potential and the Overpotential value is 494 mV. Also Lanthanum based cobalt selenate show the activity towards the OER with the small onset potential (η°= 271 mV, it define as the minimum potential at which the current density start to increases sharply) and the large current density This is because sample have the perfect sheet like structure and the successfully doping with the lanthanum increase the active site.

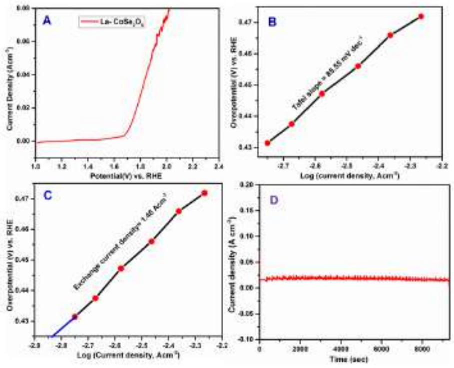

FIGURE 6. LSV polarization curve(A), Tafel plot of sample(B),measurement of the exchange current density by plot (C), bulk electrolysis for the stability curve (D).

According the literature the Tafel is also play major key role for Oxygen Evolution process which indicates the kinetics of the electrochemical process. Tafel slop is obtained by plotting the graph between the log of the current density and the Overpotential. The main equation of the measuring the Tafel slop of the electrocatalyst is as following equation (2)

$$\eta = a + b\, log\,(j) \qquad .... 2$$

Where ‘a’ for constant, b stand for slop of the Tafel plot and η and j indicates the Overpotential and the current density respectively. Low value of Tafel slop and large value of the exchange current density which was obtained by extrapolation of the Tafel plot shown is Figure 6B-C. for the efficient electrocatalyst. OER process the Overpotential is obtained by the Tafel slop (mV/dec) following equation (3)

$$\eta = E_{RHE} - 1.23 \quad ....3$$

So the Tafel slop of the La doped $CoSe_2O_5$ was found to be 85.55mVdec^{-1} and exchange current density is 1.46 mA cm^{-2}.Which suggest the sample have significant efficient for the OER process.

There are other previously reported metal composite show in Table no. 1 with corresponding Overpotential. So which can clearly show that synthesized material has efficient towards OER process (Lee et al. Shi and Zhao Gao et al. Wu et al. Chen, Kronawitter, and Koel Liu et al.).

4.2. Stability study of catalyst

Stability of the catalyst is play the crucial role to make the catalyst commercial or for the real time application. For the stability of the catalyst towards the OER process we have performed the bulk electrolysis with coulometry analysis in 1.0 M KOH. This electrolysis studied was performed for the 2.6 h with constant applied potential shown in Figure 6D. Plot indicates that the sheet like catalyst is almost constant current for the 2.6h. So the constant current suggest that catalyst has significant durable remarkable performance towards OER.

4.3. Electrochemically active surface area (ECSA) measurement

ECSA measurement of the prepared electrocatalyst using the double layer capacitance C_{dl} in the non -faradic region. For this CV were recorded with the different scan rate 20, 40, 60, 80,100 mV/s in the potential window 0.9 -1.6 V vs. RHE which is shown is Figure 7A. If the C_{dl} value is high then elctrocatalyst is having more number of the active site. The difference of the anodic current density and the cathodic current density at the different scan rate were calculated and plotted it gives the value of C_{dl} (0.111μ Fcm-2) display in Figure 7B. Electrochemically active surface area (ECSA) was calculated with the help of equation(4) (Majhi and Yadav),

$$ECSA = \frac{C_{dl}}{C_s} ....4$$

Where the Cs is the specific conductance which is depend electrolyte. For 1.0 M KOH it is taken 40 μF/cm^{-2}. So the ECSA obtained value of the Lanthanum doped $CoSe_2O_5$ is equal 19.60×10-5 cm^{-2}.

4.4. Electrochemical Impedance measurement (EIS)

For the mechanism of the electron transfer between the electrode and the electrolyte we have performed the Impedance measurement. In which we applied the frequency range 100000- 10 Hz with amplitude of 10 mV and applied the potential 0.67 V. The obtained charge transfer resistance (Rct) and solution resistance of the prepared sample from the Nyquist plot are 22.437 and 1.1755 respectively. By plotted the appropriate circuit which is displayed in Figure 7C. Shape of the Nyquist plot is semicircle arc, its smaller value suggest the faster the rate of electron transfer.

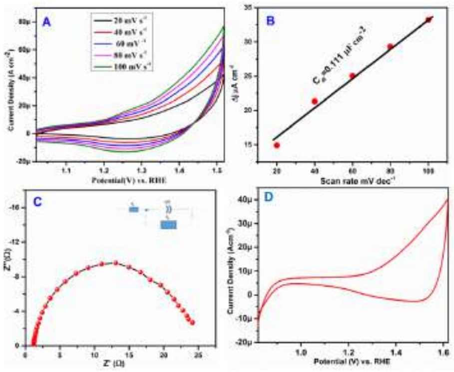

FIGURE 7. CV plot for the electrocatalyst in the non-faradic region (A), C_{dl} calculation (B), EIS Nyquist plot (C), CV curve for the TOF measurement (D)

4.5. Measurement of number of active sites (n and turnover frequency TOF)

For the measurement of the active site we have performed the CV in the potential range 0.85- 1.65 V vs. RHE with the same setup of the electrode and electrolyte and the scan rate at which the LSV we have optimized. Number of active sites of the synthesized electrocatalyst was calculated by the equation (5), (6) and (7),

$$Q = \frac{1}{V}\int_{E(1)}^{E(2)} ....5$$

$$n = \frac{Q}{4F} \quad ....6$$

$$TOF = \frac{I}{4nF} \; ....7$$

where the terms E(1), E(2),Q,V, I ,n, stand for the final and initial potential , scan rate(V/sec), charge(Coulomb) respectively. F used for the Faraday constant (98640 C mol^{-1}) and for the determination of active site n, Q is divided by 4 because four electron are involved for the 1 molecule of oxygen

TABLE 1. Table show that there are many reported electrocatalyst and there corresponding Overpotential

Electrocatalyst	**Overpotential** (η= mV for 10mA cm^{-2})	**Reference**
$Co_3O_4/2.7Co_2MnO_4$	540	9
$NiCo_2O_4$	565	10
$CoSe_2$ on GC	484	11
Co_3O_4/SWCNTS	550	12
Co_3O_4 nanocube	580	13
CoSe2 Bulk	590	14
La doped $CoSe_2O_5$	494	This work

formed. So the number of active site and TOF for the Lanthanum doped $CoSe_2O_5$ are obtained 6.935×10^{-9} mole and 0.264 s^{-1} respectively.

5. Conclusion

We conclude that in this work we successfully synthesized the cost effective electrocatalyst by facile one pot hydrothermal synthesis process. Which is characterized by the different techniques HRTEM, FESEM, Powder XRD, SAED and EDAX analysis. The prepared sheet -like Lanthanum doped Cobalt selenate was observed that the doping with the La enhance the active sites 6.935×10^{-9} mol^{-1} and the large exchange current density .This catalyst is endorsed that small value of Tafel slope 85.55mVdec^{-1}. This strategy of doping by simple one step process open up the electrocatalyst of the practical applications

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