Hydrothermal Synthesis of Zinc Cobalt Telluride Nanorod towards Oxygen Evolution Reaction (OER)

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Abstract. With an increasing demand for clean and sustainable energy which is directly related to water splitting, regenerative fuel cells, metal-air batteries, etc., exploring an efficient and inexpensive electrocatalyst with highly stable for oxygen evolution reaction (OER) is very important. In this article, here we demonstrated the nanorod Zn-Co-Te, is found to be a very good electrocatalyst for oxygen evolution reaction (OER) in alkali medium (KOH, pH= 15.14) with onset potential 1.38 V vs RHE. When this catalyst used as an electrocatalyst Zn-Co-Te nanorod obtained low overpotential 221 mV at a 10 mAcm⁻² current density with Tafel slope 91 mV/dec and high stability within three months.

Keywords: Nanorod, Oxygen evolution reaction (OER), Hydrothermal, Water splitting.

1. Introduction
Now a days the world is surviving the decreasing energy resources and increasing pollution. The hydrogen and oxygen are one of the main key elements in future sources of clean energy. The scientists are very much try to investigate the simple and ecofriendly methods for the production of oxygen. The production of oxygen from the water electrolysis is the most simplest and ecofriendly method, this method is also commercially used. Oxygen evolution reaction has more familiar in last few years in terms of various energy conversion and energy technologies. The water splitting by electrochemical is the one of the very convenient strategies to get the transformation of electric energy into the chemical energy. Basically water splitting by electrochemical consist of two half-cell reactions, oxygen evolution reaction (OER) is taking place at anode compartment and hydrogen evolution reaction (HER) is taking place at cathode compartment [1]. Among the two reactions (OER and HER), oxygen evolution is more demanding step than hydrogen evolution in water splitting [1]. Therefore, it is very much important to find an efficient and stable water splitting catalyst to enhance the overall efficiency. From the kinetics study, OER is very slow, because the first O-H bond of water molecule breaking after that O-O bond formation occurs and again which the limits for the industrial applications of water splitting [2]. The noble metals are rare in nature and also costly, hence not suitable for practical applications. Therefore, inexpensive and high efficacy towards OER is required. Earth abundant transition-metal complexes as a catalyst were found to be very good candidates for high performance towards OER [3]. IrO₂ and RuO₂
are very good catalysts for OER in acidic and alkaline medium [4], but these catalysts are costly and also low abundance. Therefore, researcher try to investigate such type catalysts which is low cost and also natural abundance. Recently, various type of transition metal chalcogenides and phosphides were reported towards OER such as CoSe$_2$ [5], NiSe$_2$ [6], CoTe$_2$ [7], Ni$_5$Se$_2$ [8] and Ni$_2$P [9], NiCoP [10] and CoMnP [11].

Various type of cobalt containing materials like sulfides, oxides, selenide and telluride shows very good catalytic activity towards OER. Since Oxygen to tellurium an electronegativity decrease leads to metallic properties increases. Again, toxicity of tellurium is less than selenium [12]. Till date only few researcher were done cobalt telluride towards OER [13]. Gao et al. were report cobalt ditelluride (CoTe$_2$) and cobalt telluride (CoTe) towards OER with overpotential 357 mV and 365 mV with current density 10 mAcm$^{-2}$ respectively [14]. Han’s group prepared cobalt telluride nanofilm towards OER with overpotential 370 mV at current density 10 mAcm$^{-2}$ [13].

Here, we first time report one spot hydrothermal synthesis of bimetallic telluride and bimetallic selenide nanalloys and compared their electrocatalytic activity like Zn-Co-Te nanorod and Zn-Co-Se nanoalloy towards OER with overpotential 221 and 560 mV at current density 10 mAcm$^{-2}$ in alkali medium respectively. Therefore, among the two nanoalloys, telluride containing nanomaterial shows very good electrocatalytic activity towards OER than selenide containing nanomaterial this is due to shape of the prepared materials. Again, our nanomaterials have high durability during three months.

## 2. Experimental Section

### 2.1. Materials

Chemicals were bought from different sources and used for experiments were analytical grade and used without further purifications. Cobalt (II) acetate [Co(CH$_3$COO)$_2$·4H$_2$O, zinc (II) acetate [Zn$_2$(CH$_3$COO)$_2$·2H$_2$O], potassium hydroxide [KOH], potassium ferrocyanide {K$_4$[Fe(CN)$_6$]} and selenium powder [Se] were purchased from Sigma-Aldrich, while the other solvents such as hydrazine hydrate [N$_2$H$_4$·4H$_2$O], ethanol [C$_2$H$_5$OH] and ethylene diamine [C$_2$H$_4$(NH$_2$)$_2$] were purchased from Merck (India) and Spectrochem Pvt. Ltd (India).

### 2.2. Synthesis Procedure

The synthesis was done by the previously reported hydrothermal methods [3]. In briefly, Synthesis of Zn-Co-Se nanoalloy, 2 mmol of cobalt acetate and 1 mmol of zinc acetate were dissolved in 30-35 ml deionized water. The solution was stirred for 10-15 min, and after that 4 mmol (0.31584 g) of selenium powder which was dissolved in 10-12 ml hydrazine hydrate and stirred for overnight in air atmosphere was added to the metal salt solution to form black solution followed by vigorous stirring for 15 min. After that, two milliliters of ethylene-diamine was added to the mixture. Finally obtained mixture was transferred into the 50 mL Teflon-lined autoclave. The autoclave was perfectly sealed and placed in oven at 200°C for 12 h. The resulting product was centrifuged at 9000 rpm, washed more time to get pure product with distilled water then washed ethanol followed by drying at 50°C for 6 h to obtained solid product was stored for characterization and further electrochemical studies. Again, Zn-Co-Te nanoalloy were synthesized in a same manner tellurium powder was used instead of selenium powder.

## 3. Characterization

### 3.1. FE-SEM analysis

The morphological study of prepared materials was done by Field emission scanning electron microscope (FESEM, Zeiss model Supra 55) analysis and FESEM images of the synthesized nanomaterials are shown in the Figure 1 and Figure 2. The FESEM images of Zn-Co-Te nanoalloy are shown in Figure 1 and Figure 2 for Zn-Co-Se nanoalloy. From the Figure 1, it is clearly seen that Zn-Co-Te nanoalloy have nanorod type shape and Zn-Co-Se don’t have perfect shape.
3.2. XRD-analysis

X-ray diffraction (XRD) analysis was used as a primary characterization tool. XRD analysis gives the information about crystallinity of the prepared catalysts, identification and quantification of their crystalline phases. X-ray diffraction pattern of the synthesized nanoalloys are shown in Figure 3. All XRD peaks of Zn-Co-Te nanoalloy corresponds to CoTe$_2$ and ZnTe was confirmed from the standard JCPDS Card No-89-1258, 80-0022, 01-0582, 74-0225, 19-1482 and 80-0009. All the Zn-Co-Se nanoalloy XRD peaks corresponds to CoSe$_2$ and ZnSe was confirmed from the JCPDS Card No-88-
1718 and 80-0021. All the peaks are gives corresponding to the particular planes, these are shown in the Figure 3. Therefore our materials were successfully synthesized, which was confirmed by XRD.

Figure 3: XRD spectra of (A) Zn-Co-Te and (B) Zn-Co-Se.

4. Electrochemical Measurement
Electrochemical measurement were performed on the CH instrument using three electrodes system. Where three electrodes are as follows saturated Ag/AgCl, Pt wire and pencil graphite (PGE, 0.7mm diameter) were taken as a reference electrode, counter electrode and working electrode respectively. Before used to pencil graphite electrode first carefully washed with 6 (N) HNO₃ and deionized water to remove the surface impurity if present in the pencil graphite electrode (PGE) followed by clean by the cotton to dry the pencil graphite electrode. The prepared catalysts were dispersed in DMSO with proper weight (1.3 mg/0.5 ml, 2.7 mg/0.5 ml, 4.0 mg/0.5 ml and 7.1 mg/0.5 ml). 80 µl dispersion solution of catalyst was drop into the small portion of the PGE (Actually 0.4 cm length) by a micro tip for electrochemical study. For the measurement of electroactive surface area & roughness factors, cyclic voltammetry (CV) analysis was performed with the range of potential was -1.2 to 1.2 V where the three electrodes were dipped in to the mixture of 1.0 (M) KCl solution and 0.1 (M) K₄[Fe(CN)₆].3H₂O, basically ferrocyanide used as an electroactive probe molecule. For the measurements of OER, we were recorded CV and linear sweep voltammetry (LSV) with the range of potential 0.0 to 2.0 V vs Ag/AgCl. Initially, the parameters such as electrolyte concentration, scan rate and loading amount were optimized for OER.

4.1. Electroactive Surface Area Study
The necessary criteria for a good catalyst possess high surface area and low roughness factor. The measurement of electroactive surface area and also roughness factor was recorded by cyclic voltammetry (CV). For this analysis (CV analysis), the three electrodes were immersed in 1.0 (M) KCl solution used as electrolyte and taking 0.1 (M) K₄[Fe(CN)₆] as a electrolytic probe molecule were taken in 10 ml breaker and CV was recorded with the range of potential range -1.2 to 1.2 V with different scan rate, the obtained results were shown in the Figure 4. In Figure 4, A & B are CV of Zn-Co-Te and Zn-Co-Se respectively with different scan rate, with increasing scan rate current also increases and C are CV of both the synthesized materials with scan rate 2 mV/s.
With the help of the most popular equation Randless-Sevick equation, we can calculate the value of electroactive surface area (A) and also roughness factor (Rf) of the electrode materials[15]. The equation is given below:

\[ I_p = (2.687 \times 10^5)n^{3/2}D^1v^{1/2}C_0^1A \]  

Where, each term has their usual significance I correspond to current, D correspond to diffusion coefficient \((D = 0.76 \times 10^{-5})\), A correspond to electroactive surface area, v correspond to scan rate, n correspond to number of electron transferred & \(C_0\) correspond to concentration of ferrocyanide.

The roughness factor (Rf) of the pencil graphite electrode (PGE) was also calculated from the given equation

\[ Rf = A/A_{geom} \]  

Where, A correspond to electroactive surface area, it can be calculated by Randless-Sevick equation of the PGE containing materials and \(A_{geom}\) is the geometrical surface area of the electrode. The values of A and Rf are calculated from the above two equations, these are shown in the table 1.
Table 1: Comparison of electroactive surface area (A) and roughness factor (Rf) of both catalysts.

| Catalyst            | Current (I) (µA) | Geometrical surface area (A_G) (cm²) | Electroactive surface area (A) (cm²) | Roughness factor (Rf) |
|---------------------|------------------|-------------------------------------|-------------------------------------|----------------------|
| Zn-Co-Te nanoalloy  | 268.914          | 0.126                               | 0.18622                             | 1.47                 |
| Zn-Co-Se nanoalloy  | 257.851          | 0.126                               | 0.17856                             | 1.41                 |

4.2. Optimization of analytical parameters

Initially the analytical parameters such as electrolyte concentration, scan rate and loading mass on the pencil graphite electrode were optimized for OER. At first, optimizing the electrolyte concentration, the concentrations (0.01 M, 0.1 M and 1.0 to 6.0 M) of potassium hydroxide solution were prepared. The electrochemical cell was set up with three electrodes and LSV were performed with the range of potential 0.0 V to 2.0 V. The electrolyte optimization was shown in the Figure 5. It was observed that 5.0 (M) KOH offered the low onset potential with high current density than others concentration. Therefore 5.0 (M) KOH was the optimized electrolyte and these electrolyte concentration was used for further OER analysis.

Similarly, the scan rate was also optimized in same manner. LSV was recorded with different scan rate (100, 10, 5 and 2 mV/s) in 5.0 (M) KOH as an electrolyte (optimized electrolyte) with the range of potential 0.0 V to 2.0 V. It was found that scan rate 2 mV/s offered low onset potential with high current density (shown in the Figure 5). So the optimized scan rate was 2 mV/s and these scan rate was used for further OER study.

Lastly, mass loading was also optimized in the same way, LSV was recorded with different amount of mass loading (0.416 mg, 0.864 mg, 1.280 mg and 2.272 mg). It was observed that modified electrode with mass loading 1.280 mg offered low onset potential with high current density (shown in the Figure 5). Therefore optimized parameters were 5.0 M KOH, scan rate (2 mV/s) and mass loading (1.280 mg), these can be used for further OER study. All the potential values were report in this article with respect to reversible hydrogen electrode (RHE), so the potential with respect RHE was done using following equation:

$$E_{\text{RHE}} = E_{Ag/AgCl} + 0.059 \times pH + E^0_{Ag/AgCl}$$  (3)
4.3. Electrocatalytic Behavior for OER

The electrocatalytic activity of OER was determined by recorded CV and LSV with three electrode system. CV and LSV was taken at the scan rate 2 mV/s, 5.0 (M) KOH as electrolyte and 1.280 mg mass loading with the potential range 0.91 to 3.3 V vs. RHE for Zn-Co-Te and Zn-Co-Se nanoalloys were shown in the Figure 6. We were found that Zn-Co-Te shows low onset potential (1.39 V) and high current density (1.44 Acm$^{-2}$ at potential 2.91 V vs. RHE) than Zn-Co-Se (onset potential=1.78 V and current density = 0.816 Acm$^{-2}$ at potential 2.91 V), this is because the Zn-Co-Te compounds have perfect nanorod shape which facilitate the oxygen evolution reaction and on the other hand, Zn-Co-Se donot have perfect shape.

Tafel plot plays very significant role towards OER, which indicates the kinetic pathway, good catalysts have low tafel slope value. A good catalyst always have low Tafel slope value, lower the Tafel slope value higher the catalytic performance for OER. Tafel plot can be obtained from the following equation, by plotting $\eta$ vs. log($j$). equation are shown below:

$$\eta = a + \frac{2.3RT}{\alpha n F} \log(j)$$

Where the each terms have their own significance role, $\eta$ correspond to overpotential (mV), $j$ correspond to current density (mAcm$^{-2}$) and $\frac{2.3RT}{\alpha n F}$ correspond to the Tafel slope (mV/dec). The overpotential can be obtained by following equation:

$$\eta = E_{RHE} - 1.23$$

Figure 5: Optimization of analytical parameters: LSV (A) Different concentration of electrolyte (KOH), (B) Different scan rate and (C) Different mass loading of Zn-Co-Te.
Tafel slope of the catalyst Zn-Co-Te was found to be 91 mV/dec and for Zn-Co-Se was found to be 135.9 mV/dec (Shown in the figure 6). Therefore, Zn-Co-Te nanoalloy have lower Tafel slope than selenium nanoalloy (Zn-Co-Se) which suggest that Zn-Co-Te nanoalloy have better electrocatalyst towards OER than Zn-Co-Se.

![Graph showing Tafel slope comparison between Zn-Co-Te and Zn-Co-Se](image)

Figure 6: OER plot (A) LSV, (B) CV and (C) Tafel Plot.

4.4. Stability Study

Although the synthesized Zn-Co-Te nanoalloys offered excellent electrocatalytic activity but stability of the compounds plays very important role to enhance the cost effective catalysts for water splitting. The stability was first checked by cyclic voltammetry (CV) study. No significant change was observed for repeated cycles of cyclic voltammetry (1st, 100th, 500th and 1000th cycles), which was shown in the Figure 7. Onset potential remains same for repeated cycles of CV and very small or minute current density changes were observed. Therefore we can say that our synthesized catalysts have high stability. Zn-Co-Te were very much stable within 3 months without altering the onset potential and also no significant current density changes were observed, which is shown in the Figure 7. These catalysts offered exactly same onset potential value as well as current density value before and after all electrochemical studies, shown in figure 7.
5. Conclusion
In this work, we were successfully synthesized by one spot simple hydrothermal method and characterized by different techniques like FE-SEM and XRD. Zn-Co-Te nanoalloy shows very good electrocatalytic activity towards OER in alkali medium. The Zn-Co-Te nanoalloy shows onset potential 1.39 V and current density 1.44 Acm$^{-2}$ at potential 2.91 V with over potential 221 mV at 10 mAcm$^{-2}$ current density with Tafel slope 91 mV/dec, but for Zn-Co-Se shows higher onset potential 1.785 V and current density 0.817 Acm$^{-2}$ at potential 2.91 V and overpotential 560 mV at 10 mAcm$^{-2}$ with Tafel slope 135.9 mV/dec and also shows high stability for several months and unchanged behavior of the catalyst, after the whole electrochemical study, which is very much important for a good catalyst.

6. References
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