Indian Journal of Pure & Applied Physics
Vol. 62, August 2024, pp. 712-717
DOI: 10.56042/ijpap.v62i8.7467

Electrocatalytic Performance of NiSe Nanoparticles Doped ZIF-67 Derived Electrocatalyst for Hydrogen Evolution Reaction

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Received 25 December 2023; accepted 25 January 2024

Herein we report an electrocatalyst for hydrogen evolution reaction (HER) by using cobalt-based zeolite imidazolate framework (ZIF67) as a synthesized precursor, along with its composites using Ni and Se nanoparticles. The morphology and structure of the samples were studied by using FESEM analysis, XRD diffraction method, IR spectra, and BET analysis. The final composite with Ni and Se doped ZIF 67 shows an over potential of 114 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 46 mV dec^{-1} compared to that of commercial Pt/C catalyst. The metal-metal interaction on the ZIF 67 frame work were found to serve as an active site. The co-doping producing a synergetic effect helps in enhancing the activity of the optimized catalyst.

Keywords: ZIF 67; Over-potential; Tafel-slope; Electrochemical Active Surface Area (ECSA)

1 Introduction

Sustainable and environment friendly energy production has become an important concern to the present world. In the past years significant efforts in research and administration have been undergone to develop green energy using solar, wind, hydrogen and biomass[1]. Among them, Hydrogen with highest energy density (142 MJ kg^{-1}) has been considered as a promising and best sustained energy source for the future. Hence Hydrogen is best for its accountability, production possibilities and as energy carrier can replace the fossil fuels thus providing an eco-friendly, clean and green technology. Hydrogen also plays important role as chemical raw material in industry such as ammonia synthesis and also in petrochemical Industries[2]. Out of many other routs to produce Hydrogen, water splitting has been regarded as the promising and efficient way to produce sustainable green Hydrogen in the area of renewable energy. This method produces hydrogen in a sustainable way where the electrolysis produces oxygen at the anode (Oxygen evolution Reaction) and Hydrogen at the cathode (Hydrogen Evolution Reaction). Oxygen at Anode is evolved along with protons and electrons where as hydrogen gets evolved using the recombination of these protons and electrons. Conventional water electrolysis is either carried out in an acidic medium or a basic medium with following respective mechanism[3].

So far, Platinum(Pt) and noble metal group metals are considered as the best electrocatalyst for HER. For *e.g.* Peng *et al.,* group have derived single atom Ru doped Mxene as a highly efficient trifunctional catalyst with the overpotential of 70 mV against HER. According to the report isolated Ru sites effectively enhances the adsorption of descriptors[4]. Wu et.al reported a low Pt content doped NiCu a hollow interior as a highly efficient HER electrocatalyst[5]. Similarly, Li *et al*., employed multi Nano particle strategy by using Pt based metal nanospheres to lower the overpotential, and achieved the ultralow onset potential of 18 mV and high mass activity. Herein, they found that Cu atom lowers the d-band position which is favourable for hydronium adsorption[6]. However, the practical applications are limited due to their “rare earth” status[4]. Hence, it is required to develop the cost effective and efficient electrocatalyst. Researches are now putting effort in developing reasonable non-noble catalyst for HER, which can match with the activity of Pt and noble metal-based catalyst. In last decade, several transition metal based catalyst have been reported which provided intact good activity and has all characteristics as well as stability to match with noble catalysts[7]. At present, tremendous breakthroughs have been put in the field of synthesis as well as design of efficient catalysts for HER[8].

Herein in this paper, development of some electrocatalysts mainly based on composites

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synthesised from ZIF 67 for efficient hydrogen evolution reaction by water splitting will be discussed in detail. Among the transition metal, Cobalt(Co) and Nickel(NI) are so far known to be one of best for its catalytic activity towards hydrogen evolution. It has been reported that a strong coupling between these two transition metals boos the position of *d*-orbital and adsorbate valance state which could lower the required over potential, further enhancing the activity of the catalyst[7]. Adding to this, Selenium (Se) a chalcogen element with lower electron affinity attracts more descriptors and promotes the HER activity[9]. In addition, the strong metallic nature of Se provided the better conductivity and the mass transfer rate of the catalyst[10]. Hence here we have synthesised composites with Se and Ni from ZIF 67 MOF as Co source.

2 Material and Methods

Cobalt nitrate hexahydrate and Nickel nitrate hexahydrate were purchased from LOBA CHEMIE pvt. Ltd. Mumbai, India, along with 2-methyl imidazole which was purchased from SPECTROCHEM, Mumbai, India were used to prepare ZIF 67 and its derivatives. Sulphuric acid (98%), KOH, methanol, acetone, and ethanol were also purchased from S.D. Fine Chemicals Ltd., Mumbai, India. Selenium powder was obtained from ALFA AESAR Ltd. Nafion solution (5%) was purchased from SIGMAALDRICH Pvt. Ltd. 20% platinum carbonpt/C-Duralyst Energy Pvt. Ltd. Deionised (DI) water was obtained from Millipore water system (ICT, Mumbai). All chemicals used were of analytical grade. All solutions were prepared using deionized water or methanol.

2.1 Synthesis of ZIF 67

ZIF 67 was Synthesized using Cobalt nitrate hexahydrate ($Co(NO3)2·6H2O$) and 2 methyl imidazole (2-MeIm). Solution A was prepared using 2.9g of cobalt nitrate in 100ml methanol and is stirred using a magnetic stirrer for 15 mins. Solution B was prepared using 6.5g of 2-MeIm in 100ml methanol and stirred for 15 mins. Later solution B was added to solution A under vigorous stirring to form a navy-blue solution C. The solution C is then kept for stirring for 12 h and thereby keeping under room temperature to settle down for about 12 h. Decantation of the top solution is then done so that purple precipitate is well collected and further centrifuged. Washing of the precipitate is done using methanol for 3 times and DI water followed by drying the sample at 60 °C to form ZIF 67 powder[11].

2.2 Synthesis of Cobalt enriched N doped Carbon (Co/NDC_{800})

For the synthesis of Co/PC, 700g of the prepared ZIF was dispersed into a ceramic/quartz boat and were evenly spread. Pyrolysis of the same is done at 800 °C with the heating rate of 3 °C/min for 2 h under Ar atmosphere to fabricate Cobalt N enriched porous carbon (Co/NDC_{800}).

2.3 Synthesis of Selenium, Nickel co-doped Cobalt enriched N doped Carbon ($Ni,Se-Co/NDC_{800}$)

Ni doped Selenised Cobalt on N enriched porous carbon is synthesised using ZIF 67, Ni $(NO3)2·6H2O$ and Se powder.(Ni, Se-Co/NDC800)/NDC was fabricated by using ZIF-67 as precursor via a facile ex-situ mixing and pyrolysis process as shown in Fig. 1. 200 mg of ZIF-67 doped with Ni as mentioned above in 3.4.3 was dispersed into motor pastor containing 400 mg of Se Powder and is vigorously mixed such that the composition is even. The powder was obtained by pyrolsis under 800 °C with the heating rate of 3 °C/min for 2 h under Ar atmosphere to fabricate Nickel doped selenised cobalt on N enriched porous carbon ($Ni,Se-Co/NDC_{800}$).

2.4 Materials Characterization

The crystal structure of the as-prepared catalyst was studied using the Rikagu ultima IV machine with the Cu Kα as the monochromatic source of radiation of a wavelength of 0.154 nm. The data were collected with a 2θ value ranging from 10° to 70° with a scan rate of 2° per minute. The morphology and elemental composition were investigated using Field emission Scanning electron microscopy (FE-SEM) by JFEI company-made Nova Nano SEM-450, equipped with Energy Dispersive Spectroscopy (EDS) and elemental mapping. The scanning was performed at 10 kV and 10 mm working distance. To quantify the Brunauer–Emmett–Teller (BET) surface area and pore size of material, N_2 sorption isotherm was measured by

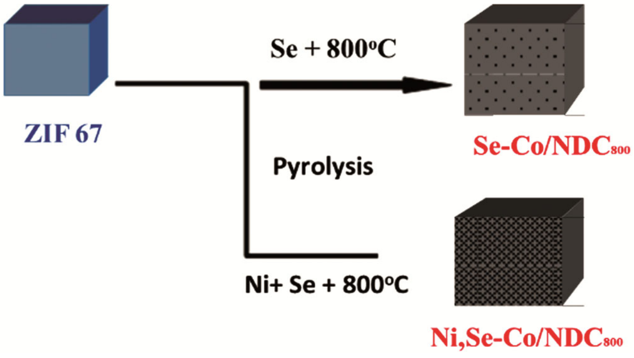

Fig 1 — Schematic representation of the electrocatalysts prepared using Metrohm BELSORP miniX instrument at 77 K with N_2 as adsorptive gas. Before N_2 sorption measurement, samples were degassed at 220 ºC for 6 hr to remove the moisture in the samples. The pore size and surface area of the catalyst were obtained by using the BET and Quenched Solid Density Functional Theory (QSDFT) method. The conductivity of the as-obtained catalyst was calculated by using the four-probe method. All the electro-chemical measurements were carried out in µ-auto lab potentiostat/galvanostat (PGSTAT) with Metrohm 663VA stand controlled by software NOVA 1.9 in three electrode cell system.

For the purpose of electrochemical activity three electrode setup was used and the electrode was prepared by using following method. Rotating GCE was cleaned with alumina slurry in DI and further rinsed with DI water. 3µl of slurry made (1 mg/ml of a sample) was drop casted on clean GCE using a micropipette. Nafion added in a suspension acts as a binder. Prepared electrode was then dried properly for getting evenly coated thin film of the catalyst material. This serves as the working electrode to examine the HER activity.

3 Results and Discussion

3.1 Structural and Morphological Study

Figure 2(a & b). represents the XRD patterns of synthesised ZIF 67 and that of carbonized ZIF 67 (Co/NDC800). The pattern of ZIF 67 were compared with that of the XRD data in literature. ZIF 67 showed prominent reflections at 2θ = 7.4°, 10.4°, 12.7°, 14.8°, 16.5°, 18.0°, 22.1°, 24.5°, 25.5°, 26.7°, 29.5°, 30.6°, 31.6° and 32.5° which correspond to (011), (002), (112), (022), (013), (222), (114), (233), (224), (134), (044), (334), (244) and (235) planes respectively[11]. The XRD pattern for Co/NDC800 illustrates two phases of cobalt coexist namely in FCC and HCP of which FCC stays as the dominant phase. The peaks observed at 2θ values of 44.35° and 75.95° correspond to (111) and (220) planes stands as the FCC phase planes of metallic cobalt along with the characteristic peak of graphitic carbon at (002) (JCPDS 15-0806). The XRD pattern of (Fig. 2c) Ni-Co/NDC800 shares a somewhat identical pattern as that of Co/NDC800 apart from the peaks being more intense. Similarly, the XRD patterns of Se-Co/NDC800 obtaining all the characteristic peaks of Co and Se at 33.3°, 44.91°, 50.57, 61.94°, and 69.94° (JCPDS no. 43-1477)[12]. The peaks are found to be intense and no

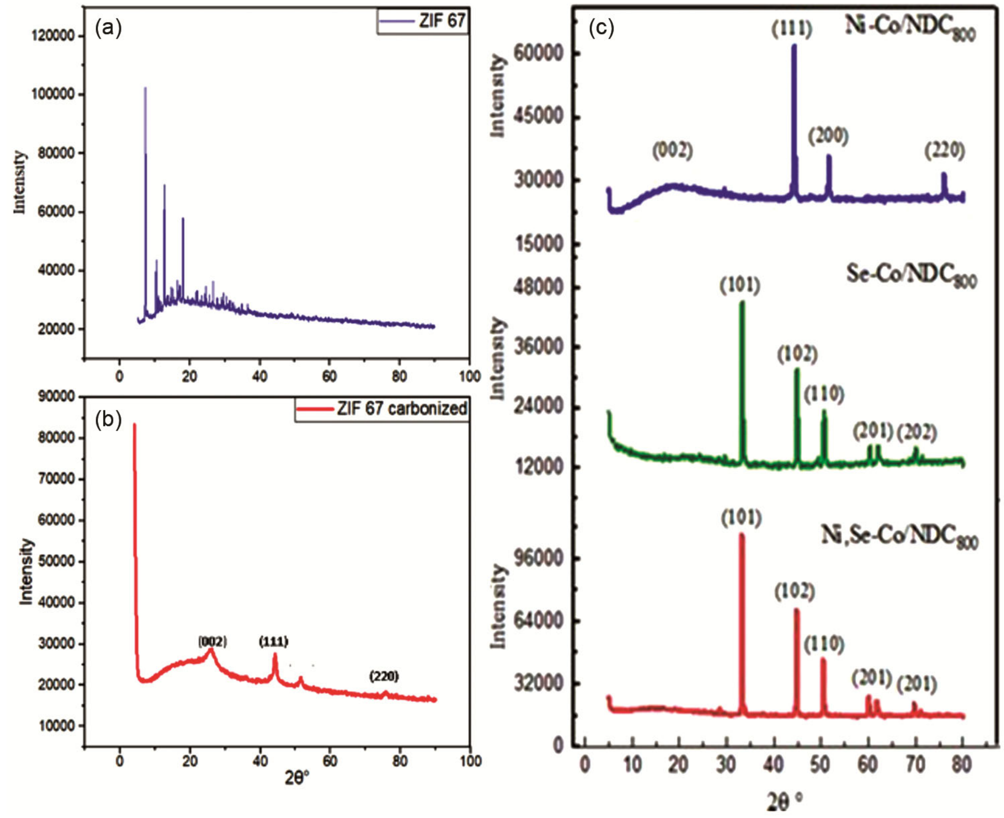

Fig. 2 — XRD analysis of (a) ZIF 67 (b) Carbonised ZIF 67 (Co-NDC800) (c) as-synthesized doped catalyst

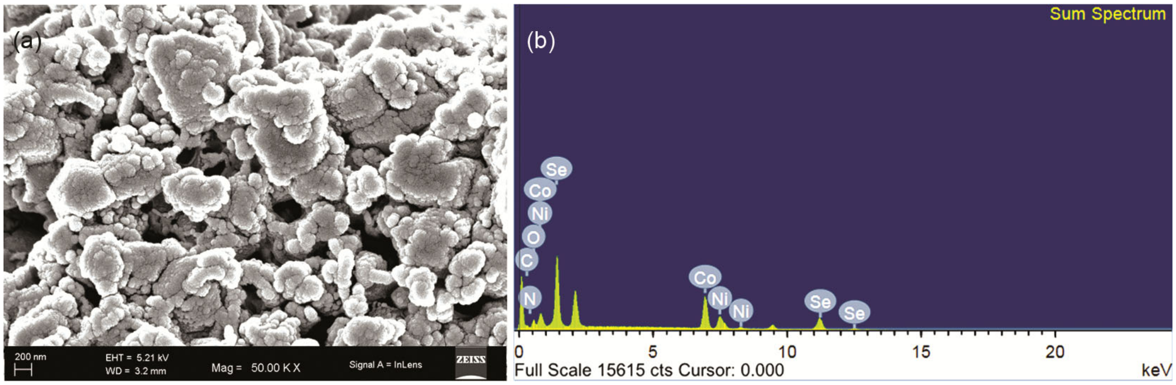

Fig. 3 — (a) FE-SEM analysis of Ni, Se-Co/NDC800 (b) EDS analysis

other extra data was observed suggesting that the material is of high crystalline nature and purity[13]. The XRD patterns of Ni, Se-Co/NDC800 where the peaks of Se, Co were exactly observed confirming its crystalline nature with long range ordering[14].

Figure 3 shows the typical morphology of the optimized catalyst that was analysed by using FESEM study. The image clearly shows that post Ni and Se nanoparticles doping on ZIF polyhedron, the morphology of the catalyst changes, and forms the dispersed/ destructed shape. Such a dispersed structure enables adsorption of more hydronium ion at active sites and promotes HER activity. Further EDS analysis confirms the presence of Co, Se, Ni, N, C and O, hence the purity of the material.

3.2 Optical Properties

FTIR analysis were obtained in order to understand the functional groups present in the samples. As illustrated in Fig. 4, the transmission peak obtained at 3270-3300 cm^{-1} suggests the N-H stretching mode along with the O-H stretching mode. The transmittance peak at 2929.13 cm^{-1} could be associated with the C-H stretching which confirms the presence of carbon in the sample. A Transmittance peak of O=C=O was observed at 2360 cm^{-1}. 1643.90 cm^{-1} shows a peak corresponding to C=C stretching. C-H bending vibration peak is obtained at 1416.31 cm^{-1}. An Intense peak of C-O stretch is obtained at 1033 cm^{-1}. Further, the transmittance of C-H, C-CH$_3$, and other were obtained in the fingerprint region. This confirms the presence of carbon in the sample and also produces a qualitative analysis of the functional groups present in the material[15]. The performed spectra confirm that despite the composition of doping, the spectra remain same, illustrating the optimum amount metal species do not affect the functionality of ZIF 67 but act as a catalyst active site to boost the performance of the material.

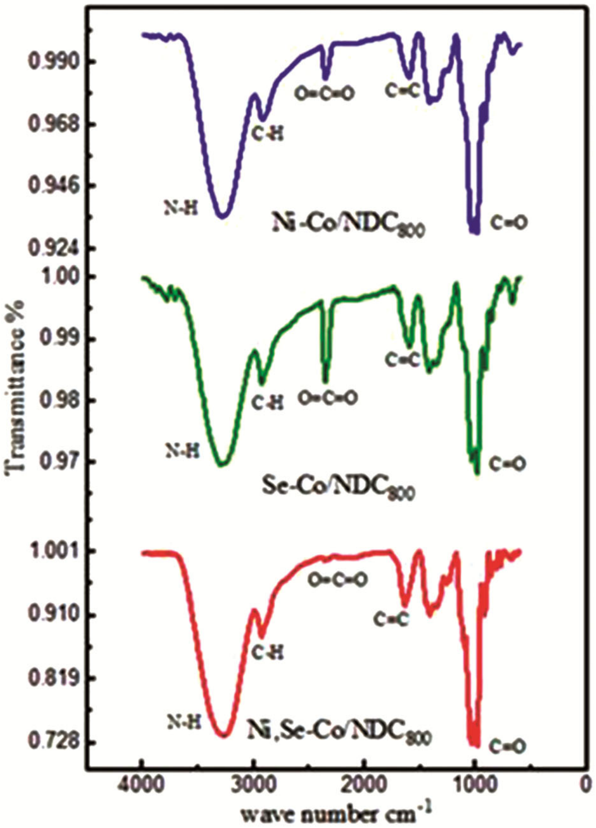

Fig. 4 — FTIR analysis of the samples

3.3 Electrochemical Study

The HER activity of all the synthesized samples was examined by using an electrochemical workstation under a three-electrode system. Fig. 5(a) provides linear sweep voltametry (LSV) obtained for all the samples which were analysed in order to understand the intrinsic HER activity of as synthesized catalyst. The overpotential obtained at 10 mA/cm^2 was found in the order of ZIF67< Se powder< Co/NDC800<Ni-Co/NDC800 < Ni, Se- Co/NDC800 which is 521 < 490 < 260 < 221 < 187 mV respectively. The obtained

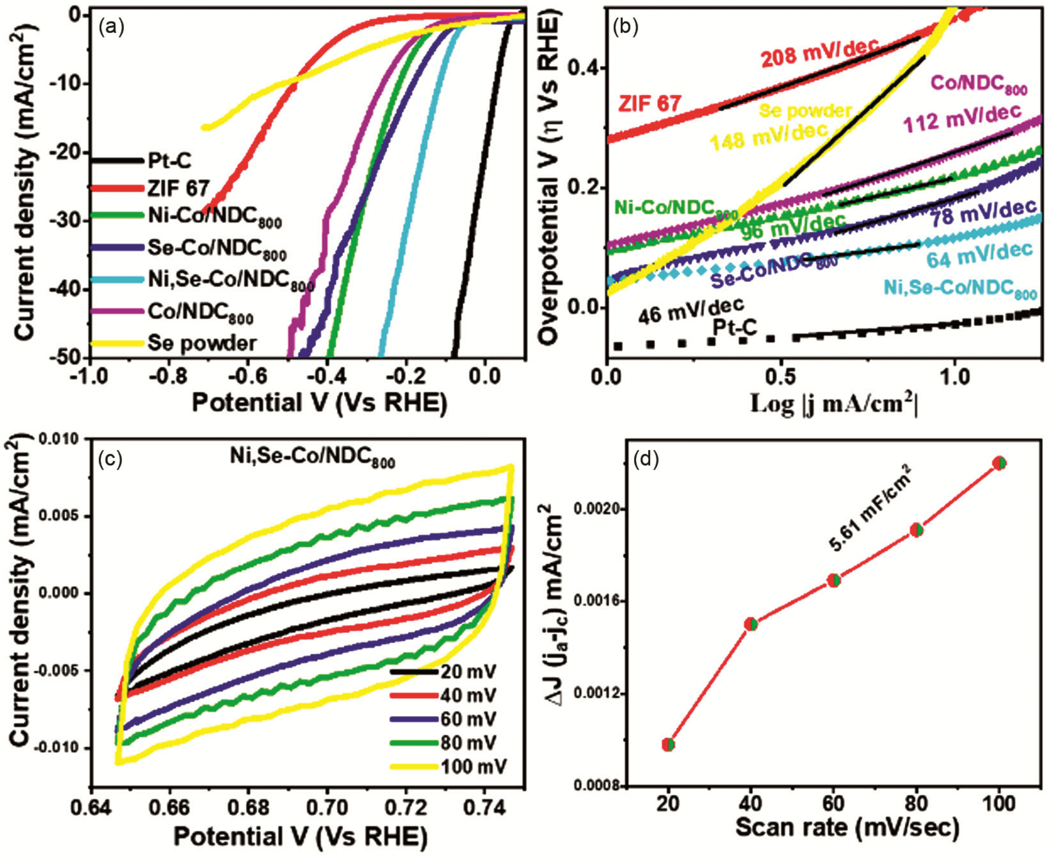

Fig. 5 — Electrochemical measurements of HER in 0.5 M H_2SO_4 electrolyte. (a) LSV curves of six samples with the current density normalized by the geometric area of the electrode at the scan rate of 10 mV s^{-1} (b) Tafel slopes (c) CV curves of Samples in the region of 0.64V-0.74V *vs* RHE (0.3 to 0.4V, non-faradaic region) at Scan rates 20,40,60,80,100 mV/s (d) along with the Linear plot of Capacitive current density *vs* Scan rate of the Samples. (a) Ni, Se-Co/NDC800

values illustrate higher catalytic activity for Ni and Se co-doped materials. This might be due to the synergistic effect of the metal-metal interaction[16]. This was further confirmed by using Tafel analysis (Fig. 5(b)), to determine the rate of reaction. The Tafel values obtained for the as-synthesized catalyst are found in the order of ZIF67< Se powder< Co/NDC800<Ni-Co/NDC800 < Ni, Se- Co/NDC800 which are 208< 148< 112< 96< 78< 64< 46 mV/dec respectively. This indicates the Volmer-Heyrovsky mechanism of hydrogen evolution ($H^* + H^+ + e^{-n} = H_2$). Whereas, pristine catalyst shows a sluggish Volmer mechanism ($H^+ + e^{-n} = H^*$) which is a rate-determining step[17]. The intrinsic catalytic activity *i.e.* double layer capacitance was calculated obtaining CV in the non-faradic region at different scan rates. The electrochemically active surface area is estimated using the electrical double-layer capacitance value along with the roughness factor. As shown in Fig. 5(c), in the Non-faradaic region selected, the current response will only be associated with the double layer charging, thus able to calculate this double layer capacitance as the slope of linear fits the plots of particular current density in the non-faradaic region against the scan rates. In the Fig. 5(c), CV curves of sample Ni, Se-Co/NDC800 was efficiently obtained and analysed to obtain the linear plot and thereby the Cdl with value 5.6 mF (Fig. 5(d)).

Further ECSA of the working electrode was mathematically calculated using the formula,

$$ECSA = C_{dl}/40\ \mu F\ cm^{-2} \qquad ...(1)$$

Thus, an ECSA of $140cm^{-2}$ was obtained for Ni, Se-Co/NDC800. The roughness factor was calculated to further confirm the intrinsic catalytic activity of the optimized catalyst, which denotes the effective ECSA per unit area of electrode accessible for catalytic activity. The ratio of C_{dl} with the 40 $\mu F\ cm^{-2}$ gives the ECSA of the studied samples. Here the roughness (which can be obtained by reciprocal of ECSA) of Ni, Se-Co/NDC800 was calculated to be 713. This denotes that the material Ni, Se-Co/NDC800 has better

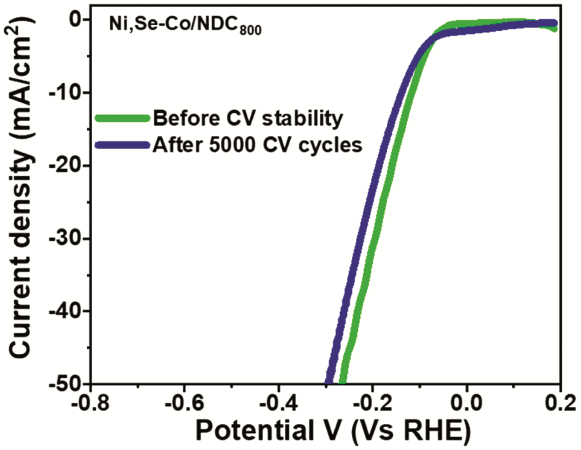

Fig. 6 — LSV analysis of Ni,Se-Co/NDC800 before and after 1000 CV cycles in scan rate of 100mV/s

electrochemical surface area accessible compared to that of near best catalyst which highly substantiates the enhanced reason for its better activity.

The optimized catalyst Ni, Se-Co/NDC800 was subjected to a stability test by degrading under 5000 CV cycles under 100 mV/s scan rate (Fig. 6). LSV analysis of the sample was obtained before as well as after the 5000 CV cycles in acidic media. The sample showed good stability towards HER after 5000 cycles giving an overpotential of 138 mV at 10 mA cm^{-2}. The shift in over potential was only 24 mV corresponding to that of the raw LSV analysis before CV cycles. This shift was attributed to the degradation of the catalyst due to the CV cycles. This showed that the material exhibits the enhanced stability towards HER reaction in acidic media.

4 Conclusion

In summary, the synthesis of Selenium, Nickel co-doped Cobalt enriched N doped Carbon (Ni,Se-Co/NDC800) has been derived by using ZIF 67 as a synthesized precursor for Hydrogen evolution reaction. Crystalline nature of the material was confirmed by the XRD analysis with Functional group studies from IR spectra. Compared to that of commercial Pt/C catalyst, which has an over potential of about 48 mV at current density 10 mA cm^{-2}, Ni, Se-Co/NDC800 produced an over potential of 114 mV at the current density 10 mA cm^{-2} which shared a decent activity towards HER compared to that of other low-cost metal-based catalyst. Reduction of over potential was attributed to the synergistic effect shared by Ni, Se and Cow here all the three collectively stands as the active sites for the Hydrogen adsorption.

Acknowledgment

This research work was sponsored by the Department of science and technology (DST/ TMD/HCF/2K18/130) and Mahatma Jyotiba Phule research programme. We would like to thank IIT Bombay and IIT Mandi SAIF department for carrying out sample analysis.

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