# **Supporting Information**

# Enhancement of HER kinetics with RhNiFe for high rate water electrolysis

Kannimuthu Karthick <sup>†,‡</sup>, Abdul Bashith Mansoor Basha <sup>1,‡</sup>, Abinaya Sivakumaran <sup>1,‡</sup> and

# Subrata Kundu<sup>†‡</sup>\*

<sup>†</sup>Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Electrochemical Research Institute (CSIR-CECRI) Campus, New Delhi, India.

<sup>1</sup>Centre for Education (CFE), CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamil Nadu, India.

<sup>‡</sup>Materials Electrochemistry Laboratory for Energy, Environment and Catalysis, CSIR-Central

Electrochemical Research Institute (CECRI), Karaikudi-630003, Tamil Nadu, India

*E-mail: skundu@cecri.res.in* and *kundu.subrata@gmail.com*.

This file contains 28 pages in which the details of reagents, electrochemical characterizations, methods of synthesis, electrochemical results, characterizations like SEM, FE-SEM and post OER and post HER SEM, FE-SEM, HR-TEM and XPS results are provided.

#### **Reagents and Instruments**

Nickel nitrate  $(Ni(NO_3)_2)$ , Iron nitrate  $(Fe(NO_3)_2)$  were purchased from Sigma-Aldrich. Rhodium Chloride RhCl<sub>3</sub>.3H<sub>2</sub>O, Ammonium fluoride (NH<sub>4</sub>F) and urea were procured from Alfa-Aesar and used as received. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) was purchased from Merck and used as received. Ni foam was procured from Sigma-Aldrich and used after surface cleaning. The electrochemical analyzer CHI-6084c was used for all electrochemical characterizations. Hg/HgO reference electrode purchased from CH instruments and carbon cloth as counter electrode from Alfa- Aesar were used along with the Ni foam with materials grown as working electrode. DI water was used in the synthetic process of growing materials over Ni foam. The as prepared catalysts with different stoichiometric ratios were characterized with HR-TEM, (Tecnai<sup>TM</sup> G<sup>2</sup> TF20) working at an accelerating voltage of 200 kV and by Talos F-200-S with HAADF elemental mapping. Color mapping and Energy Dispersive X-ray Spectroscopy (EDS) analysis were carried out with the FESEM instrument with the images (SUPRA 55VP Carl zeiss) with a separate EDS detector connected to that instrument. Scanning Electron Microscopy (SEM) analysis was carried with a Hitachi, Japan make model S-3000H instrument having magnification 30X to 300 KX with the accelerating voltage  $\sim 0.3$  to 30 kV. The XRD analysis carried out with a scanning rate of 5° min<sup>-1</sup> in the  $2\theta$  range 10-90° using a Rigaku X-ray powder diffractometer (XRD) with Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.154$  nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using a Theta Probe AR-XPS system (Thermo Fisher Scientific, UK).

#### Synthesis of sheet like structures of NiFeCHH

To synthesize NiFeCHH, Ni(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>2</sub> were added to the 40 mL of solution containing 25 mL of H<sub>2</sub>O and 15 mL of ethanol. The weight of Ni(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>2</sub> were taken as 697.92 mg and 646.4 mg respectively to have (1:0.5) ratio of (Ni:Fe) whereas 697.92 mg and 969.6 mg have been taken to have (1:1) ratio of (Ni:Fe). To this solutions, NH<sub>4</sub>F (20 mg) and urea (242.4 mg) were added and stirred for 20 min. To this clear solutions, surface cleaned (by 3 M HCl solution to remove oxide surfaces) Ni foam pieces with the dimensions of  $4.5 \times 0.5$ were added and kept in 50 mL autoclave and kept in oven at a temperature of 120°C for the duration of 6 h. After this, the NiFeCHH grown Ni foams were taken and sonicated for 10 min to exclude the loosely bound molecules and the final loading calculated to be ~0.6-0.7 mg cm<sup>-2</sup>. The prepared NiFeCHH with different ratios of (1:0.5) and (1:1) were subjected for electrocatalytic studies. From the Electrochemical studies, Ni:Fe (1:0.5) have been found to be best catalyst and subjected for the Rh<sup>3+</sup> introduction.

## Synthesis of sheet like structures of Rh<sup>3+</sup>-NiFeCHH

To synthesize  $Rh^{3+}$ -NiFeCHH, Ni(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>2</sub> and RhCl<sub>3</sub>.3H<sub>2</sub>O were added to the 40 mL of solution containing 25 mL of H<sub>2</sub>O and 15 mL of ethanol. The weight of Ni(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>2</sub> were taken as 697.92 mg and 646.4 mg respectively to have (1:0.5) ratio of (Ni:Fe) and to this RhCl<sub>3</sub>.3H<sub>2</sub>O (210.6 mg) was taken and stirred. To this solutions, NH<sub>4</sub>F (20 mg) and urea (242.4 mg) were added and stirred further for 20 min. To this, surface cleaned (by 3 M HCl solution to remove oxide surfaces) Ni foam pieces with the dimensions of 4.5×0.5 were added and kept in 50 mL autoclave and kept in oven at a temperature of 120°C for the duration of 6 h. After this, the Rh<sup>3+</sup>-NiFeCHH (1:0.5) grown Ni foams were taken and sonicated for 10 min to exclude the loosely bound molecules and the final loading calculated to be ~0.6-0.65 mg cm<sup>-2</sup>. All the prepared NiFeCHH with different ratios of (1:0.5) and (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) were subjected for electrocatalytic studies in 1 M KOH.

## **Electrochemical Characterizations**

Electrocatalytic studies were done with the conventional three electrode cell where a carbon cloth counter electrode, Hg/HgO reference electrode is used with NiFeCHH modified working electrodes where  $1\times0.5$  cm<sup>2</sup> area of NiFeCHH grown Ni foam is dipped and studied for electrocatalytic water splitting. The polarization studies were carried out a slow scan rate of 2 mV/sec. 50% iR compensation was done manually from the R<sub>s</sub> from EIS. Potentiostatic analysis was carried out for 12 h for OER, HER and total water splitting (TWS) at overpotentials of 256 mV, -76 mV and 320 mV respectively. Continuous rapid sweeping through accelerated degradation (AD) studies at a very high sweep rate of 200 mVs<sup>-1</sup> for 500 cycles was carried out in 1 M KOH for both OER and HER. The electrochemical impedance spectroscopic (EIS) analysis was carried out in the frequency range of 1 Hz to 100 kHz with an amplitude potential of 344 mV for OER study and for TWS and with 50 mV overpotential for HER study. Faradaic efficiency was calculated by collecting O<sub>2</sub> gas from the cell and analyzed in gas chromatography. The current density of 30 mA cm<sup>-2</sup> was fixed and analyzed. The GC experiment was done using

GC-2014ATF 230V R to monitor O<sub>2</sub> evolution by chronoamperometry method for 30 min with time interval of 5 min. TOF is calculated from corresponding expression, TOF= $j \times N_A / F \times n \times \Gamma$  and  $\Gamma$  (surface concentration) is calculated from the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup>.



**Figure S1**: (a-e) are the SEM images of NiFeCHH (1:0.5) taken at different magnifications showing sheet like structure.



**Figure S2**: (a-e) are the SEM images of Rh<sup>3+</sup>-NiFeCHH (1:0.5) taken at different magnifications showing sheet like structure.



**Figure S3**: (a-d) are the FESEM images of NiFeCHH (1:0.5) taken at different magnifications showing sheet like structure.



**Figure S4**: (a-f) are the FESEM mapping results of NiFeCHH (1:0.5) for area, mix, Ni K, Fe K, C K and O K respectively.



**Figure S5**: (a-d) are the FESEM images of  $Rh^{3+}$ -NiFeCHH (1:0.5) taken at different magnifications showing sheet like structure.



**Figure S6**: (a-f) are the FESEM mapping results of Rh<sup>3+</sup>-NiFeCHH (1:0.5) for area, Ni K, Fe K, Rh L, C K and O K respectively.



**Figure S7**: (a-d) are the XPS high resolution spectra of Ni 2p, Fe 2p, O 1s and C 1s respectively for NiFeCHH (1:0.5).



**Figure S8**: (a and b) are the EIS spectra of Ni foam, NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) taken before and after the AD test in OER respectively.



**Figure S9**: (a-c) are the reduction area of Ni<sup>3+</sup>-Ni<sup>2+</sup> for NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) respectively.



**Figure S10**: (a and b) are the EIS spectra of Ni foam, NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) taken before and after the AD test in HER respectively.



**Figure S11:** (a-c) are the CVs recorded for NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) respectively in a non-faradaic region with increasing scan rate for the determination of ECSA from its double layer capacitance. (d) is the corresponding plots to the measure  $C_{dl}$ .



NiFeCHH (1:0.5) for OER

Figure S12: (a and b) are the error bars at different current densities for NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) for OER and overpotentials required respectively, (c and d) are the error bars at different current densities for NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh3+-NiFeCHH (1:0.5) for HER and overpotentials required respectively and (e) error bar for NiFeCHH (1:0.5) in OER at 50 mA cm<sup>-2</sup> under O<sub>2</sub> and N<sub>2</sub> atmosphere.



**Figure S13:** Calculation of faradaic efficiency from the  $O_2$  produced in electrolysis and theoretical calculation of  $O_2$  by gas chromatography study.



**Figure S14:** Long term stability study by keeping of NiFeCHH (1:0.5) anode and Rh<sup>3+</sup>-NiFeCHH (1:0.5) cathode for 60 h.



**Figure S15**: (a and b) are the post OER and post HER plots of NiFeCHH (1:0.5), NiFeCHH (1:1) and Rh<sup>3+</sup>-NiFeCHH (1:0.5) respectively.



**Figure S16**: (a-c) are the post OER SEM images of NiFeCHH (1:0.5) and (d-f) are the post HER SEM images of Rh<sup>3+</sup>-NiFeCHH (1:0.5) respectively.



**Figure S17**: (a-d) are the post OER FESEM images of NiFeCHH (1:0.5) showing the retention in sheet like structure.



**Figure S18**: (a-f) are the post OER FESEM mapping results of NiFeCHH (1:0.5) for area, mix, Ni K, Fe K, C K and O K respectively.



**Figure S19**: (a-d) are the post HER FESEM images of Rh<sup>3+</sup>-NiFeCHH (1:0.5) showing the retention in sheet like structure.



**Figure S20**: (a-f) are the post HER FESEM mapping results of Rh<sup>3+</sup>- NiFeCHH (1:0.5) for area, Ni K, Fe K, Rh L, O K and C K respectively.



**Figure S21**: (a-d) are the post OER low and high magnified HR-TEM micrographs of NiFeCHH (1:0.5), (e) is the corresponding fine lattice fringes at higher magnification and (f) is the corresponding SAED pattern of NiFeCHH (1:0.5).



**Figure S22**: (a) is the post OER HAADF image of NiFeCHH (1:0.5) taken for mapping and (b-f) are the characteristic mapping results of mix, Ni K, Fe K, C K and O K shells respectively.



**Figure S23**: (a-d) are the post HER low and high magnified HR-TEM micrographs of  $Rh^{3+}$ -NiFeCHH (1:0.5), (e) is the corresponding fine lattice fringes at higher magnification and (f) is the corresponding SAED pattern of  $Rh^{3+}$ -NiFeCHH (1:0.5).



**Figure S24**: (a-d) are the post OER XPS high resolution spectra of Ni 2p, Fe 2p, O 1s and C 1s respectively for NiFeCHH (1:0.5).

Video Clip showing the two electrode set up	MP4 file
NiFeCHH (1:0.5) anode and Rh <sup>3+</sup> -NiFeCHH	two electrode set
(1:0.5) cathode	up.mp4

Figure S25: Video clip file showing the two electrode system for total water splitting.