

-Electronic Supplementary Information (ESI)-

Extending the accessibility of catalytic active sites through L-cysteine assisted sulphidation for promoting hydrogen evolution reaction

Prince J.J. Sagayaraj,^a Kavinkumar. S,^a Oyama,^b Naoko Okibe,^b Hyoungh-il Kim ^{c*} and Karthikeyan Sekar ^{a,c*}

^aSustainable Energy and Environmental Research Laboratory, Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, Chennai 603203, Tamil Nadu, India.

^bDepartment of Earth Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan

^cDepartment of Civil & Environmental Engineering, Yonsei University, Seoul 03722, Republic of Korea

Corresponding author Karthikeyan Sekar*

E-mail: karthiks13@srmist.edu.in

Experimental section

Chemicals

Nickel (Ni) foam 99.9% 1.6 mm thickness (MTI Korea), L-cysteine (SRL), Potassium hydroxide (Thermo Fisher Scientific Ltd.), ethanol 99.9% (Changshu Song Sheng Fine Chemicals) were purchased and used as such. Distilled water with 18.2 MΩ from NANO pure Diamond UV deionized water purification system was used for all the synthesis and studies.

Synthesis method

Hydrothermal synthesis of NiS on Ni foam (NS/NF)

Ni foam is cut into 1cm × 2cm dimensions and pretreated with 1.5M HCl to remove oxidised surface and further washed with acetone and ethanol to remove any impurities. About 2.5 mmol of L-cysteine is dissolved in 25 mL distilled water and kept for stirring until homogeneity of the solution is attained. The reaction mixture is then transferred to 25mL Teflon lined stainless steel autoclave containing cleaned Ni foam and kept in hot air oven at 120°C for 6h. The autoclave is allowed to cool naturally and the resultant foam (NS/NF) seemed to change its colour indicating the successful sulphidation process. The NS/NF is washed several times with distilled water to remove any impurities and then followed by ethanol, then dried in vacuum.

Fabrication of Pt/C on Ni foam

About 5 mg of Pt/C (10 wt % Pt content) and 5 mg RuO₂ is weighed and taken in two different sample tubes. 1 mL of catalytic ink dispersion is prepared by adding 700 μ L isopropyl alcohol, 250 μ L distilled water and 5 μ L 10% Nafion solution to the two sample tubes. The catalyst inks were then sonicated for 30 min. After that, the 20 μ L catalyst ink was deposited on two precleaned NF pieces and the loading of the catalysts was \sim 2 mg cm⁻² in each case.

Characterisation

Physical Characterisation

To confirm the crystalline phase X-ray Diffraction analysis (XRD) was done using Malvern PANalytical equipped with Empyrean Cu X-ray tube with K α radiation and Pixel3D detector running at 0.02 $^\circ$ step scan rate. The topography and morphology of the material were asserted using Field Emission Scanning Electron Microscopy (FE-SEM), Thermoscientific Apreo S and elemental mapping EDS with FEI QUANTA accelerating with 0.02 MV. Hi-resolution Transmission Electron Microscopy (HR-TEM) images was taken using JEOL Japan, JEM-2100 Plus to study the atom arrangements, defects and interplanar distances. The as-synthesized catalysts, along with references were all measured in transmission mode BL15 Ni K edge X-ray absorption near edge (XANES) spectroscopy at the Kyushu Synchrotron Light Research Centre, SAGA-LS; Tosu, Japan. Kapton tape was used to secure the samples after they were diluted with boron nitride. The Athena-Demeter 0.9.26 program in the IFEFFIT software package was used to perform a linear combination fitting analysis.

Electrochemical characterisation

The whole experiment is carried out in 1.0M KOH, pH 14 being set-up in a conventional three electrode cell model, using Hg/HgO as RE and Ni foam as CE for HER. The electrochemical

workstation CHI760E screened the electrochemical studies at room temperature. (Geographical location 12.8250223, 80.0439124). For the two-electrode system, NS/NF is connected to cathode and RuO₂ served as the anode.

HER studies: The developed electrocatalysts were activated electrochemically by cyclic voltammetry (CV) for several cycles at a scanrate of 50 mVs⁻¹ against Open Circuit Potential (OCP) to ensure optimum hydrogen saturation around the working electrode (WE). Linear Sweep Voltammetry (LSV) was done at the lowest scanrate 1 mVs⁻¹ with 100% *iR* compensation. Electrochemical Impedance Spectroscopy (EIS) is operated under catalytic turn-over conditions with AC amplitude 5mV in the wide frequency range 0.1 Hz - 100MHz from which Nyquist, Bode-absolute impedance and Bode phase angle measurements are calculated to interpret charge-transfer rate. Sampled Current Voltammetry (SCV) studies were adapted as mentioned in the previous literature¹ to avoid expendable charging current from LSV. Double layer capacitance (*C_{dl}*) method is adapted by increasing the scan from 10 to 200 mVs⁻¹ for CV in the non-Faradaic region to study charge-discharge phenomenon. The long-term stability of the material is tested by amperometry studies. All the data obtained from CHI760E is plotted and the graphs are obtained using Microsoft excel.

Firstly, 100% *iR* compensations were made and then converted into universal scale of RHE using the following equation.

$$E_{RHE} = E_{Hg/HgO} + E^{\circ}_{Hg/HgO} + \frac{2.303 RT}{F} pH \quad (S1)$$

$E^{\circ}_{Hg/HgO}$ – calibrated everytime using standard method of carrying out HER with Pt foil

R – universal gas constant (8.314 JK⁻¹mol⁻¹)

T – room temperature in °C

F – Faraday constant (96485 C mol⁻¹)

Tafel analysis was done in the HER region was calculated from the following Tafel equation,

$$\eta = a - b \log j \quad (S2)$$

where “ η ” is the overpotential $E - E_{iR}$ vs. RHE in V, “*a*” is Tafel constant, “*b*” is Tafel slope in V dec⁻¹ and “*j*” is current density in mA cm⁻².

The Tafel constant “a” was calculated by the following equations:

$$\text{Intercept, } a = \frac{2.303 RT}{\alpha n F} \log j_0 \quad (\text{S3})$$

$$\alpha n = \frac{2.303 RT}{b F} \quad (\text{S4})$$

Here “ α ” is the transfer coefficient, “ j_0 ” is the exchange current density in mA cm⁻².

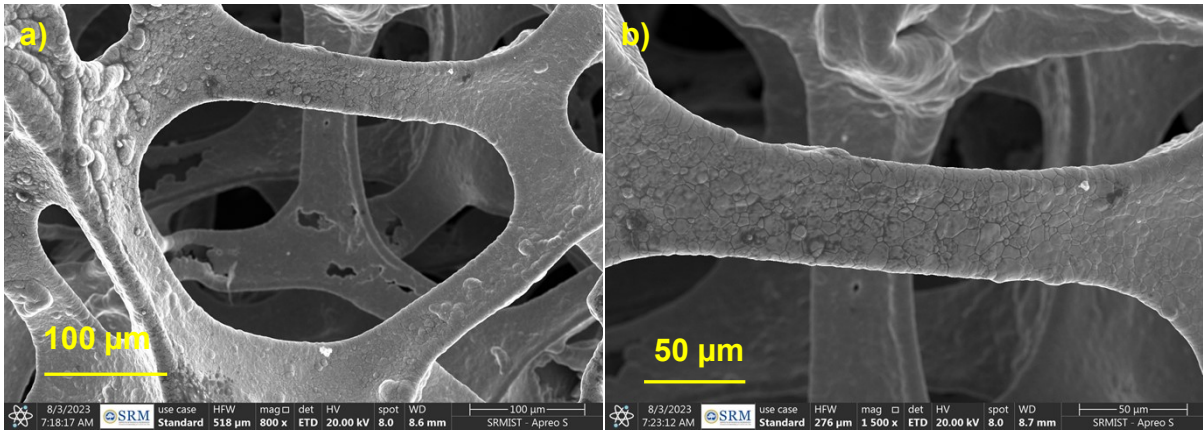


Fig.S1 (a and d) FE-SEM images of bare NF under different magnifications.

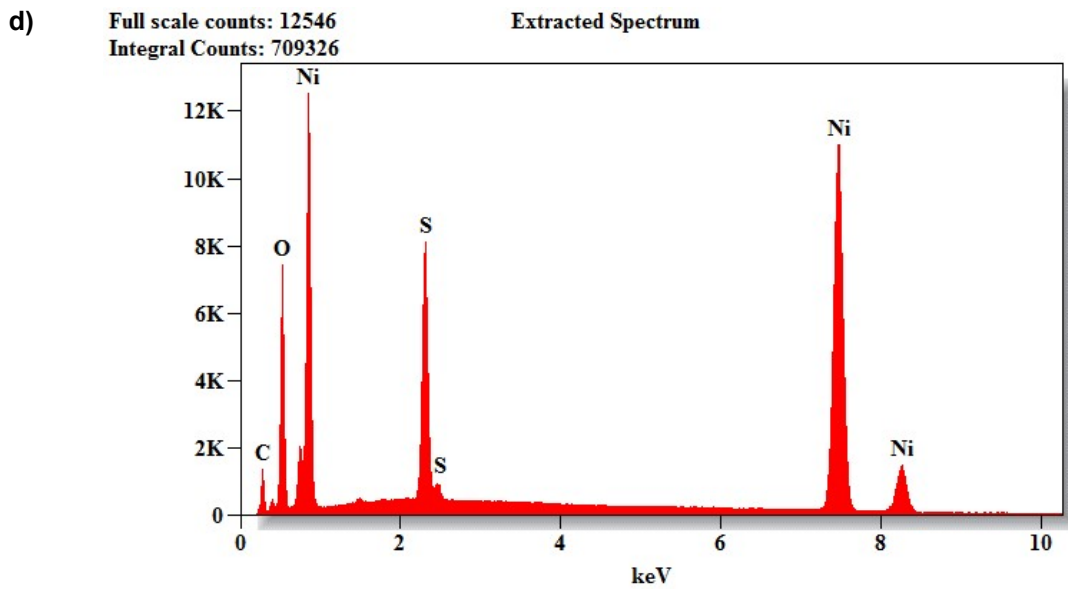
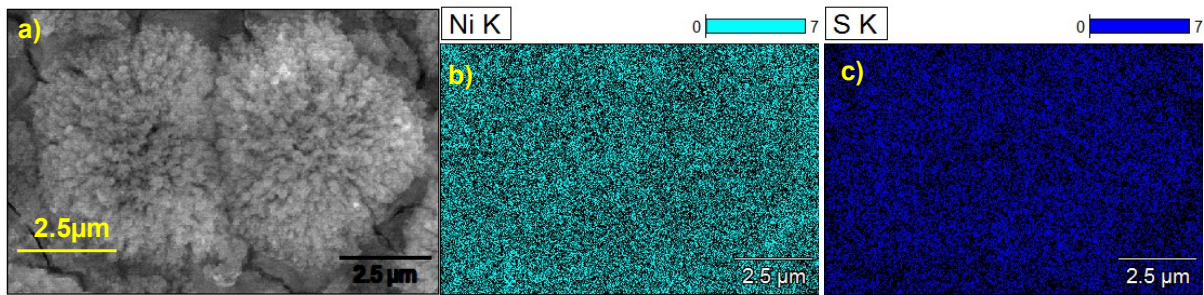


Fig.S2 (a) FESEM image and the corresponding elemental mapping for the elements (b) Ni, (c) S atom and (d) EDX spectra of NS/NF.

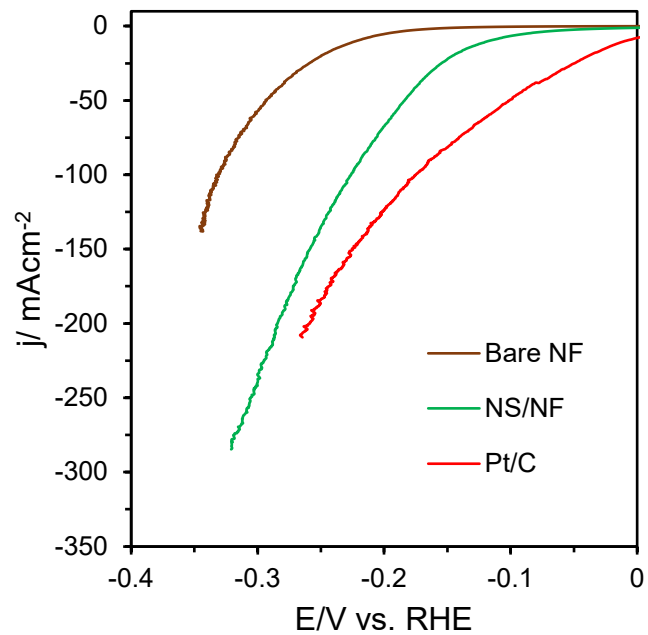


Fig.S3 LSV plot recorded at a scan-rate of 1 mVs^{-1} in 1.0 M KOH with $100\% iR$ compensation for bare NF, NS/NF and Pt/C catalysts.

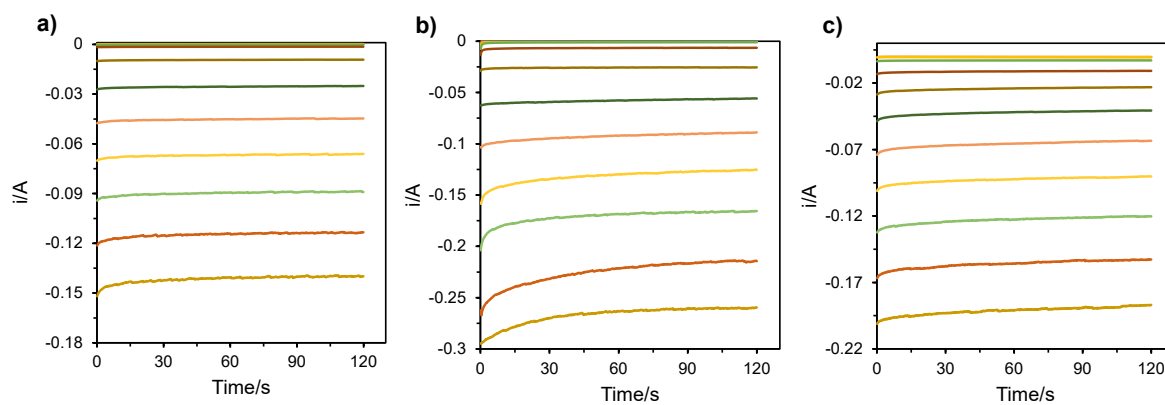


Fig. S4 CA responses at a constant potential of -0.8V to -1.8V at 100 mV interval vs.Hg/HgO for 120s of (a) Bare NF, (b) NS/NF and (c) Pt/C respectively.

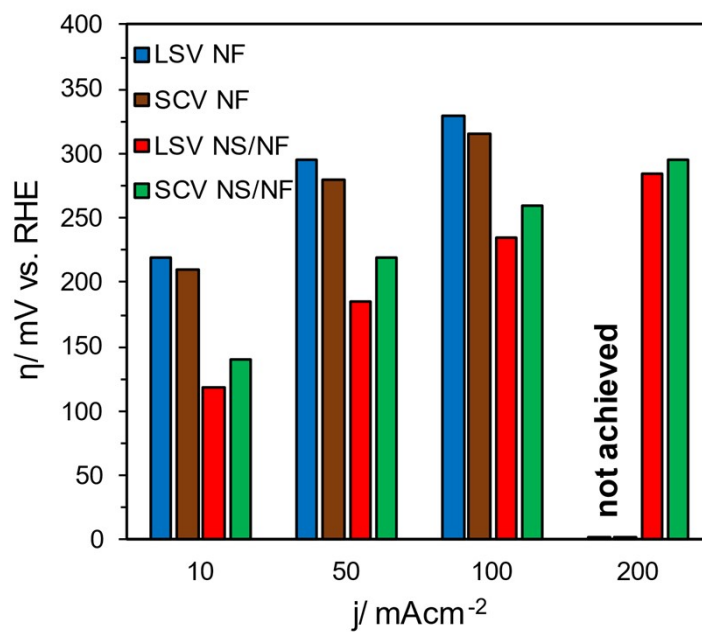


Fig.S5 Comparative plots of overpotential extracted from LSV and SCV curves at 10, 50, 100 and 200 mAcm⁻² current density for different electrocatalysts.

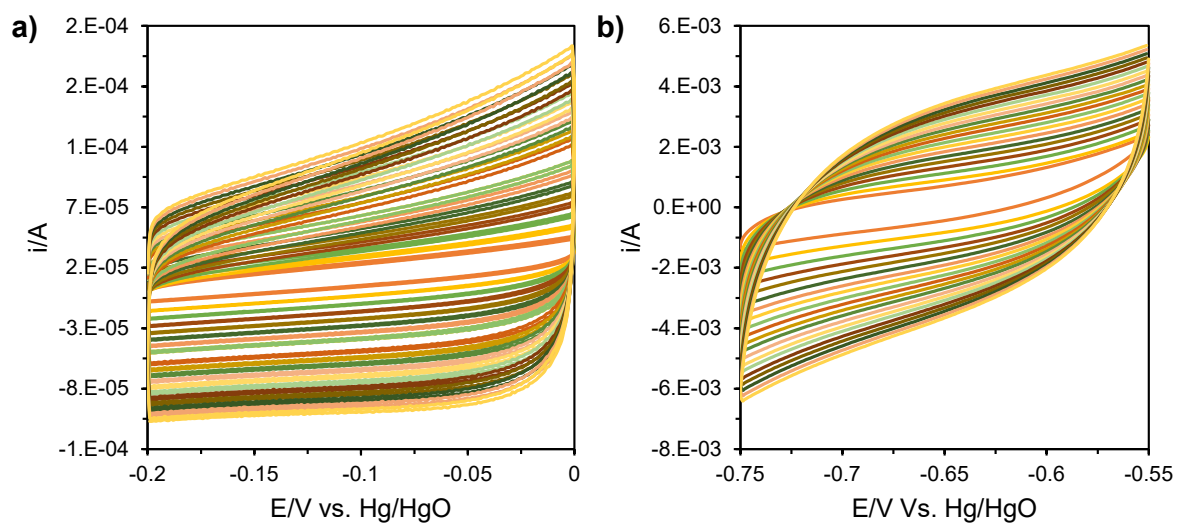


Fig. S6 CV responses in the non-Faradaic region for calculating C_{dl} values of (a) Bare NF and (b) NS/NF respectively.

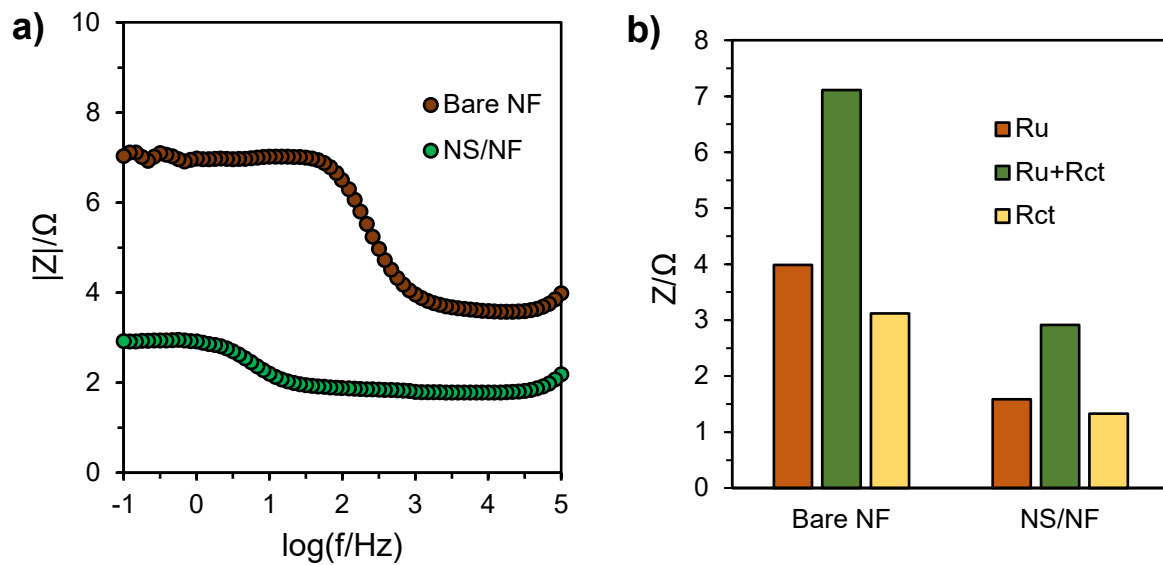


Fig. S7 (a) Bode-absolute impedance recorded at -1.2V vs. Hg/HgO at 5mV amplitude with an operating frequency between 0.1Hz and 100MHz and (c) Bar chart comparatively showing uncompensated and charge-transfer resistances for bare NF and NS/NF catalyst respectively.

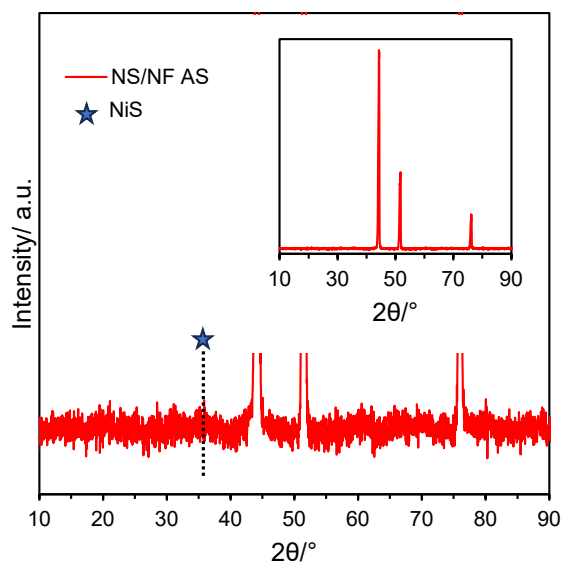


Fig. S8 XRD pattern for NS/NF catalyst after stability with inset showing zoomed-out pattern

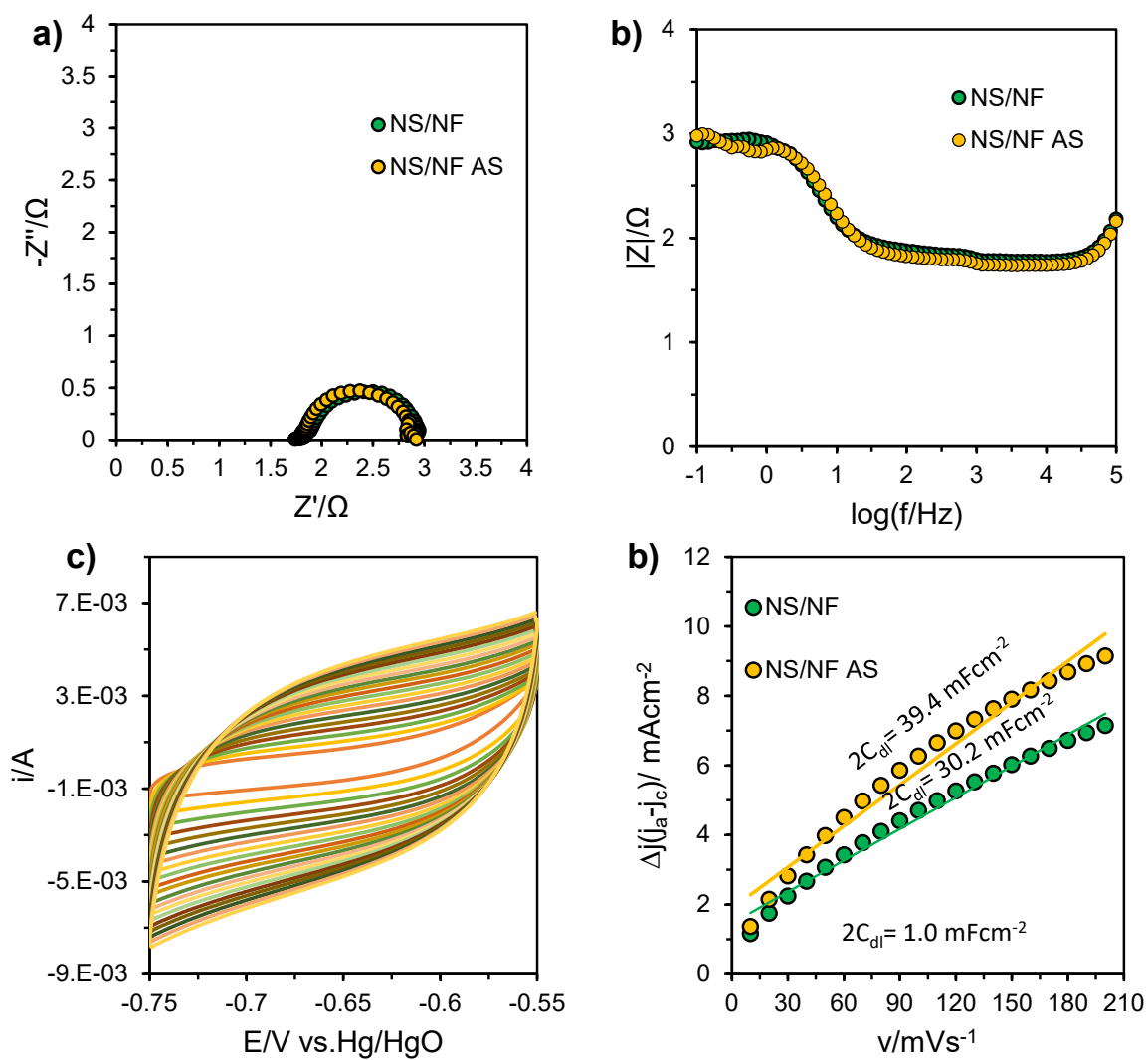


Fig. S9 (a) Nyquist plot, (b) Bode-absolute impedance plot and (c) CV responses in the non-Faradaic region of NS/NF AS and (d) Comparative linear plot of current density versus scan-rates of NS/NF before and after stability.

1. S. Anantharaj, S. Kundu and S. Noda, *Journal of the Electrochemical Society*, 2022, **169**, 014508.