

# Silicon Atom Doping in Heterotrimetallic Sulfides for Non-noble Metal Alkaline Water Electrolysis

Mohamed Barakat Zakaria Hegazy,<sup>1,2\*</sup> Leila Bahri,<sup>3</sup> David Tetzlaff,<sup>1,4</sup> Sebastian Sanden,<sup>1</sup> Ulf-Peter Apfel<sup>1,4\*</sup>

1. *Inorganic Chemistry I – Technical Electrochemistry, Faculty for Chemistry and Biochemistry, Ruhr University Bochum, 44801 Bochum, Germany,*
2. *Department of Chemistry, Faculty of Science, Tanta University, 31527 Tanta, Egypt,*
3. *Department of Chemistry, College of Sciences, University of Hafar Al-Batin, 39524 Hafar Al-Batin, Kingdom of Saudi Arabia.*
4. *Fraunhofer Institute for Environmental, Department for Electrosynthesis, Safety and Energy Technology UMSICHT, 46047 Oberhausen, Germany*

[mohamed.barakat@rub.de](mailto:mohamed.barakat@rub.de) and [ulf.apfel@rub.de](mailto:ulf.apfel@rub.de)

## Abstract

This study investigates the modification of materials by doping with foreign elements to enhance electrocatalytic activity and focuses on the engineering of an inorganic material composed of transition heterometal-rich pentlandite ( $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_8$ , FCNS) doped with silicon (FCNSSi) as a bifunctional catalyst for the overall electrochemical water splitting process. The FCNSSi electrode exhibits remarkable catalytic activity for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The OER performance of FCNSSi was evaluated in a 1.0 M KOH solution, achieving an overpotential of 313 mV at 10  $\text{mA cm}^{-2}$ . The FCNSSi electrode exhibits a current density of -10  $\text{mA cm}^{-2}$  at a remarkably low overpotential of 164 mV with a Tafel slope of 80.7 mV/dec in HER. Density functional theory (DFT) calculation suggests that Si doping adjusts the binding energies of intermediates on the surface, which weakened the \*OH, \*O, and \*OOH adsorption energies, resulting in enhanced activity for both OER and HER. Moreover, Si doping enhances the hydrogen adsorption activity of all sites. Finally, a two-electrode zero-gap cell assembly was used to investigate the durability of FCNSSi catalyst towards efficient and durable alkaline water electrolysis, demonstrating the promising potential of this catalyst for practical applications at 500  $\text{mA cm}^{-2}$ .

**Keywords:** silicon, heterotrimetallic sulfides, hydrogen, water splitting, water oxidation.

## Introduction

Climate change has emerged as a pressing global concern due to the significant changes it causes in Earth's atmosphere, temperature, and air quality, primarily resulting from the emission of CO<sub>2</sub> generated by the combustion of fossil fuels and industrial steam reforming for hydrogen production <sup>[1-2]</sup>. The development of renewable energy sources capable of replacing these environmentally damaging technologies has become an urgent requirement. Among the promising candidates for clean hydrogen production with zero CO<sub>2</sub> emission, water electrolysis has recently gained significant attention <sup>[3]</sup>. Hydrogen generated through water electrolysis is highly demanded for sustainable economic and societal development <sup>[4]</sup>. However, this process is energetically demanding and requires a minimum voltage of 1.23 V versus RHE under standard conditions <sup>[5]</sup>, which is only achievable at a much higher potential of at least 1.6 to 2.0 V vs. RHE in practice due to cathodic and anodic overpotentials <sup>[6]</sup>. Additional energy losses occur due to multiple proton and electron transfer reactions resulting in pH changes and irreversible redox reactions <sup>[7]</sup>.

To minimize the required energy and maintain continuous and efficient electrochemical water splitting for sustainable hydrogen production, the development of stable and efficient electrocatalysts is critical <sup>[8]</sup>. However, the current industrial use of scarce noble metal-based electrocatalysts, such as Pt/C and IrO<sub>2</sub>, in proton exchange membrane (PEM) technology incurs high H<sub>2</sub> production costs <sup>[9]</sup>. Similarly, the developed Ni and Co-based materials, alloys, hydroxides, etc. catalysts used in alkaline water electrolyzers still lack in efficiency compared to commercial PEM <sup>[10]</sup>.

Recent research efforts have focused on using earth-abundant elements as non-precious catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) <sup>[11-12]</sup>. Along this line, transition metal chalcogenides have emerged as promising catalysts for water electrolysis due to their abundance, cost-effectiveness, high conductivity, efficient redox chemistry, and stability <sup>[13-15]</sup>. A variety of nickel, iron, and cobalt-based transition metal-based catalysts have been developed for electrocatalytic hydrogen production to date <sup>[11-12, 16-18]</sup>. Among them, metal-rich pentlandite-type catalysts have been suggested as a promising material class <sup>[17-18]</sup>. For instance, a Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> electrode from the natural ore pentlandite achieved a current density of 10 mA cm<sup>-2</sup> at 280 mV for catalytic hydrogen evolution under acidic conditions <sup>[19]</sup>. Similarly, Co<sub>9</sub>S<sub>8</sub> nanoparticles supported by carbon nanosheets catalyst exhibited an overpotential of 294 mV at 10 mA cm<sup>-2</sup> for OER in alkaline electrolyte <sup>[20]</sup>. Our group recently adapted a mechanochemical method for making various compositions of nanosized pentlandites which work efficiently as cathodic electrocatalysts in a zero-gap PEM electrolyzer for water splitting <sup>[21]</sup>. Additionally, more insights into the electrocatalytic activity of pentlandites upon variation of the metal content were reported <sup>[22]</sup>. To further improve the HER and OER performance of these

materials, doping with non-metallic foreign elements such as nitrogen and phosphorus heteroatoms were shown as a viable strategy <sup>[16, 23]</sup>.

In addition to transition metal chalcogenides, silicon has been extensively investigated as an electrode material in electrochemical semiconductors due to its high theoretical gravimetric hydrogen storage efficiency of 14 wt.%, suggesting its excellent potential for hydrogen generation <sup>[24]</sup>. Yang and colleagues have reported that Si prepared by molten salt electrolysis has potential applications in large-scale H<sub>2</sub> production <sup>[25]</sup>. Recent studies have also shown that electrolyzed silicon can generate hydrogen when exposed to pure water <sup>[26]</sup>. This hydrogen liberation can occur in both ionic and atomic forms of silicon <sup>[26]</sup>. The chemical split of water molecules on silicon can proceed spontaneously without requiring additional external energy. In addition, silicon possesses an anodic polarization in alkaline and fluoride solutions, and hydrogen evolution is the dominant reaction at silicon electrodes in alkaline aqueous solutions <sup>[27-28]</sup>. However, pure silicon electrodes are not preferable in water splitting applications due to the formation of a silicon dioxide passivation layer, which limits its electrochemical activity <sup>[27-28]</sup>.

To connect the promising electrochemical properties of pentlandite materials and silicon for overall electrochemical water splitting, we investigated the doping of silicon into the pentlandite crystal structure. Herein, the discrepancy in atomic radius between S and Si atoms is expected to modify the overall electronic structure of the active site due to the change in bond length, the common behavior of sulfur atom in metal sulfides, originating from Si doping <sup>[29]</sup>. Thus, in this article, we propose a synthetic protocol for Si incorporation into pentlandite to regulate and investigate their electrocatalytic activity towards the overall water splitting. Moreover, we studied the effect of silicon adsorption at the pentlandite surface on the electrochemical performance compared to the doped material. The developed silicon-doped pentlandite (FCNSSi) material showed significantly improved HER and OER performances than the trimetallic pristine FCNS material. Furthermore, FCNSSi demonstrated a significantly improved catalytic HER performance after activation for 24 hours in 0.5M H<sub>2</sub>SO<sub>4</sub> during long-term chronoamperometry test at -0.1 V vs. RHE. Finally, a promising performance and durability of FCNSSi towards alkaline water electrolysis at elevated current densities was shown in membrane.

## Experimental details

**Materials:** Iron powder ( $\geq 99.0\%$ , reduced), cobalt powder (2  $\mu\text{m}$  particle size, 99.8%), nickel powder (99.9%, 3N), sulfur powder (99.5-100.5%), silicon tetrachloride (99.0%), Nafion perfluorinated resin 5% in alcohol, potassium hydroxide, and sulfuric acid were purchased from Sigma-Aldrich, Merck, Germany. Sustainion® XA-9 Alkaline Ionomer 5% in ethanol was purchased from Dioxide Materials, USA. SiLibeads Ceramic beads Type ZY-S were purchased from Sigmund Lindner GmbH, Germany. 0.05  $\mu\text{m}$  polishing alumina suspension for electrode polishing were purchased from Gamry.

**Synthesis of  $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_8$  (FCNS):** FCNS was synthesized via a modified mechanochemical synthesis recently published by our group<sup>[16]</sup>. A reaction mixture ( $m_{\text{total}} = 25$  g) composed of stoichiometric amounts of the elements iron, cobalt, nickel, and sulfur were milled employing a planetary ball mill (Fritsch Pulverisette 7, premium line) with  $\text{ZrO}_2$  milling containers ( $V = 80$  mL) and  $\text{ZrO}_2$  milling balls (100 g,  $d = 5$  mm). The reaction mixture was prepared inside a glovebox to assure an inert argon atmosphere inside the milling vessel. Ball milling was performed at a constant rotation speed of 900 rpm for 4 x 60 min, with a 60 min break after each cycle.

**Synthesis of  $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_{8-x}\text{Si}_x$  (FCNSSi) for silicon atom doping in pentlandite structure:** FCNSSi was prepared through annealing of FCNS at 800 °C in an inert nitrogen gas atmosphere with a flow rate of 80 mL  $\text{min}^{-1}$  in presence of  $\text{SiCl}_4$  as Si source (**Figure 1, right side**). FCNS powder (1.0 g) and  $\text{SiCl}_4$  liquid (3.0 g) were placed and mixed in a separate quartz-boat. A large excess of  $\text{SiCl}_4$  was used due to anticipated losses of Si e.g. by evaporation. After aging for 1 h, the annealing process was initiated by heating from room temperature up to 57 °C, the boiling point of  $\text{SiCl}_4$ , within 1 h. After continuous annealing at 57 °C for 1 h, the temperature was raised up to 800 °C within 2 h. After continuous annealing at 800 °C  $\text{min}^{-1}$  for 4 h, the powder was cooled inside the furnace at a rate of 10 °C  $\text{min}^{-1}$ . The obtained FCNSSi powder was collected for characterization and electrochemical testing.

**Synthesis of  $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_{8-x}\text{Si}_x$  (FCNSSi-RT) for silicon adsorption at pentlandite surface:** FCNSSi-RT was prepared through mixing FCNS and  $\text{SiCl}_4$  at room temperature in an inert atmosphere (**Figure 1, left side**). FCNS and  $\text{SiCl}_4$  ( $\text{wt.}/\text{wt.} = 1/3$ ) were mixed in a small vial in an inert atmosphere. The vial was aged tightly closed in a fume hood overnight. Afterwards the vial was opened and aged in the fume hood until a dry powder is obtained. The obtained FCNSSi powder was collected for characterization and electrochemical testing.

**Electrochemical measurements:** A conventional H-type three-electrode electrochemical cell or an in-house built zero-gap membrane reactor (see below) was used for OER and HER measurements. All electrochemical tests were performed on a GAMRY 1010B interface/potentiostat. A glassy carbon electrode (GCE) of a geometric surface area of 0.071  $\text{cm}^2$  and carbon paper electrode (CPE) with a geometric surface area of 0.16  $\text{cm}^2$  coated with our catalysts were used as working electrodes, saturated calomel electrode (SCE) as a reference electrode, and a platinum mesh as a counter electrode. The reported potential versus the reversible hydrogen electrode (RHE) was estimated using the following equation:  $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059 \text{ pH}$ . To prepare the ink for the working electrode, 5 mg of our catalyst was well-dispersed in a mixture of water and ethanol (950  $\mu\text{L}$ , 3:1 v/v) until obtaining a homogenous solution. 50  $\mu\text{L}$  of Nafion (5 wt %) perfluorinated resin solution was added into the prepared suspension while keeping the sonication continuous for one additional hour until affording a homogeneous ink (N.B. Sustainion® XA-9 Alkaline Ionomer 5% in ethanol is used as a binder for making ink for zero gap cell/membrane electrode assembly measurements (**Figure 8**)). Finally, 5  $\mu\text{L}$  of prepared ink was drop-casted at GCE surface and 10  $\mu\text{L}$  of prepared ink was drop-casted at CPE surface and then dried at room temperature. Linear sweep voltammetry (LSV) measurements were performed at a potential range between 1.0 V to 2.0 V vs. RHE for OER testing in KOH solution and 0.2 V and -0.8 V vs. RHE in  $\text{H}_2\text{SO}_4$  solution for HER

with a scan rate of 50 mV s<sup>-1</sup>. Tafel plots were derived from LSV curves around the onset potential region. Cyclic voltammetry (CV) measurements were performed at different scan rates to estimate the electrochemical active surface area (ECSA). The calculation of ECSA was performed according to the formula,  $ECSA = R_f S$ , in which S represents the geometric surface area of the smooth electrode, equivalent to the geometric area of the working electrode. The roughness factor ( $R_f$ ) was obtained from the formula,  $R_f = \frac{C_{dl}}{C_s}$ , in which the double layer capacitance ( $C_{dl}$ ) was equal to the slope of the double layer charging current versus the scan rate slope using this formula  $i = vC_{dl}$ . The general specific capacitance  $C_s$  corresponded to the average double layer capacitance of a smooth surface about 20-40  $\mu\text{F cm}^{-2}$  [30]. Electrochemical impedance spectroscopy (EIS) measurements were performed to determine the charge transfer speed. Finally, chronoamperometry and chronopotentiometry tests were performed for 24 h to determine the catalyst durability and stability for long-term OER and HER performance.

**Zero-gap cell assembly:** An in-house made zero-gap cell with an active area of 2 cm<sup>2</sup> was employed for all experiments at high current densities [31-32]. The compression and position of the porous transport electrodes were adjusted by polytetrafluorethylene (PTFE) gaskets. We focused our investigation on AEM-based zero-gap electrolyzers, for which chalcogenide materials hold greater promise for both the anodic and cathodic side. The employed Fumasep FAA-3-PK-130 membrane was conditioned in 1.0 M KOH for one day prior the electrochemical measurements. KOH (1.0 M) was used as an electrolyte for both the anode and the cathode and were flooded through the used titanium parallel flow-fields with a flow rate of 10 mL min<sup>-1</sup>.

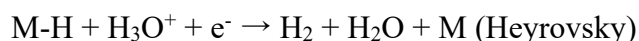
**Characterizations:** Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D2 Phaser diffractometer equipped with a Lynx Eye XE-T detector operating at 30 kV acceleration voltage and 10 mA emission current using Cu K- $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). The data was recorded in a range from 10–70° 2 $\theta$ . The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using Netzsch STA 449 F3 Jupiter equipped with nitrogen-purged SiC-Oven (<1550°C), DSC-Sample holder. The device was properly calibrated using the pure elements In, Zn, Al, Ag and Au. The FTIR spectra were collected using Shimadzu IR Tracer-100 with a Pike miracle ATR unit. Scanning electron microscopy (SEM) was performed on a ZEISS Gemini2 Merlin HR-FESEM equipped with an OXFORD Aztec Energy X-ray microanalysis system for energy dispersive X-ray spectroscopy (EDX). The SEM images were recorded at an acceleration voltage of 4 kV while EDX mappings were performed from 0-20 kV. XPS measurements were carried out in an ultra-high-vacuum (UHV) setup equipped with a polychromatic Al K $\alpha$  X-ray source (1486.6 eV) or Mg K $\alpha$  X-ray source (1253.6 eV) and a hemispherical analyzer (type CLAM2, VG, Scientific, Thermo Fischer Scientific). The base pressure in the measurement chamber was maintained at about 10<sup>-9</sup> mbar. All spectra were recorded with a pass energy of 100 eV at beam current of 13 mA and a high voltage of 14 kV, which equals a Power of 13\*14=182 W. ICP was performed to measure the elements Fe, Ni and Co after microwave digestion on an Analytik Jena Model ContrAA800 AAS. The nitrogen gas adsorption-desorption isotherms were obtained using a Autosorb-1,

Quantachrome Instruments. The pore size distribution was calculated based on the DFT model. Prior the measurements the materials have undergone preheating treatments at 100 °C for 24 h.

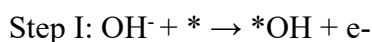
**Online gas chromatography (GC) measurements:** An Agilent 7820A GC system for gas analytics was used for qualitative and quantitative analysis of O<sub>2</sub> and H<sub>2</sub> gases and for faradaic efficiency (FE%) calculations. The gas chromatography system is equipped with two columns (HaySep Q and molesieve 5A), a flame ionization detector (FID) and a thermal conductivity detector (TCD). Argon was used as carrier gas for standard measurements.

**Computational methods:** The spin-unpolarized DFT calculations with the Perdew-Burke Ernzerhof (PBE) exchange-correlation functional were performed using the Vienna ab initio simulation package (VASP) [33]. The projector augmented wave method (PAW) [34], with a plane-wave kinetic energy cutoff of 400 eV, was used, with the Gaussian smearing of 0.05 eV. The Brillouin zone was sampled by only the 3\*3\*1 K-point. The pentlandite Fe<sub>3</sub>Co<sub>3</sub>Ni<sub>3</sub>S<sub>8</sub> (111) surface was modeled by a (2\*3\*2) supercell, and a vacuum layer of 15 Å was added to eliminate artificial interactions between periodic images for modeling surface chemistry. We substituted the surface sulfur atoms with silicone for doped pentlandite systems (FCNSSi sample) to evaluate the dopant effects. All atoms were allowed to relax during geometry optimization, and the atomic positions were optimized until the forces were less than 0.02 eV/ Å. The effects of van der Waals corrections were modeled using Grimme's method, with Becke-Johnson damping [35]. The adsorption energy of hydrogen atom (EH<sub>ad</sub>) is defined as the energy difference before and after the adsorption with respect to the gas-phase H<sub>2</sub> molecule as shown in the following equation:  $EH_{ad} = E_{total} - E_{surface} - \frac{1}{2} EH_2$ , where EH<sub>ad</sub>, EH<sub>2</sub>, and E<sub>total</sub> are the energies for the clean surface, H<sub>2</sub> molecule in the gas phase, and hydrogen atom adsorbed on the surface, respectively. The Gibbs-free energy of H adsorption (ΔGH) is obtained by applying the entropy correction as shown in the equation  $\Delta GH = \Delta EH + \Delta EZPE - \Delta SH$ .

The HER takes place on the surface of the cathode via multi-step electrochemical process. Specifically, in acidic conditions the multi-step electrochemical process occurs via the following reactions [36-37].



The OER performance of Pentlandite system can be predicted using the Gibbs-free-energy (ΔG) profiles for the following sequence of elementary OER sub-steps, according to Rossmeisl et al. [38]:



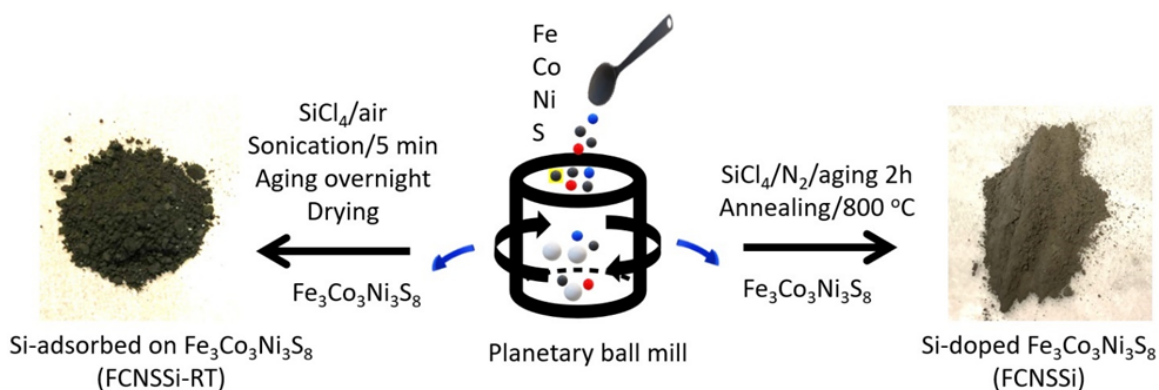
where \* represents the bare site and \*OH, \*O, \*O<sub>2</sub>, and \*OOH denote the surface featuring different chemisorbed species. The free energy difference for all the elementary steps above ( $\Delta G_{OH^*}$ ,  $\Delta G_{O^*}$ ,  $\Delta G_{OOH^*}$ ) involve an electron transfer is calculated by the equation  $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}$ , where  $\Delta E$ ,  $\Delta ZPE$ , and  $\Delta S$  correspond to the energy difference between adsorption energy, zero-point energy, and entropy, respectively. The  $\Delta ZPE$  and  $T\Delta S$  values were obtained from harmonic vibrational frequency calculations and DFT.  $\Delta G_U = -eU$ , where  $U$  represents a potential based on a standard hydrogen electrode.

Under ideal conditions, the OER reaction with a total energy change of 4.92 eV can be driven at 1.23 V, whereas the free energy of each elementary reaction would be equally divided into 1.23 eV. Thus, the overpotential ( $\eta$ ) is introduced to represent the additional required potential and rationalize the catalytic performance of the catalyst, which is defined in theoretical calculations as:  $\eta(PLS) = \max(\Delta G(1,2,3,4))/e - 1.23 \text{ eV}$

## Results and discussion

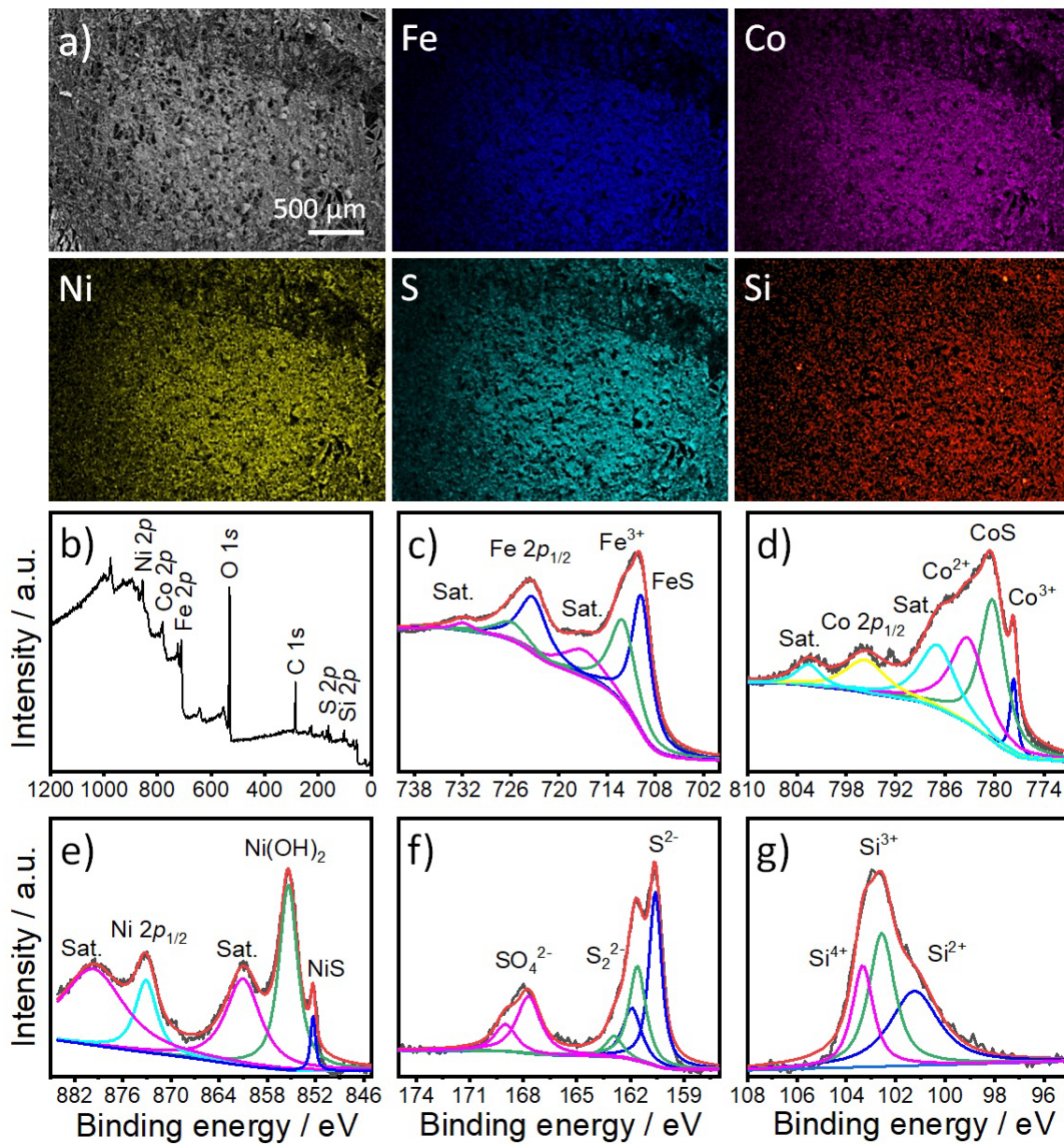
### Materials characterization

Using a combinatorial chemical synthesis approach that involves planetary ball milling followed by monitored annealing in an inert atmosphere and in the presence of SiCl<sub>4</sub>, we were able to successfully obtain Si-doped pentlandite powder (as depicted on the right side of **Figure 1**). Likewise, to prepare Si adsorbed at the surface of pentlandite, we conducted an additional control experiment at room temperature as shown on the left side of **Figure 1**. The sample obtained through annealing is denoted as FCNSSi, while the sample obtained at room temperature is labeled as FCNSSi-RT.



**Figure 1** Schematic illustration of the synthetic pathway of Si-doped trimetallic pentlandite (FCNSSi) and Si-adsorbed at trimetallic pentlandite (FCNSSi-RT) surface





**Figure 2** a) Top-view SEM and the corresponding atoms (Fe, Co, Ni, S, and Si) mapping images of FCNSSi on carbon paper electrode. b) Wide scan XPS survey of FCNSSi powder and high-resolution XPS spectra of c) S 2p, d) Si 2p, e) Ni 2p, f) Fe 2p, and g) Co 2p orbitals.

We first analyzed the crystal structure and phase purity of the materials using PXRD diffraction (**Figure S1**). All materials exhibited diffraction peaks consistent with the trimetallic pentlandite phase (*PDF card no. 30-0444*)<sup>[39]</sup>. The dominant diffraction peaks of FCNSSi also matched the pentlandite phase, indicating that the doping of Si atoms into FCNS had no significant impact on the pristine crystal structure (**Figure S2**). Additionally, the peaks' intensity and sharpness increased, suggesting an improvement in the overall crystallinity of the material. While some peaks associated with NiS and Ni<sub>31</sub>Si<sub>12</sub> phases were detected (**Figure S1**)<sup>[40]</sup>, they were minor compared to the main pentlandite phase in terms of peak intensity, likely due to phase preferential crystallization.



To examine the morphology and composition of FCNSSi on carbon paper electrodes, we used SEM in combination with an energy-dispersion X-ray system (EDX). The microscale particles of FCNSSi (1-10  $\mu\text{m}$ ) were distributed across the electrode surface (as displayed in **Figure 2a**). The EDX images (**Figure 2**) and spectra (**Figure S3**) revealed the presence and overlapping distribution of Fe, Co, Ni, S, and Si atoms throughout the entire FCNSSi electrode surface.

X-ray photoelectron spectroscopy (XPS) analysis was then conducted to determine the oxidation state of the elemental and material composition of FCNSSi powder (**Figures 2b**). The photopeaks corresponding to Fe  $2p$ , Co  $2p_{3/2}$ , Ni  $2p_{3/2}$ , S  $2p$ , and Si  $2p$  orbitals were clearly observed in the XPS survey scan (**Figure 2b**). The Fe  $2p$  orbital photopeak was deconvoluted into two splits that are assignable to the Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  orbitals (**Figure 2c**)<sup>[16]</sup>. The peak at 709.8 eV for FCNSSi is attributed to the Fe-S bond in pentlandite phase<sup>[41]</sup>. The Co  $2p_{3/2}$  photopeaks were then deconvoluted into four peaks which indicate not only presence of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  species at tetrahedron and octahedron positions in pentlandite, but high intensity photopeak at 780.2 eV is assigned to Co-S phase<sup>[42]</sup>. Similarly, Ni  $2p_{3/2}$  is deconvoluted into three peaks at 852.4eV, 855.35eV, and 860.85 eV attributed to NiS, Ni(OH)<sub>2</sub>, and a shake-up satellite, respectively<sup>[43]</sup>. The S  $2p$  photopeak was deconvoluted into two peaks at 160.6 eV and 161.9 eV, characteristic of S  $2p_{3/2}$  and S  $2p_{1/2}$  orbitals in metal-sulfur bond in pentlandite phase, respectively<sup>[44]</sup>. An additional doublet at 161.7 eV and 163.0 eV can be assigned to disulfide phase<sup>[45]</sup>. The signals at 167.6 eV and 168.9 eV corresponding to S  $2p_{3/2}$  and S  $2p_{1/2}$  orbitals can be assigned to sulfate species<sup>[45]</sup>. Finally, the S  $2p$  signal is deconvoluted to one dominant peak at 101.22 eV and two additional peaks at 102.5 eV and 103.4 eV characteristics of  $\text{Si}^{2+}$ ,  $\text{Si}^{3+}$ , and  $\text{Si}^{4+}$ , respectively<sup>[46-47]</sup>. We are assuming that the peak observed at 101.22 eV originates from the silicon-metal bond due to silicon doping as proposed by the DFT calculations (see below) and/or  $\text{Ni}_{31}\text{Si}_{12}$  alloy<sup>[48]</sup>. The additional peaks at 102.5 eV and 103.4 eV are assigned to oxidized silicon<sup>[49]</sup>.

To further confirm the successful doping of the pentlandite materials, the chemical composition of the materials was determined using Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES). The compositional analysis confirmed the presence of Si in pentlandite as a part of the material's composition (**Table S1**). The chemical composition of the FCNS sample was determined as  $\text{Fe}_{2.97}\text{Co}_{2.98}\text{Ni}_{3.01}\text{S}_8$ , while that of FCNSSi was  $\text{Fe}_{2.82}\text{Co}_{2.84}\text{Ni}_{2.8}\text{S}_{7.7}\text{Si}_{0.3}$ , which is almost typical of the composition of the pentlandite phase. Notably, a low content of silicon doping was preferred to avoid passivation caused by silicon dioxide formation intentionally. At the same time, incorporation of an large amount of Si may disrupt the crystal structure of pentlandite phase as a common behavior of sulfur bonded atom<sup>[29]</sup>. On the other hand, the Si-adsorbed FCNSSi-RT sample had a chemical composition of  $\text{Fe}_{3.1}\text{Co}_{2.94}\text{Ni}_{2.95}\text{S}_{8.61}\text{Si}_{2.21}$ , which is not in accord with the chemical composition of the pentlandite phase and provided evidence of Si adsorption and/or  $\text{SiO}_2$  formation at the surface of FCNS at room temperature. This observation is further explained in XPS spectra that provide evidence to the surface modification of the FCNS sample after aging in  $\text{SiCl}_4$  at room temperature (**Figure S4**). The Si  $2p$  orbital peak was deconvoluted into several peaks, revealing the presence of Si with different oxidation states, as expected from

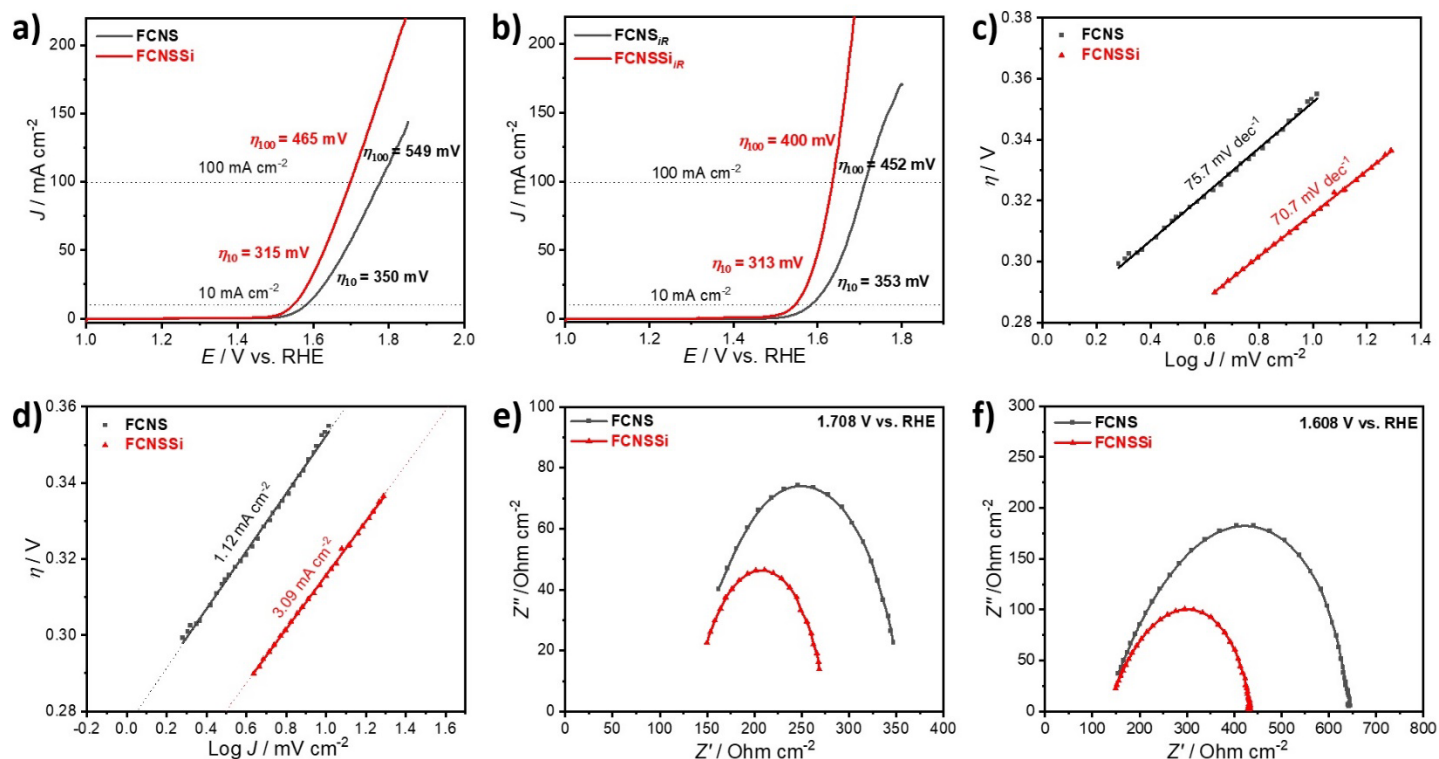
SiCl<sub>4</sub>. Additionally, deconvolution of the high-resolution XPS scan of the S 2*p* orbital shows a peak at around 103.5 eV that could be attributed to oxidized silicon at FCNS surface [49].

To investigate the effect of silicon on the porous nature of FCNS and FCNSSi powders, we performed nitrogen gas adsorption-desorption isotherms (**Figure S5a**). There was a clear change in sorption behavior, which could be attributed to the incorporation of Si atoms and resulted in a remarkable increase in the BET surface area of FCNSSi (120.19 m g<sup>-1</sup>) compared to FCNS, which had a BET of 93.49 m g<sup>-1</sup> (**Figure S5a**). Surprisingly, the FCNSSi-RT shows a significant improvement in the specific surface area (230.08 m g<sup>-1</sup>) reflecting the significant changes in the surface due to Si adsorption, but without support to the electrocatalytic activity (**Figure S5a**). The average pore size distribution curves are depicted in **Figure S5b**. The three samples each showed an average pore size distribution of 170 nm within the range of macroporous materials according to IUPAC classifications [50], which might indicate that porosity originated from the interlayer spaces. In addition, FCNSSi-RT sample shows one more different average pore size distribution of 70.4 nm within the macropores change as well. This result might be additional evidence for foreign phase formation at FCNS surface due to treatment with SiCl<sub>4</sub> at room temperature.

### ***OER performance of FCNS and FCNSSi***

To assess the OER performance of our catalysts, we subsequently analyzed the materials using LSV both with and without iR compensation. Figure 3a and 3b illustrate the results obtained. To precisely evaluate the catalyst performance, we performed the measurements before and after iR compensation (between 4 to 7 Ω) for the whole electrodes. We found that FCNSSi exhibited superior OER performance, with an overpotential of 315 mV at 10 mA cm<sup>-2</sup>, outperforming pristine FCNS, which showed an overpotential of 350 mV (**Figure 3a**). At elevated current density of 100 mA cm<sup>-2</sup>, still FCNSSi shows superior performance (465 mV) compared to pristine FCNS (549 mV) (**Figure 3a**). In particular, FCNSSi showed an overpotential of 313 mV at 10 mA cm<sup>-2</sup>, compared to FCNS, which showed an overpotential of 353 mV (**Figure 3b**). The improvement is significant at higher current density (100 mA cm<sup>-2</sup>), whereas FCNSSi displays an overpotential of 400 mV, which is significantly better than that of pristine FCNS (452 mV) at identical conditions (**Figure 3b**).

To gain additional insight into the kinetics of oxygen formation on our catalysts, we calculated the Tafel slopes and exchange current densities (*J*<sub>0</sub>) (**Figure 3c and 3d**). Our results indicate that the FCNSSi sample exhibited fast oxygen formation kinetics with the lowest Tafel slope of 70.7 mV dec<sup>-1</sup> (**Figure 3c**) and a high *J*<sub>0</sub> of 3.09 mA cm<sup>-2</sup> (**Figure 3d**). These findings represent a significant improvement over previously published results (see Table S2).



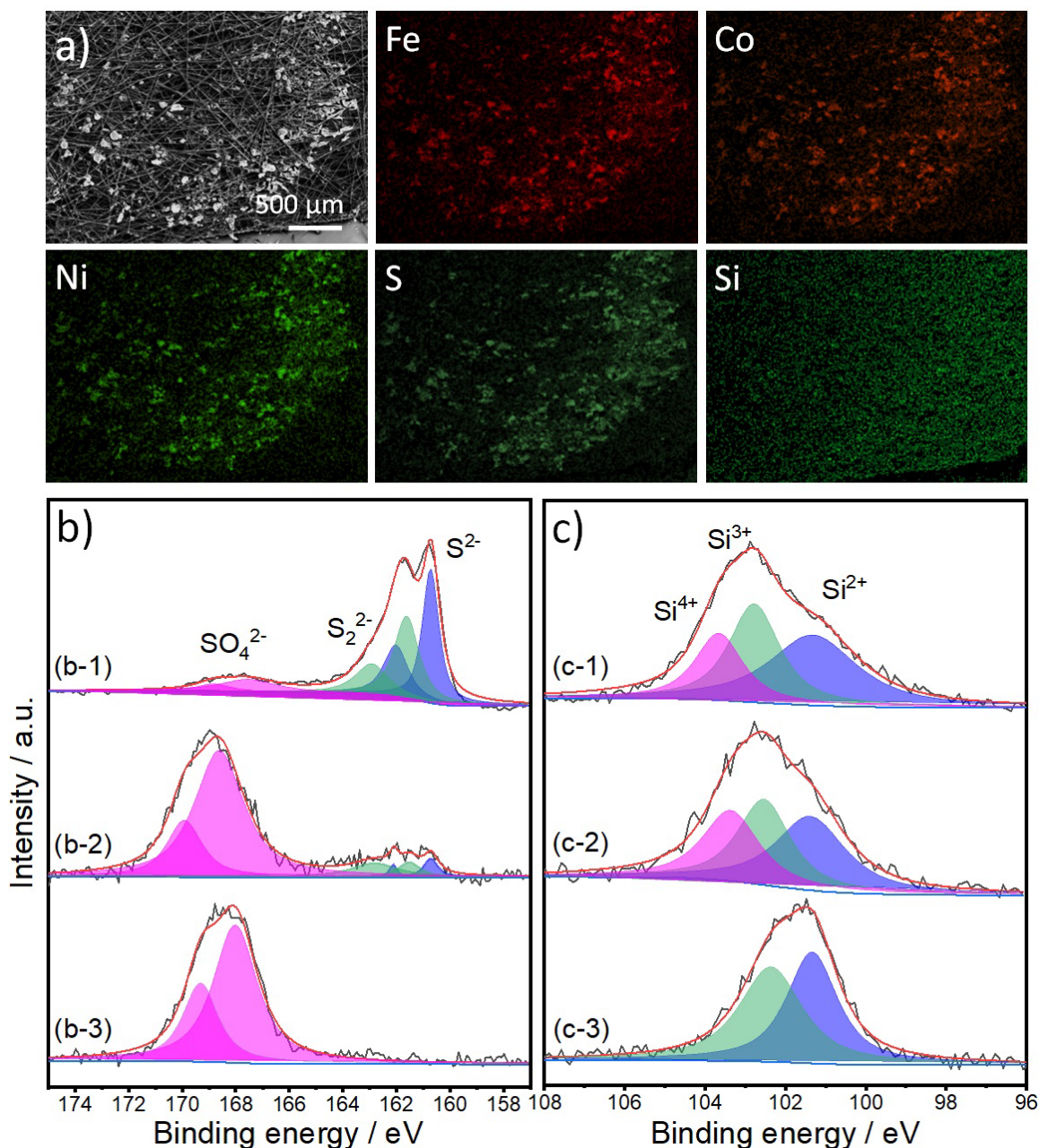
**Figure 3** LSV curves a) before and b) after  $iR$  compensation in 1.0 M KOH solution at scan rate of 10 mV s<sup>-1</sup>, c) derived Tafel plots from LSV curves, d) the estimated exchange current density ( $J_0$ ), and EIS at e) 1.708 V vs. RHE and f) 1.608 V vs. RHE of our materials on glassy carbon electrode.

To elucidate the charge transfer speed, we conducted Electrochemical Impedance Spectroscopy (EIS) at different potentials at 1.71 V and 1.61 V versus RHE to enable polarization at the catalyst surface (refer to **Figure 3e,f**). It is widely recognized that pentlandites have high conductivity due to their high metal-to-sulfide ratio [51]. The FCNSSi sample displayed a very narrow Nyquist arc (117  $\Omega$  cm<sup>-1</sup> at 1.71 V vs. RHE and 275  $\Omega$  cm<sup>-1</sup> at 1.61 V vs. RHE), indicating a fast charge transfer at the interface between electrode and electrolyte, supporting its excellent OER performance. We calculated the electrochemical surface-active area (ECSA) by measuring the dielectric charging current in a non-faradic region using cyclic voltammetry at various scan rates (refer to **Figure S6**). The FCNSSi material demonstrated a higher  $C_{dl}$  value (2.66 mF cm<sup>-2</sup>), implying a high ECSA (6.39 cm<sup>2</sup>), which represents a twofold increase over pristine FCNS (1.28 mF cm<sup>-2</sup> and 3.07 cm<sup>2</sup>). This result, combined with an improved specific surface area/BET, supports our initial hypothesis that Si doping can increase the number of active sites for better OER performance.

To identify the gases produced during the oxidation process, we analyzed the gases obtained in an inert argon gas carrier using gas chromatography (GC) at 20 mA cm<sup>-2</sup> for 1 hour (refer to **Figure S7**). It is evident that the primary product is O<sub>2</sub> gas. Catalyst stability is a crucial factor for its potential industrial applications; therefore, we performed a long-term stability test of our materials for 24 hours at a high current density of 100 mA cm<sup>-2</sup> (**Figure S8a**). FCNSSi exhibited an increase in performance in the first few hours followed by almost stable catalytic OER

performance, reflecting its high durability compared to pristine FCNS, which continuously loses its OER activity over time. At the same time, we examined the surface structure, morphology, and composition of the FCNSSi sample on carbon paper electrode after the stability test using Scanning Electron Microscopy (SEM) (**Figure 4a**), XPS (**Figure 4b,c**), Energy-Dispersive X-ray Spectroscopy (EDX) (**Figure S9**), PXRD (**Figure S8b**). The SEM and atom mapping images clearly depict the homogenous distribution of Fe, Co, Ni, S, and Si atoms on the surface of carbon paper, even after the long-term stability test (**Figure 4**).

The high resolution XPS spectra of S 2*p* orbital collected from FCNSSi/CPE is like those of the as-prepared powder (**Figure 4b-1**). There are three doublets that are assignable to sulfides, disulfides, and sulfate species. After one hour of performance the doublet corresponding to sulfides and disulfides species are decreased in intensity and, at the same time, the doublet corresponding to sulfate species are remarkably increased (**Figure 4b-2**). After 24 hours of performance the whole surface is oxidized ((**Figure 4b-3**), which is in agreement with the XRD patterns (**Figure S8**) reflecting that the surface tends to oxidize during OER performance, forming a more thermodynamically stable transition metal oxyhydroxide shell, which is in line with our previous work <sup>[16]</sup>. The XRD peaks are assigned to carbon paper <sup>[52]</sup>, iron and cobalt oxyhydroxide <sup>[53]</sup>, nickel oxyhydroxide <sup>[54]</sup>, and iron oxides <sup>[55]</sup>. This phenomenon has been extensively studied previously, as transition metal oxides and hydroxides (oxyhydroxides) are more thermodynamically stable than transition metal chalcogenides, particularly sulfides <sup>[56-58]</sup>. On the other hand, XPS spectra of the Si 2*p* orbital collected from the as-prepared FCNSSi/CPE and after one-hour OER performance are similar to the spectra collected from the as-prepared powder (**Figure 4c-1, c-2**). The peak at 103.4 eV disappeared, which suggests the dissolution of some oxidized silicon species after long term OER performance (**Figure 4c-3**) <sup>[49]</sup>. The decrease in sulfur content herein was determined by EDX after long-term OER performance (24h at 100 mA cm<sup>-2</sup>) on FCNSSi (Fe<sub>3.01</sub>Co<sub>3.078</sub>Ni<sub>2.93</sub>S<sub>4.98</sub>Si<sub>0.95</sub>) (**Figure S9**). All previous results indicate that sulfur from the surface is oxidized during OER, and the surface is dominantly composed of Si, S, and O atoms which we anticipate is significant contribution to OER catalytic performance.



**Figure 4** a) Top-view SEM and the corresponding atom mapping images of FCNSSi on carbon paper electrode after chronopotentiometry test at  $100 \text{ mA cm}^{-2}$  for 24h. High resolution XPS spectra of b) S 2p and c) Si 2p orbitals of the prepared electrode, and after 1h and 24h OER.

Due to its low boiling point of  $57.6^\circ\text{C}$  and tendency to evaporate at room temperature, we also tested the doping process of  $\text{SiCl}_4$  on pentlandite ( $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ ) at ambient conditions (**Figure 1**, left side). To characterize the morphology and composition, we performed SEM and EDX measurements on FCNSSi-RT powder (**Figure S10**). The SEM images suggest that either a phase segregation occurred, or that more than one phase is produced (**Figure S10a**). The element mapping images reveal that the overlapping of Fe, Co, Ni, S, O, and Cl, while the Si signals are not overlapping. These results, in addition to presence of chloride ions, may likewise indicate an unsuccessful Si doping at room temperature, which suggests that the Si atoms may have been only adsorbed on

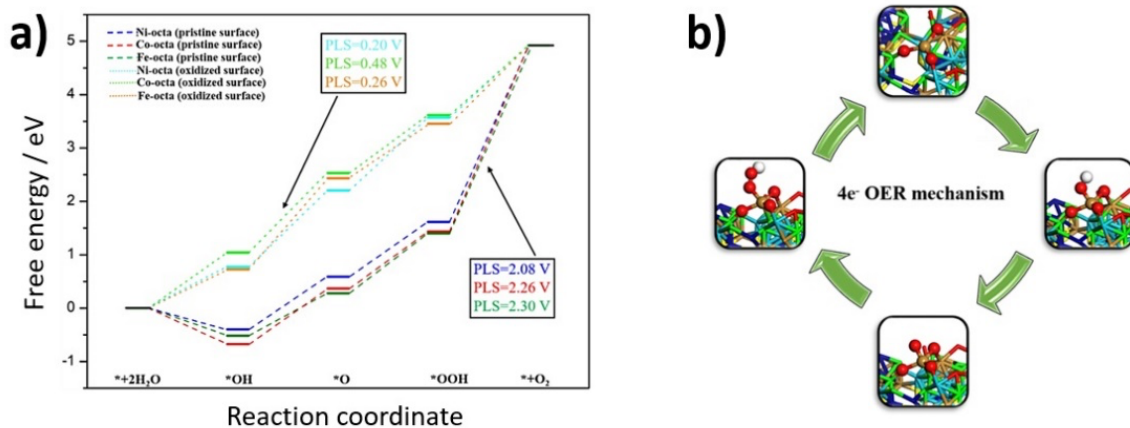
the surface (**Figure S10b**). Notably, XRD analysis showed typical diffraction peaks characteristic of pentlandite, indicating that the FCNS crystal structure was retained (**Figure S11a**). Despite this observation, the FCNSSi-RT sample exhibited poor OER and HER performances compared to FCNSSi obtained at 800°C (**Figure S11d,e**), supporting the idea that Si doping in FCNS is preferable to Si adsorption on FCNS for OER. It is expected that Si adsorption may block the active centers on the metal surface, leading to a decrease in OER catalytic activity.

### ***Theoretical study of FCNSSi on OER***

To understand the observed enhancement of OER activity for FCNSSi, DFT calculation was conducted to analyze the whole process of the four-electron OER reaction on different metal site moieties embedding in FCNSSi matrix. Considering the conditions of OER in our previous work the surface of catalyst was oxidized as is the case here the surface would oxidize to be covered by 7/4 ML of O\* <sup>[16]</sup>. The calculations were performed on the optimized (111) surface. As expected, the oxidation of the surface lead to the formation of self-assembled amorphous metal oxide (**Figure S12**), where similar observations were noted for pentlandite doped by nitrogen and phosphorus in our previous work by combining systematic experimental and theoretical studies <sup>[16]</sup>. These findings may explain the outstanding OER activity of the pentlandite catalyst compared to other crystalline catalysts since the amorphous catalysts are reported to show better activities of water splitting reaction than their crystalline counterparts <sup>[59]</sup>.

To quantify further OER activity of the FCNSSi, we investigated the atomic-scale mechanism of OER on the clean FCNSSi and FCNSSi oxidized surface, as depicted in **Figure 5**. We found that the potential limiting step for the unoxidized FCNSSi surface corresponds to the oxidation of \*OOH intermediate to form the O<sub>2</sub> product. The calculated overpotential on clean FCNSSi surface was 2.08, 2.26 and 2.30 V for Ni, Fe, and Co metal sites, respectively. The high overpotential can be ascribed to the strong binding between \*OOH and metal atoms. However, as described in **Figure 5a**, oxidation of FCNSSi surface significantly adjusts binding of the intermediates on the surface, which weakened the \*OH, \*O and \*OOH adsorption energies compared with those on clean FCNSSi surface. Therefore, the calculated theoretical overpotential significantly decreased to 0.20, 0.26 and 0.48 V on Ni, Fe, and Co metal site, respectively in oxidized FCNSSi. By comparing the OER energy profile of Si with the N and P dopant in our previous publication <sup>[16]</sup>, it is clear that Si dopant leads to moderate adsorption energy of intermediates closer to the ideal energy profile showing the advantage of Si doping over the pristine FCNS and N and P dopants as well.





**Figure 5** a) Quantum-theoretical calculations at the level of density functional theory (DFT) on the electrocatalytic OER performance in FCNSSi, and b) the computational optimized OER intermediates on Fe in FCNSSi.

### HER performance of FCNS and FCNSSi

As mentioned in the introductory part, both ionic and metallic forms of silicon show promise for hydrogen production. Therefore, it is necessary to also evaluate the potential of FCNSSi for HER. The catalytic HER performance of the FCNSSi sample was thus subsequently assessed using LSV measurements on a glassy carbon electrode (GCE). While the HER performance of the as-prepared FCNSSi electrode was significantly improved compared to the pristine FCNS, it achieved a current density of only  $-10 \text{ mA cm}^{-2}$  at a high overpotential of 425 mV (**Figure 6a**).

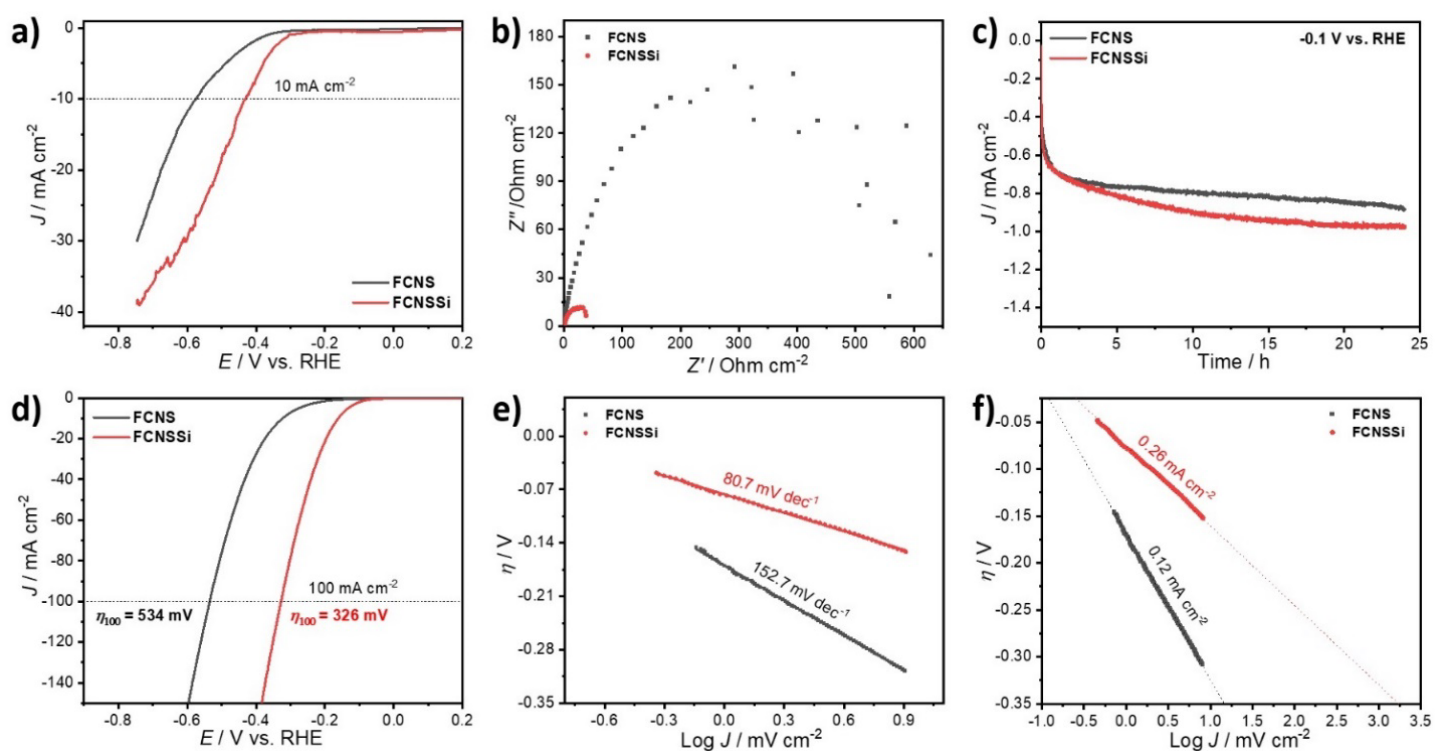
However, the FCNSSi electrode showed a much smaller Nyquist arc around  $45.0 \Omega \text{ cm}^{-2}$ , compared to FCNS ( $600 \Omega \text{ cm}^{-2}$ ) (**Figure 6b**), indicating a faster charge transfer between the electrode-electrolyte interface. After 24 hours of FCNSSi electrode performance, a significant HER improvement was observed (**Figure 6c**) and the activated FCNSSi electrode achieved a current density of  $-10 \text{ mA cm}^{-2}$  at an overpotential of 164 mV and a low Tafel slope of  $80.7 \text{ mV dec}^{-1}$ , which was significantly better than the pristine FCNS materials (316 mV and  $152.7 \text{ mV dec}^{-1}$ , respectively) at identical conditions (**Figure 6d and e**). These results were also better than those reported for previously published pentlandite materials in terms of energy required for water reduction and kinetics of hydrogen formation (**Table S3**). Additionally FCNSSi ( $\eta_{100} = 326 \text{ mV}$ ) significantly displays HER performance better than pristine FCNS ( $\eta_{100} = 534 \text{ mV}$ ) at  $-100 \text{ mA cm}^{-2}$  (Figure 6c). To obtain further information concerning the HER rate and kinetics, we estimated the exchange current density ( $J_0$ ) from the intercept between the equilibrium potential at an overpotential of zero (**Figure 6f**). The calculated  $J_0$  for FCNSSi was  $0.26 \text{ mA cm}^{-2}$ , which is almost twice the value for FCNS reflecting the faster hydrogen formation rate in case of FCNSSi electrocatalyst ( $0.12 \text{ mA cm}^{-2}$ ).

Furthermore, to identify and estimate the amount of  $H_2$  produced through hydrogen evolution in acid solution, we performed gas chromatography (GC) (**Figure S13**). We applied a current density of  $-20.0 \text{ mA cm}^{-2}$  for 10 hours



and injected the GC one time every hour. The chromatogram showed that the main product was  $\text{H}_2$  gas, with negligible traces of  $\text{O}_2$  and  $\text{N}_2$  that might have been due to air inside the tubes (Figure S14a). The faradic efficiency was calculated to be  $109 \pm 10 \%$  for FCNSSi and  $94 \pm 10 \%$  for FCNS on a carbon paper electrode at identical conditions (Figure 7b) (Table S4). To receive postmortem information on a FCNSSi on a carbon paper electrode before and after chronopotentiometry tests at  $-20.0 \text{ mA cm}^{-2}$  for 10 hours, we performed PXRD analysis (Figure S14). The pentlandite crystal structure was well-preserved, indicating high structural stability and durability of FCNSSi during  $\text{H}_2$  evolution in acidic solution.

The HER results in combination with the OER clearly demonstrate that the FCNSSi electrode is a highly active and stable bifunctional electrocatalyst for both HER and OER. To investigate its potential and durability for overall water splitting, we designed a two-electrode cell in which FCNSSi served as both anode and cathode in an alkaline solution (Figure S15 and S16).



**Figure 6** a) LSV curves of the as-prepared FCNS and FCNSSi in 0.5 M  $\text{H}_2\text{SO}_4$  solution at scan rate of  $50 \text{ mV s}^{-1}$ , b) EIS at  $-0.155 \text{ V vs. RHE}$ , c) chronoamperometry test at  $-0.1 \text{ V vs. RHE}$ , d) LSV curves after HER performance for 24 e, f) the derived Tafel plots of FCNS and FCNSSi samples on glassy carbon electrode.

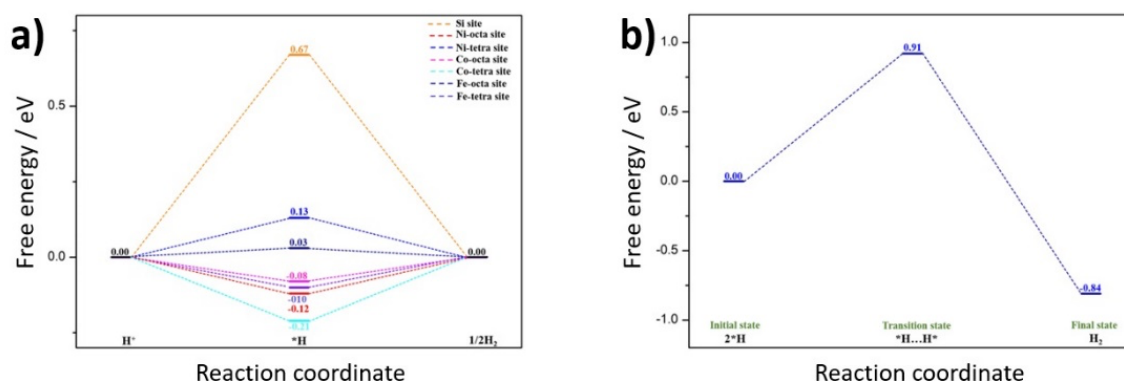
### Theoretical study of FCNSSi on HER

To further understand the HER activity and nature of active sites on the hypothetical silicon doped FCNS, the adsorption free energy of hydrogen for the possible sites were calculated to estimate their catalytic activity toward HER (Figures S17a). The hydrogen adsorption free energy is calculated at a potential  $U = 0$  relative to the

standard hydrogen electrode (SHE) at pH = 0. Although our synthesis strategy envisioned doping of FCNS with Si, we considered Si adsorption as an alternative possibility for the modification of the material (**Figures S17b and S17c**). We proposed Si atom adsorbed and atomically dispersed on the surface. After optimization of the structure, we found that the adsorption of a single Si atom on the surface is unstable. The DFT calculation suggests that the adsorbed Si atoms lead to aggregate forming small clusters  $\text{Si}_3$  or  $\text{Si}_4$  atoms on the metal site (Fe, Co and Ni) on the surface leading to blocking hydrogen adsorption active sites, which agrees with our experimental results (**Figures 7 and S11b**). In this case the Si sites were supposed to be the only possible site for HER. The calculated free energy illustrated in **Figure 7a** shows that the Si site exhibit a high  $\Delta G^*\text{H}$ , indicating its limited HER activity due to excessive binding strength.

On the other hand, compared to Si adsorbed at FCNS (FCNSS-RT), Si doping in FCNS (FCNSSi) enhances the hydrogen adsorption activity of all sites. We found the global minimum energy of hydrogen adsorption on each type of metal site tends to be much closer to zero, where the  $\Delta G^*\text{H}$  in the range of (0.10, -0.2) eV, as depicted in **Figure 7a**. Moreover, DFT calculations have shown that  $\text{H}^*$  adsorbs on the surface as bridging two metal atoms explaining the improvement of H adsorption activity over the sites following Heyrovsky mechanism (**Figure S15c,d**).

Alternatively, the hydrogen evolution could proceed *via* the Tafel reaction. Therefore, we studied the Tafel reaction energetics on Fe octahedral site as an example (**Figure 7b**). The results show that the Tafel reaction requires an energy barrier of 0.91 eV. The overall reaction energy from  $2\text{H}^*$  to  $\text{H}_2(\text{g})$  is -0.84 eV (exothermic). This result indicates that the Tafel reaction seems to be kinetically unfavorable compared to Heyrovsky reaction in our study. This result is in accordance to our previous work, whereas a Volmer-Heyrovsky mechanism is favorable to the pristine FCNS [17]. Smialkowski et al. found that the content of Co plays a significant role in manipulating the HER mechanism and kinetics [17]. The Co-rich FCNS adapts a Volmer-Heyrovsky mechanism, while the mechanism shifts to a Volmer-Tafel mechanism with increasing Fe or Ni content.



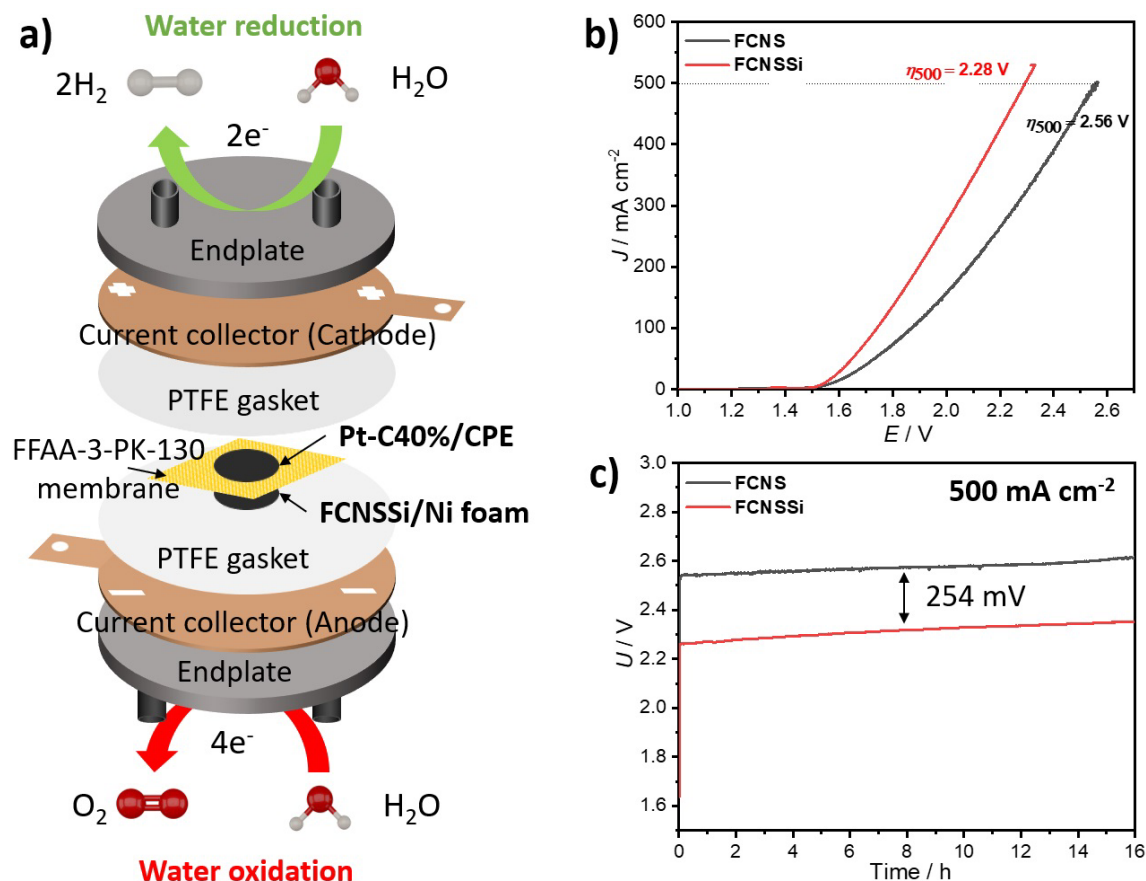
**Figure 7** Quantum-theoretical calculations at the level of density functional theory (DFT) on the electrocatalytic HER performance in FCNSSi *via* a) Volmer-Heyrovsky and b) Volmer-Tafel mechanisms.

### ***Zero-gap Cell Experiments***

To assess the effectiveness of the materials presented here on an industrial scale, we constructed a zero-gap cell in-house using FCNssi deposited through thermal drop casting at 90 °C on Ni-foam on the anodic side (FCNssi/Ni foam), and Pt/C(40%) on CPE on the cathodic side (Pt-C/CPE) for alkaline water electrolysis (**Figure 8a**). The results of LSV measurements showed that FCNssi had better performance towards water oxidation compared to the pristine FCNS electrode (**Figure 8b**). The overpotential estimated for the FCNssi/Ni foam electrode at 500 mA cm<sup>-2</sup> is 2.28 V, outperforming the pristine FCNS/Ni foam electrode (2.56 V). The long-term chronopotentiometry test at an elevated current density of 500 mA cm<sup>-2</sup> further confirmed the high performance and durability of FCNssi/Ni foam, with an overall cell potential of approximately 2.31 V for 16 h (**Figure 8c**). There is a potential increase of around 23.0 mV after 16h of consecutive performance at 500 mA cm<sup>-2</sup>, which represents a loss of 0.99% (3 mV h<sup>-1</sup>) in the overall cell voltage (**Figure 8c**). It is currently unclear if this drop stems from an overall material decomposition or mechanical faults of the electrode assembly/membrane. In contrast, the pristine FCNS/Ni foam electrode demonstrated lower performance, with a higher cell potential of 2.58 V.

As a reference cell, we constructed a zero-gap cell using bare CPE as the cathode and FCNssi/Ni foam and bare Ni foam as anodes. The chronopotentiometry test at 500 mA cm<sup>-2</sup> showed an improvement in the FCNssi/Ni foam electrode compared to bare Ni foam by 679 mV, reflecting the significant contribution of the FCNssi catalyst towards the water oxidation activity (**Figure S18**).

Likewise, to evaluate the HER catalytic performance in 1.0M KOH, we constructed a zero-gap cell in which FCNssi/CPE acted as the cathode against bare Ni foam as the anode (**Figure S19a**). The cell achieved a cell voltage of 2.56 V at -100 mA cm<sup>-2</sup>, with an average steady FE% of 104±5% within 10 hours of performance (**Figure S19b**), which agrees with the three-electrode set up results (**Figure S13b**).



**Figure 8** a) Zero-gap cell assembly using FCNssi on Ni foam at anodic side against Pt/C (40%) on CPE at cathodic side, and b) LSV measurements, and c) chronopotentiometry test at  $500 \text{ mA cm}^{-2}$  for 16 h of both pristine FCNS and FCNssi on Ni foam electrodes.

## Conclusion

In this study, we successfully doped heterotrimetallic pentlandite (FCNS) with silicon (Si) atoms through controlled annealing at  $800^\circ\text{C}$  in an inert atmosphere of pristine FCNS and  $\text{SiCl}_4$  mixture. The obtained FCNssi exhibited superior performance and durability towards electrochemical OER in alkaline solution with an overpotential 313 mV at  $10 \text{ mA cm}^{-2}$  and a Tafel slope of 70.7 mV/dec and HER in acid solution with an overpotential 164 mV at  $-10 \text{ mA cm}^{-2}$  and a Tafel slope of 80.7 mV/dec for overall electrochemical water splitting, outperforming pristine FCNS. Moreover, the FCNssi electrode exhibited exceptional durability and robustness for long-term HER and OER. For comparison, the pristine FCNS was treated with  $\text{SiCl}_4$  at room temperature to obtain FCNssi-RT. We found that the FCNssi-RT has neither improved OER nor HER implying that heating is necessary for Si atom doping. The DFT calculation suggested that the surface oxidation of FCNssi during OER improved its performance by weakening the adsorption energy of  $\text{*OH}$ ,  $\text{*O}$  and  $\text{*OOH}$ . Additionally, Si doping in FCNS structure led to moderate adsorption energy of intermediates closer to the ideal energy profile, showing the advantage of Si doping over the pristine FCNS. Furthermore, Si doping in FCNS structure enhanced the

hydrogen adsorption activity of all sites, where the global minimum energy of hydrogen adsorption on each type of metal site tended to be much closer to zero, thereby improving the HER performance.

Our results suggest competitive performance of FCNSSi with previously published materials towards overall electrochemical water splitting. The zero-gap cell testing further confirmed the excellent FCNSSi activity and robustness for long-term alkaline water electrolysis. Si doping of metal sulfides is therefore an effective strategy to improve catalytic activity by adsorption of hydrogen on unoxidized pentlandite and \*OOH on oxidized pentlandites and possibly other metal chalcogenides.

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