Seleno-analogues of pentlandites (Fe_{4.5}Ni_{4.5}S_{8–y}Se_y, Y = 1–6): tuning bulk Fe/Ni sulphoselenides for hydrogen evolution†

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We herein present a series of hitherto unprecedented seleno-pentlandites (Fe_{4.5}Ni_{4.5}S_{8–y}Se_y). By analysing the influence of S/Se exchange on the catalyst structure and activity in the electrochemical hydrogen evolution reaction we herein showcase the potential and limitations of homologous S/Se exchanges within pentlandite HER catalysts.

The electrocatalytic splitting of water using renewable energy is widely recognized as a promising process to establish a sustainable hydrogen production (hydrogen evolution reaction, HER) and to replace traditional fossil fuel-based technologies which are strongly connected to detrimental effects on the environment.1,2 Consequently, developing catalysts made from cheap and abundant materials has become a central issue to improve the inherently sluggish kinetics of the HER and to supersede costly noble metal catalysts, e.g. Pt.3 In this respect, non-noble metal chalcogenides, especially transition metal sulphides of Mo_xS_y, W_xS_y, Co_yS_z, Mo_yS_z, W_yS_z and Ni^{15–17} were reported in recent years.18,19 Despite being efficient HER catalysts, most of these materials suffer from intrinsically low conductivity and/or limited durability which makes sophisticated nanostructuring and conductive support materials a necessity.18 These downsides can potentially be overcome by employing chalcogen minerals of the pentlandite type (M_xS_y, e.g. Fe_{4.5}Ni_{4.5}S_{8} and Ni_{4.5}Co_{4.5}S_{8}) with their pseudo-metallic character and high robustness under acidic and alkaline conditions.20–22 In particular Fe/Ni-containing pentlandites, which can be regarded as mineral analogues of hydrogenase active sites, offer enormous potential to replace platinum in the HER.20,23

Recently, we reported on the bulk mineral pentlandite (Fe_{4.5}Ni_{4.5}S_{8}) as a stable and efficient HER catalyst reaching an overpotential as low as 190 mV at 10 mA cm^{-2}. Remarkably, this material was shown to withstand even potent sulphur-containing catalyst poisons, such as H_2S. The overall activity of Fe/Ni-pentlandites was found to crucially depend on the exact Fe/Ni-ratio employed and enables to modulate the metal–metal interactions, electronic properties of the surface and thus the hydrogen absorption sites.24 Similarly, it can be assumed that substitution of sulphur with its higher homologue selenium will affect the material’s catalytic efficiency due to the altered bond lengths and electronic properties introduced by Se with its increasing metallic character. In particular, since reports on Ni- and Co-diselenides suggest an elevated HER activity compared to their disulphides, investigations on selenium-containing pentlandites appear highly desirable.25 We thus herein report on the synthesis, the characterisation and catalytic performance of a series of pentlandites with the general intended formula Fe_{4.5}Ni_{4.5}S_{8–y}Se_y (Y = 0–8).

Synthesis of the materials and pentlandite (Pn) for comparative reasons was attempted via a high-temperature solid state method directly from a mixture of the respective elements. The ratio of S:Se employed was adjusted to the desired stoichiometry according to the formula Fe_{4.5}Ni_{4.5}S_{8–y}Se_y (Y = 1–8, Se_1–Se_8). Powder XRD measurements were performed on all obtained materials and a comparison to synthetic Pn is depicted in Fig. 1A. The obtained reflexes of the compounds Se_Y (Y = 1–5) indicate an overall similar structure, which agrees well with that of synthetic Pn. However, it is evident from the PXRD spectra that compounds Se_6, Se_7 and Se_8 show major contribution of non-pentlandite phases that were identified as mixed iron nickel sulphides and selenides (Fig. S1, ESI†). Although the pentlandite phase is still present in Se_6, it diminishes in Se_7 and is not observed in Se_8 indicating that Pn with a high selenium content is not accessible via this synthetic route.

These findings are also supported by differential scanning calorimetry (Fig. 1B). Here, the characteristic pentlandite-type...
phase transitions in Se1–Se5 between 600°C and 650°C and 800°C and 875°C are observed. Starting from Se6, these transitions are less pronounced in Se7 and not observed in Se8.

To shed light on the structure of Se-containing pentlandites, single crystals of Pn, Se1 and Se4 were grown from the bulk materials by the vapor transportation method upon exclusion of air.26 After several weeks, small hexagonal and cubic crystals with gold-metallic shine were obtained. The single crystal diffraction experiments confirmed the expected cubic space group $Fm\bar{3}m$ with lattice constants of 10.12 Å and 10.41 Å for Se1 and Se4, which are larger than those of Pn (10.11 Å). A schematic representation of the structures is presented in Fig. 1C (see the ESI† Section S2.4 for details). Se1 and Se4 are found to be isostructural compared to Pn with Fe/Ni as well as the chalcogenides adopting two distinct sites each in the asymmetric unit. By analogy to Pn, Fe and Ni seem interchangeable on both metal-containing crystallographic sites in Se1 and Se4. The structural solutions further indicate that S and Se are, to some extent, interchangeable. For both selenium-materials, however, the most consistent models were obtained by preference occupation of the Wyckoff position 8c with sulphur (yellow dots in Fig. 1C, S exclusively for Se1 and Se < 10% for Se4), whereas the Wyckoff position 24e (Fig. 1C, blue dots) appears capable of hosting both S and Se without noticeable preference. Assuming that the site 8c can host exclusively sulphur implies an upper bound of the Se : S ratio of about 3 : 1 for selenium-containing pentlandites, which is consistent with the observation that Se6 (ratio Se : S, 3 : 1) is the first compound of the synthetic series to experimentally yield phase impurities. This is further in line with the PXRD data of Pn phases of Se7 and Se8 not being accessible.

A key role for the catalytic activity of pentlandites is attributed to the distance between the different metal sites.27 For Se4, values of 2.64 Å (metal cluster) and 3.59 Å (metal atoms next to site 8c) were found, which are significantly larger than Pn (2.55 Å and 3.54 Å, respectively) and expected to notably influence the catalytic behaviour of the material. In the same fashion, the distances between the metals and the chalcogens are significantly enlarged in Se4 (Table S2, ESI†). In contrast, Se1 (2.56 Å and 3.54 Å) remains comparable to Pn.

Additionally, the morphology of the bulk materials was evaluated by SEM measurements (Fig. S2, ESI†). In all cases, no specific nanostructuring was observed and the particle size and the shape appear to be randomly distributed. Much like Pn, the resulting catalytic properties of the materials are thus solely ascribed to the intrinsic material properties.28 EDX measurements were performed to analyse the surface composition of Se1–Se5 (Fig. S4, ESI†). As expected, the selenium content on the surface gradually increases from Se1 to Se5, whereas the amount of sulphur decreases and reflects the trends observed in the bulk material. For catalytic experiments, only the phase-pure materials Se1–Se5 were evaluated and compared with the previously described Pn catalyst. Custom-made and polished pellet electrodes,28 exhibiting a defined surface area of 0.071 cm$^{-2}$, were conditioned electrochemically by cyclic voltammetry (CV) until at least five reproducible CV curves were obtained.

After the electrochemical conditioning, the HER activity of the catalyst materials was analysed by linear sweep voltammetry. The overpotentials at $-10$ mA cm$^{-2}$ were determined to be in a range between 273 mV and 339 mV vs. RHE for all investigated compounds. The curves are shown in Fig. 2A. It is evident that the electrocatalytic activity is severely influenced by the amount of selenium incorporated. The overall trend

![Fig. 1](https://example.com/fig1.png) **Fig. 1** Comparison of powder diffraction patterns of synthesised materials Se1–Se8 and Pn (A), differential scanning calorimetry of SeY and Pn (B) and schematic representation of the crystal structure of Pn/SeY (C). For Pn the blue S/Se positions are exclusively occupied by sulphur.

![Fig. 2](https://example.com/fig2.png) **Fig. 2** Linear sweep voltammograms of Pn and Se1–Se5 before (A) and after (B) electrolysis. (C) Tafel analysis of Pn and Se1–Se5.
indicates that most overpotentials are increased by the progressive sulphur–selenium exchange, representing a decreased activity for the HER. However, it is encouraging that Se1 shows a slightly improved overpotential of 273 mV at –10 mA cm⁻² compared to Pn (280 mV at –10 mA cm⁻²). In contrast, Se2 shows a significantly decreased HER activity with an overpotential of 336 mV, which is ~56 mV higher than Pn. The performance of Se2 is the lowest in the entire series, whereas compounds Se3 (306 mV), Se4 (300 mV) and Se5 (296 mV) show a better performance. However, their overpotentials are still ~30 mV above that of Se1, indicating that further sulphur–selenium exchange negatively influences the HER activity of pentlandites. It is interesting to note that progressive S/Se exchange does not lead to a monotonic decrease in the HER activity but rather an erratic behaviour. This observation indicates a complex interplay of competing factors ultimately influencing the overall activity.

Recently, the activation mechanism of Pn was elucidated via operando phonon studies.²⁷ The mechanism involves sulphur detachment from the surface during long-term electrolysis at a potential of ~500 mV vs. RHE, leading to a significant improvement of the overpotential over time to a value as low as 190 mV vs. RHE at 10 mV cm⁻².

To determine if a similar activation process occurs using seleno-pentlandites, the same experiment was implemented for the compounds from Se1 to Se5. A potential of ~500 mV vs. RHE was applied to the working electrode for 20 h. Subsequently, potential changes were recorded by linear sweep voltammetry. A significant change in the electrocatalytic behaviour was revealed for all materials (Fig. 2B). The overpotentials generally decrease, indicating an increased HER activity. It is clearly visible that the activation ability of the respective compounds heavily depends on the level of S/Se exchange. The compounds with a low content of selenium, from Pn to Se2, reveal major activation effects. For Se1, an overpotential of as low as 172 mV (Δη = 101 mV) was achieved, even lower than activated Pn (190 mV, Δη = 90 mV). Se2 also undergoes an eminent activation process with an overpotential lowered from 336 mV to 230 mV (Δη = 106 mV). For the compounds with a selenium-content above 2 equivalents the improvement in the catalytic HER performance is significantly smaller.

The difference Δη in the overpotential of the activated versus the non-activated catalyst is in the range between 34 mV and 54 mV for compounds Se3, Se4 and Se5. For Pn, the formation of sulphur vacancies at the Wyckoff position 8c was recently considered crucial and allows for the adsorption of hydrogen in a substitutional manner before less favorable interstitial adsorption sites are occupied.²⁷ Considering the preferential occupation of sulphur sites in the position 8c it seems likely that sulphur depletion is preserved as the key step in activation for Se1–Se5. This observation is consistent with the observed activation behavior which gradually decreases in materials with the increasing selenium content due to the decreasing availability of depletable sulphur. Notably, the overall morphology of the electrodes did not markedly alter in the course of the electrochemical process (Fig. S3, ESI†) suggesting that the increase in current density originates from a change in the surface composition. To test this hypothesis, the differences between the electrochemical active surface area before and after electrolysis were recorded (ESI† Section S3.2) and likewise support that material activation is sulphur dependent. In addition, the differences in the surface composition between non-activated and activated seleno-pentlandites were subsequently investigated by XPS using Se1 and Se4 as representative samples (Fig. 3). The results show that activation of Se1 and Se4 leads to a substantial depletion of surface sulphur (S₂⁻) in Se1 and Se4 consistent with the previously proposed mechanism (Fig. 3, ESI† Section S2.5).²⁷ The spectra of Se1 mainly reveal surface reduction of sulphur, whereas the XP spectra of Se4 are dominated by surface reduction of Se(w) species to Se(0). In the case of Se4, Se apparently depletes from the surface which might account for the increasingly hampered activation-margin Δη with the increasing Se content. Taken together, catalyst activation is attributed to extensive reductive processes at the surface combined with depletion of sulphur, most likely from the Wyckoff position 8c.

Considering the decreased overall activity of Se2–Se5 and assuming a similar mechanism compared to Pn, we believe that H-adsorption at the position 8c is less efficient in Se2–Se5 possibly even leading to additional or preferential H-adsorption at other (interstitial) binding sites. This assumption is supported by the elongation of the average metal–metal distances for the position 8c (S-detachment site and H-adsorption site), which increases from 3.54 Å (Pn) to 3.59 Å (Se4) and certainly influences the absorption properties. In line with this assumption is the observation that metal–metal distances in Se1 are close to that of Pn, but apparently providing even slightly better structural and electronic conditions for H₂ formation.

Although deposited Pt from the counter electrode can contribute to the observed phenomena, control measurements with a glassy carbon counter electrode and measurements utilizing an H-type cell revealed the same trends as observed before (Fig. S8, ESI†). Thus, Pt deposition is not a major factor in our study.

Further information on the reaction mechanism can be deduced from Tafel analysis (Fig. 2C). Notably, the Tafel plots show an increase of the slopes of the selenium-containing compounds by ~40 mV dec⁻¹ compared to the selenium-free compounds. Thus, instead of the reaction between two adsorbed hydrides in the bimetallic centers of the catalyst,
which corresponds to a Volmer–Tafel-like reaction path, it seems more likely to assume a Volmer–Heyrovsky-like reaction path for the seleno-pentlandites. Here, an adsorbed hydride reacts with a solvated proton from the electrolyte. The high values (>100 mV dec⁻¹) of the selenium-containing compounds indicate that the proton adsorption step (Volmer) is rather limiting than the subsequent reaction steps. This is consistent with our assumption that hydrogen-adsorption properties are severely affected, rendering recombination of adsorbed hydrogen-species less likely in Se₁–Se₅. We conclude that introducing low amounts of Se (Se₁) seems to improve the balance between optimal adsorption and subsequent reactivity of adsorbed H-species by modulating the geometric and electronic properties of the H-adsorption sites. The faradaic efficiencies for the HER (Fig. S10, ESI†) were also determined (FE 94–99%) for all compounds and are comparable to those measured for Pu (FE 90%) during 4 h electrolysis (the experimental error is ±5%).

In conclusion, a series of hitherto unprecedented seleno-substituted pentlandites with the general formula Fe₄₋ₓNiₓ₄₋ₓS₈₋ₓSeₓ (Y = 1–5) was successfully synthesized and characterised. Notably, pentlandites with a high selenium content (Se:S ratios ≥ 3:1) are not accessible via this route and instead show major phase impurities. All phase-pure materials are highly efficient for HER catalysis and were found to undergo pronounced activation during electrolysis due to the surface reduction processes and sulphur depletion. In this series, only Se₁ showed a decreased overpotential of 172 mV at −10 mA cm⁻² outperforming the benchmark material Pu (190 mV) and providing evidence for the possibility to further tune Fe/Ni-chalcogenide catalysts via S/Se substitution. Our results likewise show that the incorporation of Se leads to significantly changed interatomic distances and electronic properties on sulphur-depletion sites, which serve as H-adsorption sites in pentlandites. In return, alterations of the adsorption properties of Pu will eventually control its HER performance as reflected in the hampered performance of seleno-pentlandites Fe₁₋ₓNiₓ₄₋ₓS₈₋ₓSeₓ with a high Se content (Y = 2–5).

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Conflicts of interest

There are no conflicts to declare.

References