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Article

Fe/Co and Ni/Co-pentlandite type electrocatalysts for the hydrogen evolution reaction

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ABSTRACT

Metal-rich transition metal sulfides recently gained increasing attention as electrocatalysts for the hydrogen evolution reaction (HER), as they are capable to overcome major challenges faced by sulfide-rich metal catalysts such as limited conductivity and the necessity of nanostructuring. Herein, we present the synthesis, characterization and electrocatalytic investigation of ternary metal-rich sulfide composites $\text{Fe}_x\text{Co}_{9-x}\text{S}_8$ as well as $\text{Ni}_y\text{Co}_{9-y}\text{S}_8$ ($x = y = 0-4.5$), which possess pentlandite-type structures. In this study, we show a stepwise alteration of the binary cobalt pentlandite Co_9S_8 and report on the replacement of cobalt with up to 4.5 equivalents of either iron or nickel. These altered pentlandite composites facilitate the proton reduction in acidic media at different temperatures. We furthermore show that the stoichiometric variation has a decisive influence on the electrochemical activation/deactivation behavior of the catalysts under reductive electrocatalytic conditions. Here, Co-deficient composites display an improved HER performance in contrast to Co_9S_8 . Notably, Ni/Co compounds generally tend to show higher catalytic activities towards HER than their respective Fe/Co compounds.

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1. Introduction

Transition metal chalcogenides, in particular sulfides, are attracting widespread interest as cheap and efficient alternatives to costly noble metal catalysts for the electrocatalytic hydrogen evolution reaction (HER) [1–3]. Recently, especially metal-rich formulations, i.e. phases with a stoichiometric excess of metal atoms or phases providing at least a significant degree of metal-metal bonding were shown to be capable to overcome prevailing challenges encountered for many other metal chalcogenides in the electrocatalytic formation of hydro-

gen [4]. In particular, using the Fe/Ni-containing pentlandites, $(\text{Fe,Ni})_9\text{S}_8$, our group showed that metal-rich metal sulfides benefit from a high metallic character leading to significant improvements in conductivity. In this way, the high metal contents support a high catalytic activity even in bulk form which greatly reduces the need for sophisticated nanostructuring and consequently simplifies and cheapens the production process of these materials [5,6]. Furthermore, these systems provide a high durability with an apparent initial increase in catalyst performance under reductive potentials which was attributed to the formation of additional H-adsorption sites upon deple-

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tion of sulfur from the surface [7,8].

It is well known that the compositional alteration of catalysts, that is the stoichiometric substitution of the corresponding metals and chalcogenides or functional doping with foreign elements [9–11] can have dramatic influences on the overall catalyst performance. Consequently, we probed the influences of the Fe : Ni ratio on the catalytic activity and established that an equal ratio of Fe : Ni provides the highest catalytic performance [6]. Likewise, we showed that substituting one equivalent of sulfur for selenium can increase the catalysts HER properties [12]. However, pentlandite type HER catalysts are not solely restricted to Fe/Ni-containing systems and several transition metals with broad stoichiometric variations are potentially compatible to the pentlandite structure [13]. Especially cobalt containing pentlandites derived from Co_9S_8 have been a subject of intensive investigations for catalyzing the HER, OER as well as for the overall water splitting [14–20]. Up to now, little is known about the HER performance of Co-containing pentlandites with variable ratios of pentlandite related 3d-transition metals Fe and Ni. Along this line, Gao and coworkers showed that the mixed Ni/Co-pentlandite $\text{Ni}_{4.3}\text{Co}_{4.7}\text{S}_8$ can be used as an efficient electrocatalyst for HER and OER [21]. Furthermore, Zhang and coworkers prepared mixed $(\text{Ni}, \text{Co}, \text{Fe})_9\text{S}_8$ /N-doped carbon composite catalysts for water splitting [22]. However, in both cases the catalysts were not applied in their bulk form, but drop-coated on Ni foam with acetylene black and PTFE or coated on glassy carbon electrodes using Nafion as an additive, respectively, which display promising electrode activities but do not necessarily showcase the intrinsic materials properties. Further motivation to explore pseudo-metallic mixed Co/Fe/Ni-sulfides arises from the successful applications of non-pentlandite materials containing the same elements such as CoFeS [23], FeS_2 [24], CoS_2 [25], NiS_2 [26] or Ni_3S_2 [27] which clearly emphasizes the huge potential of non-noble metal sulfides for HER-catalysis. Herein, we explore the possibility of a gradual incorporation of Fe or Ni into cobalt-pentlandite (Co_9S_8) via high temperature synthesis. Likewise, we assess the catalytic activity of the obtained bimetallic Ni/Co- and Fe/Co-pentlandites for the formation of dihydrogen under ambient as well as elevated temperatures.

2. Experimental

2.1. Chemicals

Iron (Sigma Aldrich, 99%), Nickel (abcr, 99.9%) Cobalt (abcr, 99.8%) and sulfur (Sigma Aldrich, 99.5%) were purchased from commercial vendors and used without further purification.

2.2. Synthesis of mixed metal sulfides

The high-purity elements iron, nickel, cobalt and sulfur were thoroughly mixed in a mortar to obtain a homogeneous powder mixture which was transferred to a quartz glass ampule. This ampule was evacuated and sealed under conservation of the reduced pressure of 3×10^{-2} mbar for 24 h. The ampule was

then placed inside of a tubular furnace. Depending on the desired composition, an appropriate temperature profile was applied to produce a composite with a predominant pentlandite phase (see supporting information). The temperature ranged between 700 and 1000 °C covering a period of 24–90 h to obtain a light to dark gray ingot with metallic luster in the inside. This ingot was crushed and ground to a fine grey powder for characterization and electrochemical experiments.

2.3. Characterization

Powder X-ray diffractometry (PXRD) was performed on an X'Pert Powder X-ray diffractometer from Malvern Panalytical or on a Bruker D8 Advance using a Cu radiation source ($\lambda = 1.5406 \text{ \AA}$) at 45 kV and 40 mA at step size of 0.02° .

Scanning electron microscopy (SEM) was performed on a ZEISS Gemini2 Merlin HR-FESEM equipped with an OXFORD AZtecEnergy X-ray microanalysis system for energy dispersive X-ray spectroscopy (EDX) or on a JEOL JSM-6510 plus a SSD-detector EDX unit made by remX GmbH. SEM images were recorded at an acceleration voltage of 20 kV while EDX measurements were performed from 0–20 kV.

The samples were investigated via differential scanning calorimetry (DSC) utilizing a Netzsch STA 449 Jupiter. The samples were heated in covered corundum crucibles from 28 to 1000 °C and cooled to ambient temperatures by a rate of $10^\circ \text{C min}^{-1}$. Nitrogen gas was used as protective and purging gas with a flow rate of 50 mL min^{-1} and 20 mL min^{-1} , respectively. Temperature and device sensitivity were calibrated against high purity In, Zn, Ag and Au standard samples.

The ground material was pressed into pellets with a diameter of 3 mm and height of 2–4 mm. The pellets were then immobilized with a conductive silver epoxide glue into a Teflon housing providing an electric contact via a brass rod. The glue was cured at 60 °C over a period of 12 h. The electrode surface was polished by the help of sanding and polishing paper with gradually finer grit size to obtain a flush and flawless surface with a surface area of 0.071 cm^2 .

2.4. Electrochemical measurements

Electrochemical measurements were performed utilizing a three-electrode setup connected to either a Gamry Reference 600+ or Gamry Reference 1010B potentiostat. The temperature-controlled cell was composed of two compartments filled with 0.5 M sulfuric acid and separated by a Fumasep cation exchange membrane (FUMATECH). The working electrode (WE), consisting of an as prepared pellet electrode, was placed next to the reference electrode (RE, Ag/AgCl, conc. KCl) in the cathodic and the counter electrode (CE, Pt-mesh) in the anodic compartment. All measured potentials have been converted referring to the reversible hydrogen electrode (RHE) according to the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + x + 0.059\text{pH}$ ($x = 0.197 \text{ mV}$ for sat. KCl) and were corrected for the ohmic drop between the WE and RE. At first, the electrode was conditioned by cycling the potential with scan rate of 100 mV s^{-1} in a range of 0–200 mV vs. RHE until the last five cyclic voltammograms match

seamlessly. The electrochemical surface area (ECSA) was determined by measuring cyclic voltammograms in the non-faradaic range starting from 210 to 290 mV vs. RHE scanning at speeds of 160, 80, 120, 40, and 200 mV s⁻¹ in this order. Linear sweep voltammetry (LSV) was performed sweeping the potential from 0 mV to -400 mV vs. RHE by 5 mV per second. Chronoamperometry was carried out during application of constant -400 mV vs. RHE over a period of 20 h. All currents were converted to the current density regarding the working electrodes' geometrical area. For all experiments, the double walled cell was connected to a thermostat and the electrolyte temperature was set to either 25 °C for experiments at room temperature or 75 °C for the elevated temperature experiments.

3. Results and discussion

3.1. Synthesis and characterization

For the synthesis of binary Fe/Co and Ni/Co containing pentlandites with the general formulas Fe_xCo_{9-x}S₈ and Ni_yCo_{9-y}S₈ ($x = y = 0-4.5$) we used a modified procedure recently described by our group [6,28]. In short, we heated pure elemental mixtures containing Co, S as well as Fe or Ni, respectively, under vacuum to obtain the desired pentlandite-containing catalyst materials. The respective elemental ratios were adapted to the desired stoichiometric formula of the respective target materials.

Fig. 1 displays the PXRD patterns of the as-synthesized materials and a comparison to pure cobalt pentlandite Co₉S₈ [29]. All synthesized materials show equivalent reflexes to the Co₉S₈ reference unambiguously showing the presence of pentlandite as the main phases. However, attempts to introduce more than two metal-equivalents of Fe (Fe_xCo_{9-x}S₈ ($x = 2-4.5$)) to the Co-pentlandite lattice resulted in the formation of troilite (FeS) as significant byproduct. Likewise, the XRD pattern of the Ni-containing pentlandites Ni_yCo_{9-y}S₈ ($y = 2-3$) shows additional reflexes which can be assigned to the thiospinel phase of linnaeite (Co₃S₄). Notably, in case of applying equal ratios between Co and Ni, aiming for Ni_{4.5}Co_{4.5}S₈, small amounts of

heazlewoodite (Ni₃S₂) were detected. Thus, XRD analyses clearly show that the incorporation of nickel and iron into the cobalt pentlandite structure is only possible to a limited extent.

The elemental composition of the different Fe_xCo_{9-x}S₈ and Ni_yCo_{9-y}S₈ ($x = y = 0-4.5$) materials was further evaluated via EDX analysis (Table 1). The obtained data confirms the expected elemental compositions for the Fe_xCo_{9-x}S₈ as well as Ni_yCo_{9-y}S₈ ($0 \leq y \leq 3$) materials. The apparent discrepancies found for Ni_{4.5}Co_{4.5}S₈ and Fe_{4.5}Co_{4.5}S₈ are ascribed to the presence of heazlewoodite and troilite respectively as a result of the applied synthetic procedure. These phases form additional domains within the pentlandite material leading to deviations from the expected elemental compositions. Thus, the synthesized materials can be described as sulfidic composites of Ni/Co as well as Fe/Co with a high ratio of pentlandite type phases.

For further characterization, the materials were subjected to differential scanning calorimetry (DSC) in order to reveal influences of amorphous compounds in the samples and to analyze the phase purity. The most intensive signals visible in each DSC curve are assigned to the transitions of the respective main pentlandite phase.

In accordance to previously reports, Co₉S₈ features two major signals at 834 and 936 °C respectively [30]. The signal at 834 °C is attributed to a transition between a low temperature form of pentlandite and its corresponding high temperature form. The second signal at 936 °C expresses the breakdown of the high temperature form into a monosulfide solid solution and its subsequent melting. A third, much less intensive, signal with an onset temperature of 789 °C is attributed to the decomposition of an amorphous binary cobalt sulfide phase not visible in the powder XRD. Fig. 2(A) displays the DSC curves for Fe/Co pentlandites with incrementally increasing Fe-content. These curves reveal significant shifts for the onset temperatures of the aforementioned phase transitions and decompositions. The onset temperature for degradation of the high-temperature form gradually decreases from an initial 936 °C (Co₉S₈) to 841 °C (Fe_{4.5}Co_{4.5}S₈) with an increasing Fe content. A similar shift to lower temperatures is also observed for the transition of low to high temperature forms. However, the

Fig. 1. PXRD patterns of Fe/Co (A) and Ni/Co (B) materials obtained from high temperature synthesis.

Table 1

Comparison of expected stoichiometry and obtained elemental composition from EDX. Elemental compositions from EDX are derived from at least 4 independent measurements.

Estimated sum formula	Fe equiv.	Co equiv.	Ni equiv.	S equiv.	Composition obtained from EDX analysis
Ni _{4.5} Co _{4.5} S ₈	—	5.33	4.94	6.73	Co _{5.33} Ni _{4.94} S _{6.73}
Ni ₃ Co ₆ S ₈	—	6.51	3.44	7.05	Co _{6.51} Ni _{3.44} S _{7.05}
Ni ₂ Co ₇ S ₈	—	7.17	1.92	7.91	Co _{7.17} Ni _{1.92} S _{7.91}
NiCo ₈ S ₈	—	8.01	0.92	8.06	Co _{8.01} Ni _{0.92} S _{8.06}
Co ₉ S ₈	—	9.01	—	7.99	Co _{9.01} S _{7.99}
FeCo ₈ S ₈	0.70	7.91	—	8.40	Fe _{0.70} Co _{7.91} S _{8.40}
Fe ₂ Co ₇ S ₈	2.64	7.24	—	7.12	Fe _{2.64} Co _{7.24} S _{7.12}
Fe ₃ Co ₆ S ₈	2.77	6.32	—	7.91	Fe _{2.77} Co _{6.32} S _{7.91}
Fe _{4.5} Co _{4.5} S ₈	4.01	8.04	—	4.96	Fe _{4.01} Co _{8.04} S _{4.96}

Fig. 2. DSC curves for the synthesized Fe/Co (A) as well as Ni/Co materials (B). DSC results for Co₉S₈ are added for comparison. Heating was performed from RT to 1000 °C with a rate of 10 °C min⁻¹.

maximum shift to 756 °C was already obtained for Fe₂Co₇S₈ and remained constant for materials with higher Fe-content. It is striking that an initial significant broadening of the signals occurs with an increasing Fe:Co ratio indicating the coexistence of the low- and high temperature form over a somewhat broader temperature of approximately 30 °C, in good accordance to results obtained by Kitakaze *et al.* [30]. In case of Fe₃Co₆S₈, a flat shoulder appears directly after the first sharp pentlandite phase transition, which we hypothesize is caused by interactions of the pentlandite with the troilite phase. For Fe_{4.5}Co_{4.5}S₈ containing troilite as the main phase, the shoulders disappear in favor for small sharp signals because of the decreasing ratio of pentlandite type phases. A similar behavior was likewise found for the mixed Co/Ni materials. In particular, the pentlandite phase transitions shift from initial 834 °C (0 eq. Ni) down to 653 °C (4.5 eq. Ni), whereas the onset temperature for decompositions is shifted from 936 °C (0 eq. Ni) to 878 °C (4.5 eq. Ni) with increasing Ni-content. Furthermore, the aforementioned signal broadening also occurs with an increasing Ni ratio. In contrast to the iron compounds, where no additional signals were observed below temperatures of ~800 °C, all nickel compounds show at least one diminutive signal between 470 and 550 °C. The compound Ni_{4.5}Co_{4.5}S₈ even shows two of these signals, which are attributed to minor contributions of the above-mentioned cobalt-thiospinel and heazlewoodite.

Although the presence of heazlewoodite and troilite was clearly confirmed by PXRD measurements, an unambiguous assignment in our DSC measurements proved challenging in view of their minor contribution in the majority of cases. Despite of the rather minor influence of the non-pentlandite phases on DSC measurements, their presence in the material cannot be neglected in electrocatalytic measurements. A comparison of onset-temperatures (i.e. start temperature of the respective phase transitions) obtained for the synthesized materials is depicted in Fig. S1.

3.2. Electrocatalytic hydrogen evolution reaction measurements at room temperature

Stoichiometric alterations, concerning the metal as well as chalcogenide content, can dramatically influence the catalytic activity of pentlandite-based metal sulfide electrocatalysts. In view of our recent successful application of mixed Fe/Ni- and seleno-substituted pentlandites for the hydrogen evolution reaction we herein probe our obtained materials for their suitability for electrocatalytic H₂-formation [6,12]. Furthermore, the identified additional components from our applied thermal synthesis are in fact metal sulfides which are suitable for HER catalysis. Consequently, the presented materials can be understood as pentlandite-rich catalysts involving additional shares

Fig. 3. ECSA slopes before (grey) and after (green) chronoamperometry at -400 mV vs. RHE (A) and recorded overpotentials before (grey) and after (green) chronoamperometry (B). The green bars indicate the difference between the respective data points.

of troilite, heazlewoodite or cobalt thiospinel.

For electrocatalytic evaluation the compounds were assembled into electrodes according to a method recently reported by our group [28].

At room temperature, the prepared electrodes were electrochemically conditioned to ensure the removal of traces of surface impurities. After electrochemical cleaning, the electrochemical surface area (ECSA) was determined via cyclic voltammetry to obtain the initial active surface area. Subsequently, LSV was performed to determine the respective catalysts overpotential vs. RHE at 10 mA cm^{-2} (η_{10}) (Fig. 3(B), Table 2). In terms of overpotentials for dihydrogen formation, all materials range between 256–357 mV. Up to an incorporation of about two equivalents of Fe or Ni, only small deviations of the overpotentials in comparison to Co_9S_8 are observed. However, a remarkable improvement is found for $\text{Ni}_3\text{Co}_6\text{S}_8$ with an overpotential of 256 mV at 10 mA cm^{-2} , thereby even outperforming the mixed Fe/Ni pentlandite $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ (280 mV at 10 mA cm^{-2}) [5]. The overall trend of overpotentials is qualitatively reflected in the ECSA slopes of the respective materials. Consequently, the highest ECSA slope was obtained for $\text{Ni}_3\text{Co}_6\text{S}_8$ ($0.01539 \text{ mA s cm}^{-2} \text{ mV}^{-1}$). Interestingly, Co_9S_8 exhibits the second highest value for the ECSA slope ($0.01128 \text{ mA s cm}^{-2} \text{ mV}^{-1}$), but its moderate overpotential of 333 mV at 10 mA cm^{-2} is significantly lower and a rationalization solely based on a quantitative assessment of electrocatalytically active sites represented by the ECSA slope is insufficient. Thus, the apparent

improvement in overpotential for $\text{Ni}_3\text{Co}_6\text{S}_8$ might be attributed to a geometric as well as electronic improvement of the active sites due to the presence of Ni.

Chronoamperometric long-term measurements at a fixed potential of -400 mV vs. RHE were subsequently performed after the ECSA and LSV measurements (Fig. 4(A)). $\text{Ni}_3\text{Co}_6\text{S}_8$ exhibits the highest current density starting at around -80 mA cm^{-2} and steeply rising up to -180 mA cm^{-2} after 20 h of electrolysis. Along this line, $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$, which shows a slightly increasing current density of around -50 mA cm^{-2} over the period of 20 h. In contrast, NiCo_8S_8 , $\text{Ni}_2\text{Co}_7\text{S}_8$ as well as the reference substance Co_9S_8 reveal much lower, but constant current densities ranging from -20 to -30 mA cm^{-2} . The benchmark substance Co_9S_8 itself shows the highest initial current density at around -27 mA cm^{-2} but has a slight decrease down to a final value of -22 mA cm^{-2} after 20 h. The Fe-containing materials feature current densities comparable to the Ni/Co-pentlandites with low Ni content.

In contrast to the reference compound Co_9S_8 , the iron-rich compound $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$ catalyzes the hydrogen evolution reaction with a lower current density starting at -24 mA cm^{-2} in the beginning of the chronoamperometric experiment but has a steep increase within the first two hours up to -35 mA cm^{-2} . Afterwards, the current density severely decreases and finally approaches the current density of the benchmark compound Co_9S_8 exhibiting a final value of -22 mA cm^{-2} . A completely different behavior is found for compound $\text{Fe}_3\text{Co}_6\text{S}_8$ which starts

Table 2
Overpotentials and ECSA before and after chronoamperometry at -400 mV vs. RHE and 25°C .

Compound	η before Chronoamperometry (mV)	η after Chronoamperometry (mV)	$ \Delta\eta $ (mV)	ECSA before Chronoamperometry ($\text{mA s cm}^{-2} \text{ mV}^{-1}$)	ECSA after Chronoamperometry ($\text{mA s cm}^{-2} \text{ mV}^{-1}$)	ΔECSA ($\text{mA s cm}^{-2} \text{ mV}^{-1}$)
$\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$	336	293	43	0.00823	0.01546	0.00723
$\text{Ni}_3\text{Co}_6\text{S}_8$	256	283	27	0.01539	0.02313	0.00774
$\text{Ni}_2\text{Co}_7\text{S}_8$	334	347	13	0.00442	0.00805	0.00363
NiCo_8S_8	345	328	17	0.01032	0.01714	0.00682
Co_9S_8	333	319	14	0.01128	0.01996	0.00869
FeCo_8S_8	334	348	14	0.00241	0.00841	0.00599
$\text{Fe}_2\text{Co}_7\text{S}_8$	357	352	5	0.00886	0.01021	0.00135
$\text{Fe}_3\text{Co}_6\text{S}_8$	354	296	58	0.00109	0.00642	0.00532
$\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$	327	286	41	0.00620	0.02800	0.02180

Fig. 4. Electrolysis at -400 mV vs. RHE over 20 h for (A) iron- and (B) nickel-containing compounds in 0.5 M H_2SO_4 .

at ca. -10 mA cm^{-2} and then shows a significant increase ending at -48 mA cm^{-2} . The compounds FeCo_8S_8 and $\text{Fe}_2\text{Co}_7\text{S}_8$ show rather similar curve progressions with current densities averaging between -10 mA cm^{-2} and -12 mA cm^{-2} , whereas the latter one represents the lower limit. Post-chronoamperometric measurements for the ECSA and LSV reveal that the ECSA slopes of all compounds have increased.

The average increase of the ECSA is slightly larger for Ni/Co (between 0.00363 and 0.00774 $\text{mA s cm}^{-2} \text{mV}^{-1}$) materials than for Fe/Co (between 0.00135 and 0.00599 $\text{mA s cm}^{-2} \text{mV}^{-1}$) materials which is well in line with the respective current densities reached after 20 h of electrolysis. Herein, $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$ represents an exception undergoing a much larger ECSA-increase with 0.02180 $\text{mA s cm}^{-2} \text{mV}^{-1}$.

Apart from $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$, the highest increase was observed for $\text{Ni}_3\text{Co}_6\text{S}_8$, rising from 0.01539 $\text{mA s cm}^{-2} \text{mV}^{-1}$ to 0.02317 $\text{mA s cm}^{-2} \text{mV}^{-1}$. Conversely, the measured potential for H_2 -evolution at 10 mA cm^{-2} indicates a lowered activity after electrolysis, going down from initial 256 to 283 mV ($\Delta\eta = 27$ mV). This contrasts the behavior observed for Fe/Ni pentlandites which undergo substantial activation during electrolysis due to depletion of sulfur at the active site of the catalysts which was previously reported for pentlandite-based materials [6,12]. We recently demonstrated that a reductive influence on the pentlandite lattice causes the depletion of sulfur from the Wyckoff position 9c in the crystal lattice, thereby liberating a favorable binding motif for protons on the catalysts surface [7]. The overall H-binding efficiency at this position is however strongly dependent on the intermetallic distances at this site (and thus also the electronic conditions) which itself is a function of the exact stoichiometric composition of the pentlandite material. In other words, S-depletion liberates active sites with different H-reduction capability depending on the stoichiometric composition. It is therefore reasonable to assume that apparent differences in the activation might be closely related to the sulfur depletion process. Based on this study, assuming a similar activation process for Co-rich pentlandite phases does not seem justified as phases with high amounts of Co ($\text{Co} \geq 6$ equiv.) merely undergo any comparable electrochemical activation or deactivation. For these cases, the process leading to higher ECSA values thus appear to be surface decomposition

reactions not affecting the structure or electronics of the active sites. This assumption is further supported by the fact that activation/deactivation becomes more prominent with decreasing Co-content and might indicate that Co is in fact hampering the depletion of sulfur to form additional active sites. Thus, the apparent slightly higher increase of ECSA for Ni/Co-pentlandites compared to Fe/Co-pentlandites might point to somewhat facilitated depletion of sulfur in Ni/Co-pentlandites, similar to activating mechanisms previously observed for Fe/Ni-containing materials [6,7,12]. Another electrochemical processes leading to a higher ECSA might be a decomposition of troilite or heazlewoodite/cobalt thiospinel in the Fe or Ni-containing composite materials respectively which corresponds to previous reports showcasing that sulfidic materials should not be considered entirely inert under acidic conditions [32–34]. However, we believe that these processes alone do not explain the observed differences in ECSA-increase as for all pure phases and the majority of composites comparable ΔECSA -values within the same order of magnitude are observed. The observed ECSA-increases can thus be understood as an interplay between surface alteration reactions not affecting the active sites (predominant in Co-rich pentlandites) as well as beginning sulfur depletion which becomes a relevant factor with increasing amounts of Fe or Ni (respectively low amounts of Co). This is well in line with the observation that Fe-rich $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$ underwent the highest increase in ECSA while simultaneously providing significant activation during electrolysis. Furthermore, we hypothesize that electronic and geometric effects on the active site are the predominant factor influencing the observed activation/deactivation tendencies. Indeed, a careful control of the stoichiometric composition and thus of metal-metal as well as metal-chalcogen distances can be a key-factor affecting the catalytic activity of these metal chalcogenide catalysts [12]. Suboptimal compositions can thus hamper H_2 -formation despite of an increasing sulfur depletion, e.g. in NiCo_8S_8 and $\text{Ni}_3\text{Co}_6\text{S}_8$ leading to substantial deactivation. In case of other Ni-containing materials, incorporation of high amounts of Ni seems to support a material activation process. The overpotential of $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$ decreased after electrolysis by 43 down to 293 mV at 10 mA cm^{-2} , while the ECSA slope increased from 0.00823 to 0.01546 $\text{mA s cm}^{-2} \text{mV}^{-1}$, which is rather similar to the ECSA increase of $\text{Ni}_3\text{Co}_6\text{S}_8$. We hypothesize

that the activation is then attributed to beginning sulfur depletion with decreasing Co-content and preferential electronics at the active site. In case of $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$, however, the presence of an additional HER-active material (heazlewoodite) [4] complicates the situation for this composite. Superficially, these composite materials outperform the pure Co_9S_8 pentlandite with a much higher rate of activation, but it remains yet unclear if these materials benefit from synergistic effect between the present phases. An additional possibility for the observed activation would be the HER-activity of heazlewoodite through exposed {210}-facets [35], which might overcompensate for a deactivating process in the otherwise pure $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$ phase. The situation for the Fe-containing pentlandite phase confirms the trend that continuous substitution of Co leads to higher tendencies for activation within HER. Notably, the Fe/Co phases with high Fe content undergo substantial activation. Again, due to the comparably high ECSA-enlargement a decomposition of the troilite phases in the composite accompanied by depletion of sulfur may be anticipated. A representative Tafel-analysis (SI Section 3.3) at ambient conditions as well as elevated temperature (vide infra) using $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$, FeCo_8S_8 , NiCo_8S_8 as well as $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$ (Fig. S6) indicate an initial Volmer-type adsorption step ($\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$) followed by a Heyrovsky step ($\text{H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2$) which corresponds well to our previous results on HER-active pentlandites [12].

Here, it can be concluded that incorporation of Fe or Ni into the pentlandite phase complicates the synthesis and leads to composite materials. The resulting catalysts like $\text{Ni}_1\text{Co}_8\text{S}_8$ and $\text{Fe}_3\text{Co}_6\text{S}_8$ are much more prone to activation while $\text{Ni}_2\text{Co}_6\text{S}_8$ and $\text{Fe}_1\text{Co}_8\text{S}_8$ tend to deactivate during electrolysis. However, these modified cobalt-pentlandite derivatives potentially outperform the parent Co_9S_8 and underline the rationale of doping/stoichiometric substitution approach.

3.3. Electrocatalytic hydrogen evolution reaction measurements at 75 °C

For the industrial realization of the HER mainly two pathways are pursued, namely alkaline and PEM (acidic) electroly-

sis. Both are commonly performed at elevated pressures of <30 bars. Optimized electrolyzers operate at cell voltages of 1.8 to 2.4 V which is the sum of all overpotentials including the cathodic reactions where HER is going on. For the industrial application it is furthermore desirable to achieve current densities well above 500 mA cm^{-2} . Likewise, commercially competitive devices for electrocatalytic hydrogen production usually operate at elevated temperatures. Commonly, the applied temperature ranges between 50–90 °C for alkaline as well as PEM electrolyzers [36]. Consequently, we likewise evaluated the electrocatalytic performance at an elevated temperature of 75 °C. Throughout this study, the remaining parameters such as potential, reaction setup and electrolyte were conserved to ensure a high comparability to experiments at room temperature.

The electrodes were tested for their initial overpotentials (LSV) and the ECSA (CV)). Subsequently, electrolysis at -400 mV vs. RHE was performed for 20 h and the ECSA and overpotential were determined after the experiment. Compared to the measurements at room temperatures the results indicate a much lower overpotential at 75 °C (Fig. 5). The initial overpotentials range from 270 mV (FeCo_8S_8) to 182 mV ($\text{Ni}_3\text{Co}_6\text{S}_8$) at -10 mA cm^{-2} . After activation, the range slightly increased from 278 mV (FeCo_8S_8) to 176 mV ($\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$). On average, the overpotential remained approximately constant with small changes of $\pm 16 \text{ mV}$ or less (Fig. 6, Table 3). However, $\text{Ni}_2\text{Co}_7\text{S}_8$ represents an exception, undergoing a stronger activation process lowering its overpotential from 239 to 200 mV. This behavior is underlined by a major increase of its ECSA ($\Delta\text{ECSA} = 0.0156 \text{ mA s cm}^{-2} \text{ mV}^{-1}$). Interestingly, the $\text{Ni}_2\text{Co}_7\text{S}_8$ is the only example at 75 °C where a notable change in activity can be observed. In contrast, changes in catalyst activity were significantly greater when measured at room temperature. The aforementioned effects-like decomposition of either troilite phases or heazlewoodite/cobalt spinel as well as the sulfur depletion-causing an activation/deactivation seem to balance each other, resulting in much smaller alterations. Nevertheless, the trend of higher activity for Co-deficient compounds persists. Apparently, this trend becomes even more pronounced at

Fig. 5. ECSA slopes before (grey) and after (green) chronoamperometry at -400 mV vs. RHE (A) and recorded overpotentials before (grey) and after (green) chronoamperometry (B) with green bar graphs indicating the difference between the respective data points. All values obtained at 75 °C cell temperature.

Fig. 6. Chronoamperometric curves obtained at -400 mV vs. RHE and 75 °C for Fe/Co- (A) and Ni/Co- (B) compounds.

elevated temperature.

The chronoamperometric measurements at -400 mV vs. RHE and 75 °C (Fig. 6) show another interesting difference compared to the data obtained at room temperature: Not only is the overall activity-represented by the obtained current densities - much higher for all compounds, but the activity of the Ni-containing compounds is significantly higher than the iron-containing compounds. While the Fe/Co compounds are in a range of -100 to -200 mA cm $^{-2}$, the Ni/Co compounds comprise current densities between -450 to peaking -4500 mA cm $^{-2}$. This might be due to the intrinsic higher conductivity of the identified nickel compounds compared to the iron compounds [36–39]. While at room temperature a higher activity was previously observed only for $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$ and $\text{Ni}_3\text{Co}_6\text{S}_8$, a higher activity of the nickel-compared to the iron compounds is now clearly seen in the measurements of all Ni-compounds. However, it is surprising that the activation-behavior is not represented by the LSVs and the corresponding overpotentials after electrolysis, which have the same order of magnitude and might be explained by a quick consecutive surface-oxidation after electrolysis. The intrinsic changes in conductivity are again reflected in the chronoamperometric curve of $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$, which protrudes from all other curves in Fig. 6 with impressive current densities of approx -3.5 A cm $^{-2}$. The corresponding iron-composite $\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$, however ranges between -150 to -100 mA cm $^{-2}$ —~25-times lower. The reasons for the high currents observed for $\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$, however, remain completely

unknown and will be investigated in detail in the future.

4. Conclusions

We herein report on the synthesis of bimetallic Fe/Co and Ni/Co pentlandite materials and their application for the hydrogen evolution reaction at different temperatures. These materials display altered Fe:Co and Ni:Co metal ratios and form pentlandite-rich composites. All materials represent effective electrocatalysts for the hydrogen evolution reaction at -0.5 V vs. RHE. In general, the rational incorporation of heteroatoms like Fe or Ni into Co_9S_8 potentially leads to an increased activity for HER. The Ni/Co pentlandite materials outperform the corresponding Fe/Co pentlandite materials with $\text{Ni}_3\text{Co}_6\text{S}_8$ ($\eta_{10, \text{RT}} = 256$ mV, $\eta_{10, 75^\circ\text{C}} = 182$ mV) showing the lowest overpotentials at 10 mA cm $^{-2}$ at RT and 75 °C. All materials display an increased ECSA after electrolysis, which is attributed to an interplay between surface-decomposition reactions not affecting catalytically active sites, depletion of sulfur and potentially decomposition of foreign phases like troilite (FeS), linnaeite (Co_3S_4) and haezlewoodite (Ni_3S_2) in the sulfidic composite materials. However, it is evident that an increased ECSA does not necessarily correspond to an improved activity after electrolysis leading to the conclusion that consecutive substitution of Co in Co_9S_8 for foreign metals such as Fe or Ni does not solely affect the structural integrity of the materials but likewise decisively influences the electro-geometric properties of the active

Table 3

Values for overpotential and ECSA before and after chronoamperometry at -400 mV vs. RHE and 75 °C.

Compound	η before Chronoamperometry (mV)	η after Chronoamperometry (mV)	$ \Delta\eta $ (mV)	ECSA before Chronoamperometry (mA s cm $^{-2}$ mV $^{-1}$)	ECSA after Chronoamperometry (mA s cm $^{-2}$ mV $^{-1}$)	ΔECSA (mA s cm $^{-2}$ mV $^{-1}$)
$\text{Ni}_{4.5}\text{Co}_{4.5}\text{S}_8$	213	207	6	0.00845	0.01162	0.00318
$\text{Ni}_3\text{Co}_6\text{S}_8$	182	192	10	0.02248	0.02786	0.00538
$\text{Ni}_2\text{Co}_7\text{S}_8$	239	200	39	0.01067	0.02626	0.01559
NiCo_8S_8	246	233	13	0.00984	0.01276	0.00291
Co_9S_8	247	252	5	0.01193	0.01538	0.00346
FeCo_8S_8	270	278	8	0.00546	0.00894	0.00348
$\text{Fe}_2\text{Co}_7\text{S}_8$	241	235	6	0.01097	0.01937	0.00840
$\text{Fe}_3\text{Co}_6\text{S}_8$	227	239	12	0.00721	0.01250	0.00529
$\text{Fe}_{4.5}\text{Co}_{4.5}\text{S}_8$	192	176	16	0.01919	0.04440	0.02521

Graphical Abstract

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Fe/Co and Ni/Co-pentlandite type electrocatalysts for the hydrogen evolution reaction

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A series of Ni/Co- and Fe/Co- sulfide composites based on Co_9S_8 pentlandite have been synthesized and tested for their HER performance at different temperatures, revealing a higher activity for Co-deficient compounds due to a complex phase-dependent interplay.

sites for H_2 -formation.

Electronic supporting information

Supporting information is available in the online version of this article.

Conflicts of interest

There are no conflicts to declare.

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Fe/Co和Ni/Co镍黄铁矿型析氢反应电催化剂

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摘要: 作为析氢反应的电催化剂, 富金属的过渡金属硫化物因能克服富硫金属催化剂所存在的如导电性有限和缺乏必要的纳米结构等不足, 近年来受到越来越多的关注。本文介绍了具有镍黄铁矿型结构的三元富金属硫化物复合材料 $\text{Fe}_x\text{Co}_{9-x}\text{S}_8$ 和 $\text{Ni}_y\text{Co}_{9-y}\text{S}_8$ ($x = y = 0-4.5$)的合成、表征及其电催化研究。首先, 研究了二元钴化合物 Co_9S_8 中Co逐步被Fe或Ni取代直至4.5当量的变化过程。硫镍黄铁矿复合物中组分的变化有助于不同温度下酸性介质中的质子还原。其次, 在还原电催化条件下, 复合物中元素化学计量变化对其电化学活化/失活行为有决定性的影响。与 Co_9S_8 相比, Co缺陷复合材料表现出了更高的HER性能。Ni/Co化合物通常表现出比类似结构Fe/Co化合物更高的电催化析氢活性。

关键词: 氢气; 镍黄铁矿; 金属硫化物; 过渡金属; 电催化

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