Supporting Information for

Extreme accumulation of ammonia on electroreduced mackinawite: An abiotic ammonia storage mechanism in early ocean hydrothermal systems

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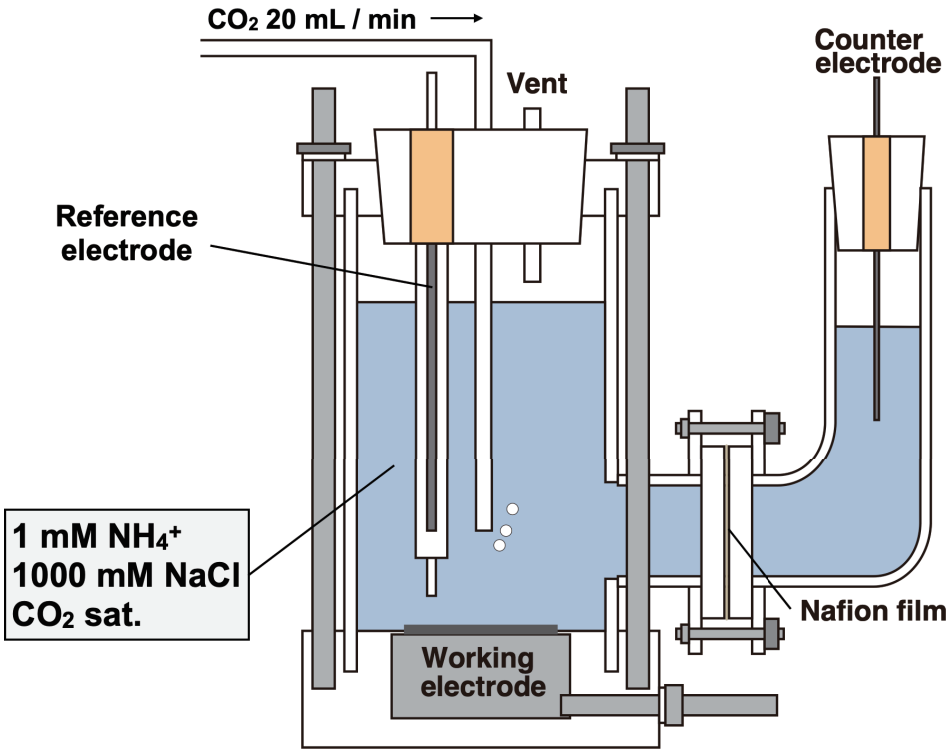

Fig. S1. Schematic of the electrochemical cell. The cell is made of a Pyrex glass tube sandwiched between a polyoxymethylene (POM) cap and a basement, which were tightened together with stainless screws and knurled nuts. The cell has two compartments: a large working electrode side (~100 ml) and a small counter electrode side (15 ml) that are separated by a proton exchange membrane (Nafion 117; DuPont). On the working electrode side, a titanium cylinder (purity 99.5%) is placed at the center of the POM basement and is coated with carbon paper (5.7 cm^2) with silicon and POM packings. An Ag/AgCl electrode (in saturated KCl) is used as the reference and is fixed at a distance of less than 5 mm from the working electrode to reduce solution resistance. On the counter side, a platinum coil is inserted into the glass tube and is used as the counter electrode.

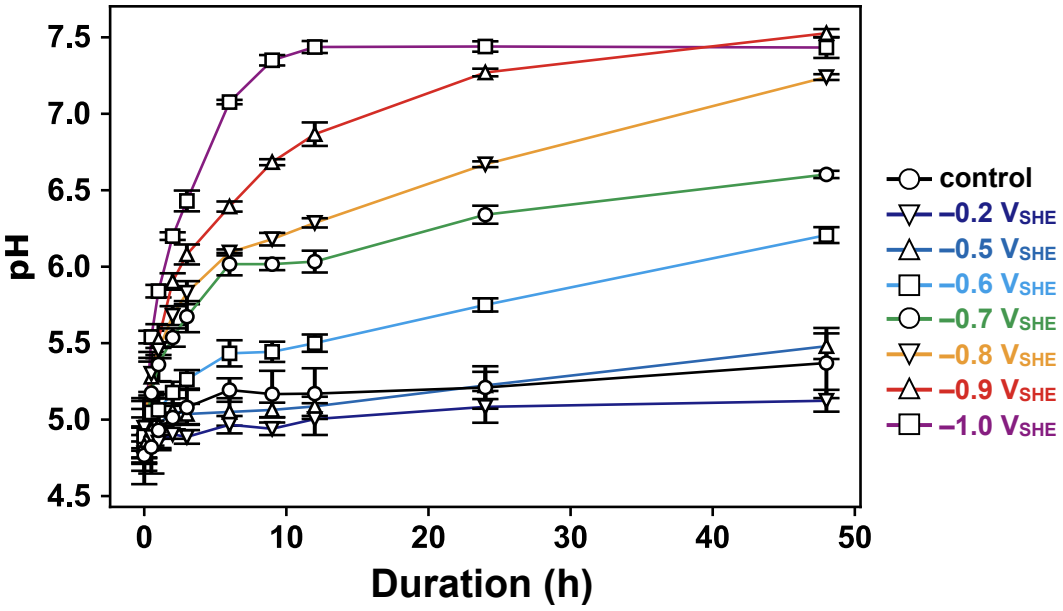

Fig. S2. Changes in the solution pH during mackinawite electrolysis. Error bars are the standard deviation of three independent experiments. The control experiment was performed in an electrochemical cell (Fig. S1) without an externally imposed electric potential.

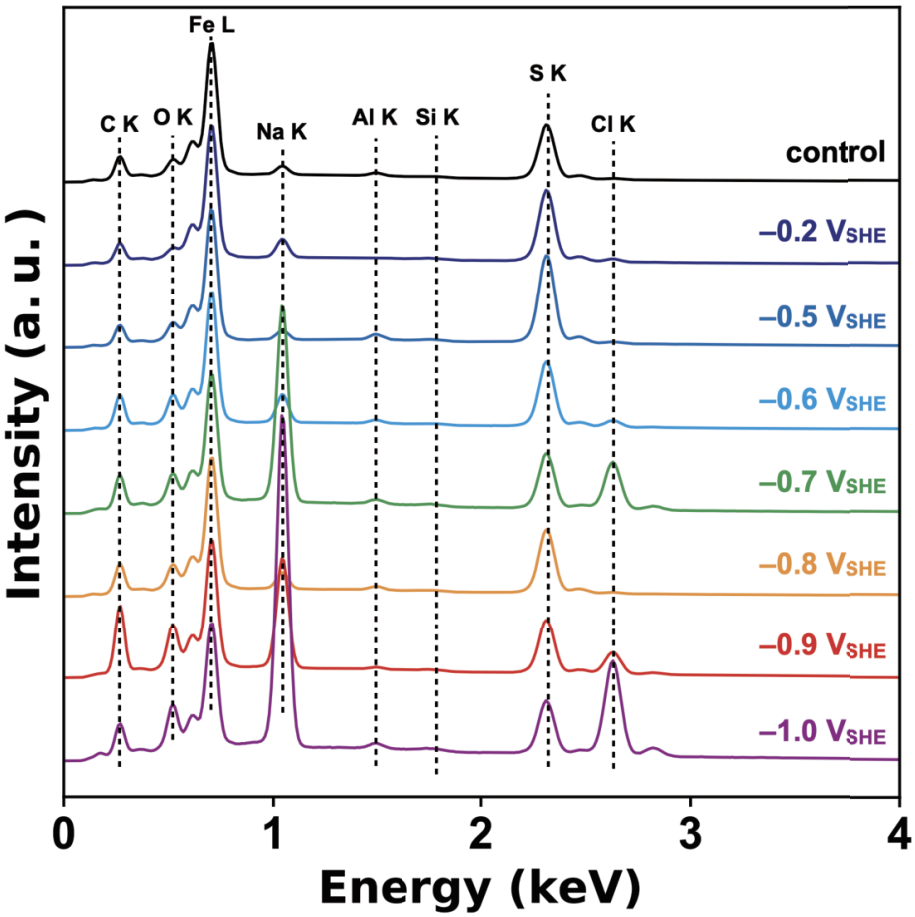

Fig. S3. EDS spectra of mackinawite after the 48 h electrolysis at the potential indicated. The control experiment was performed in an electrochemical cell (Fig. S1) without an externally imposed electric potential.

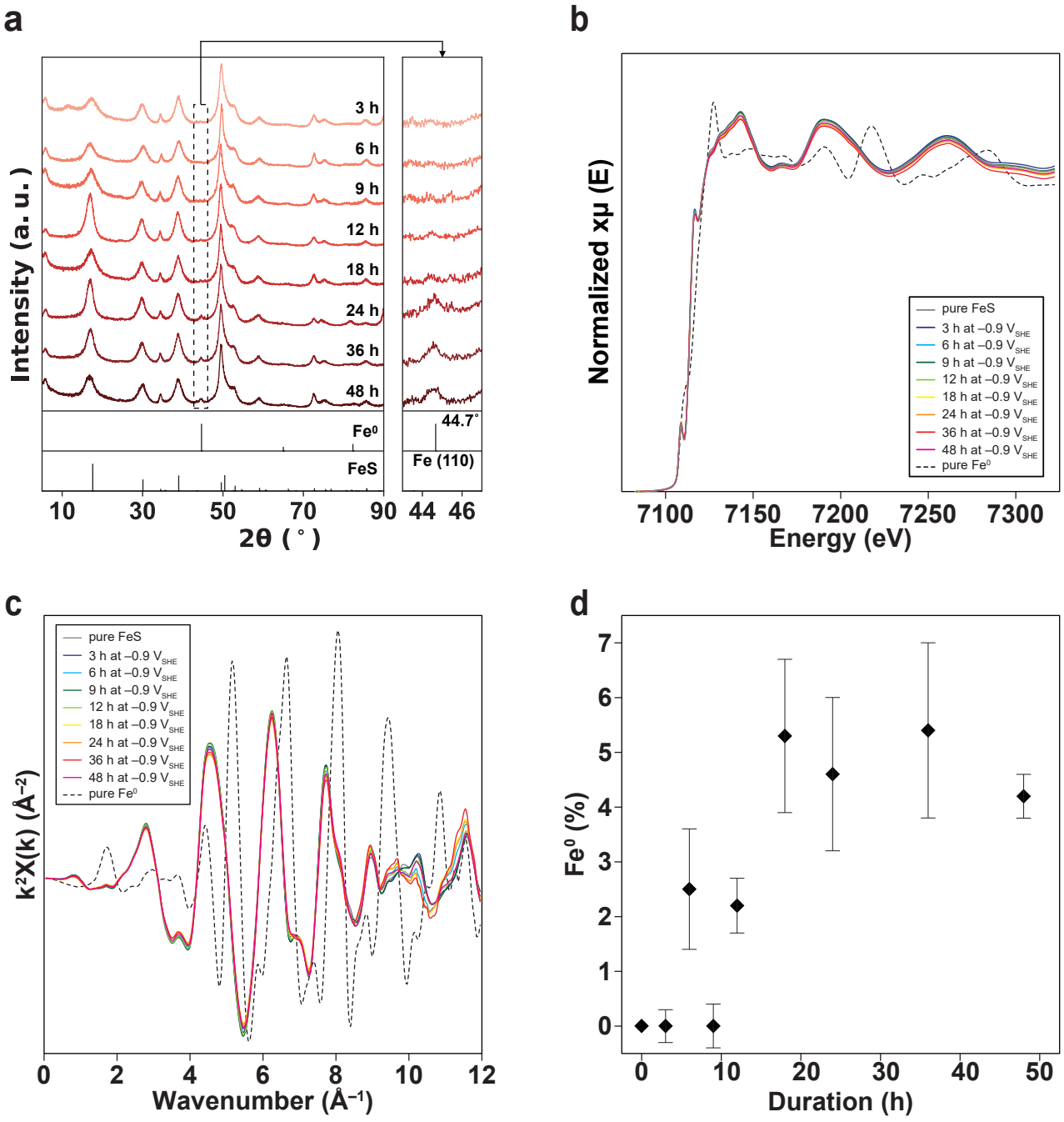

Fig. S4. (a) XRD, (b) iron K-edge XANES, and (c) iron K-edge EXAFS of the FeS electrolyzed for 3, 6, 9, 12, 18, 24, 36, and 48 h at $-0.9\,V_{SHE}$. (d) Percentages of Fe^0 quantified by a least-squares fitting of the sample EXAFS spectra with those of pure FeS and pure Fe^0. The spectral profiles of XANES and EXAFS reflect the size and morphology of sample as well as its valence state (1); smaller particles in several nm scale tend to exhibit lower signal intensities in the EXAFS spectra. Therefore, using pure Fe^0 nanoparticles with a diameter of 95-105 nm (from EM Japan) as a reference may not accurately capture the spectral properties of Fe^0 formed in the electroreduced mackinawite structure.

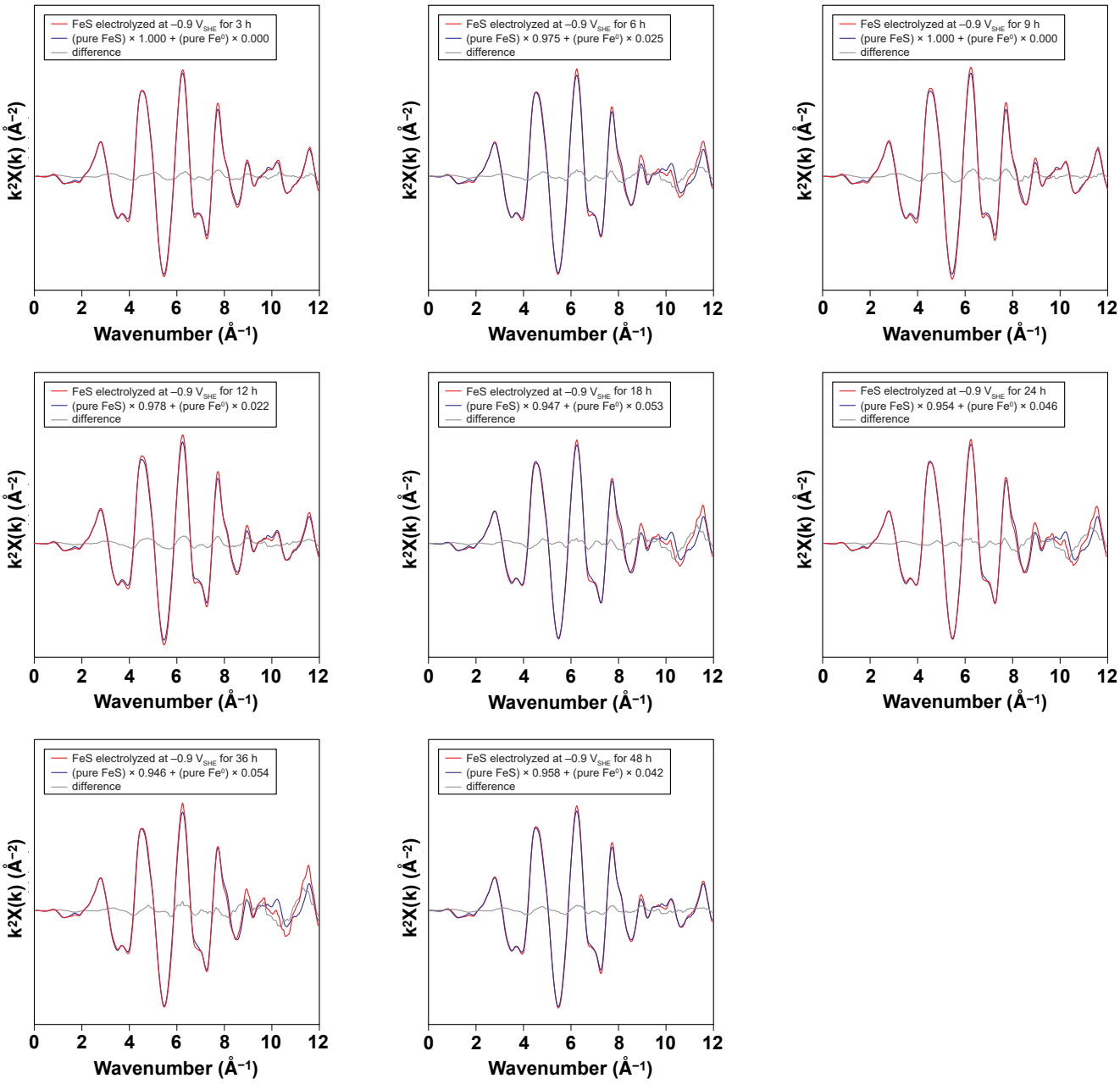

Fig. S5. Iron K-edge EXAFS of the FeS electrolyzed for 3, 6, 9, 12, 18, 24, 36, and 48 h at −0.9 V_{SHE} (red) and the best fitting results with the spectra of pure FeS and pure FeS (blue). The residuals are shown with dotted black lines.

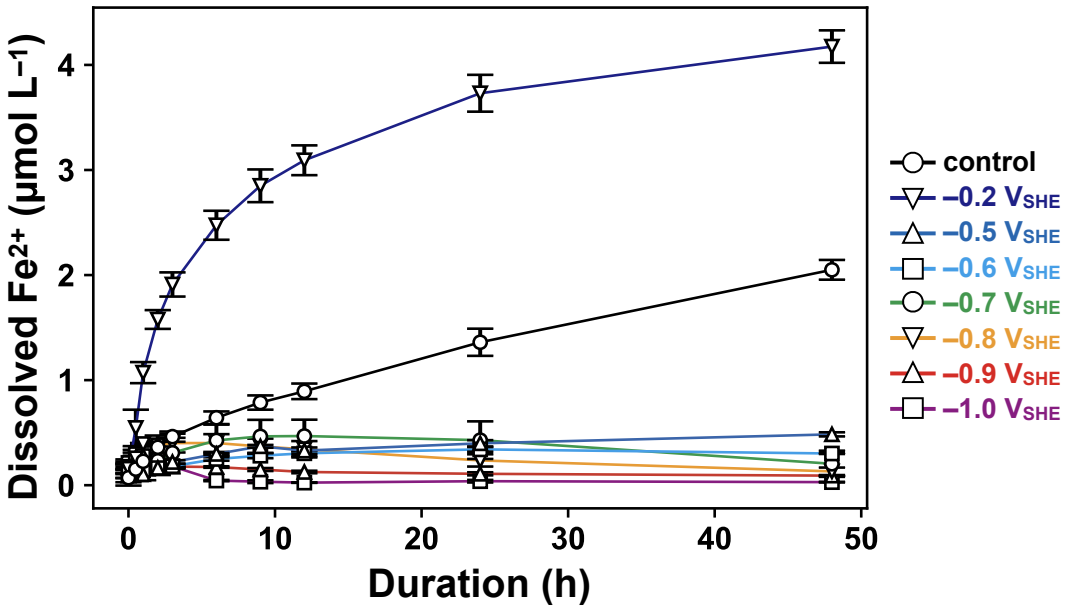

Fig. S6. Changes in the dissolved Fe^{2+} concentration during mackinawite electrolysis. The control experiment was performed in an electrochemical cell (Fig. S1) without an externally imposed electric potential. Error bars are the standard deviation of three independent experiments.

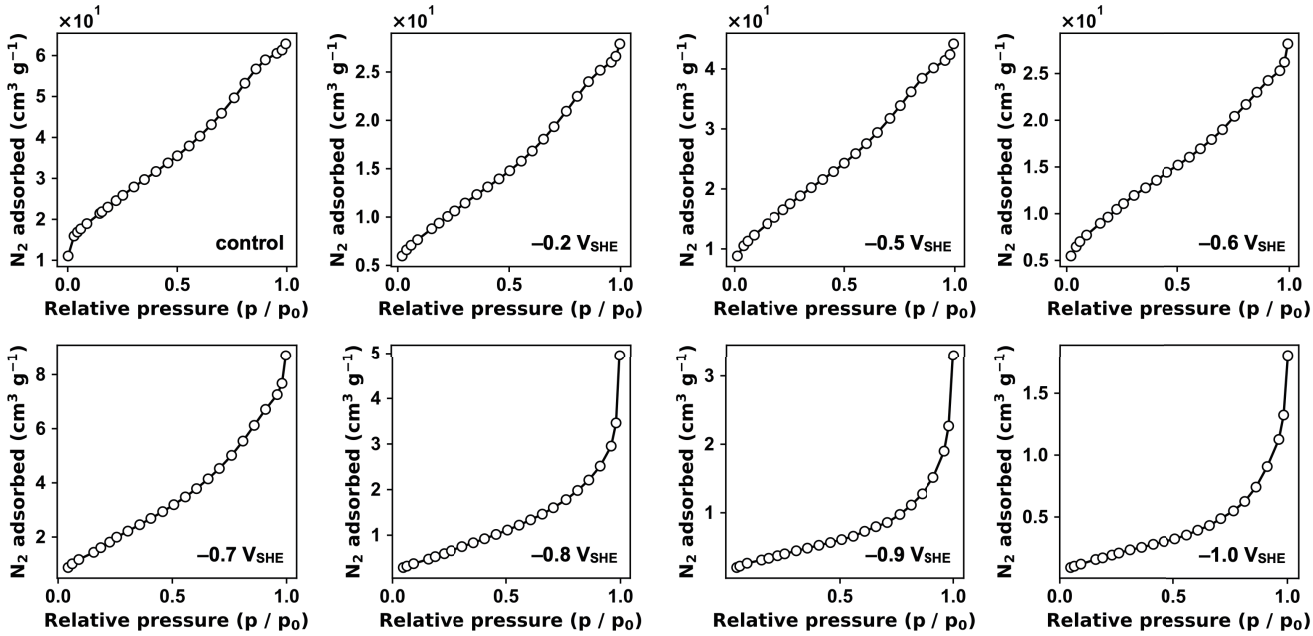

Fig. S7. N_2 adsorption isotherms on mackinawite measured by a BET surface area analyzer.

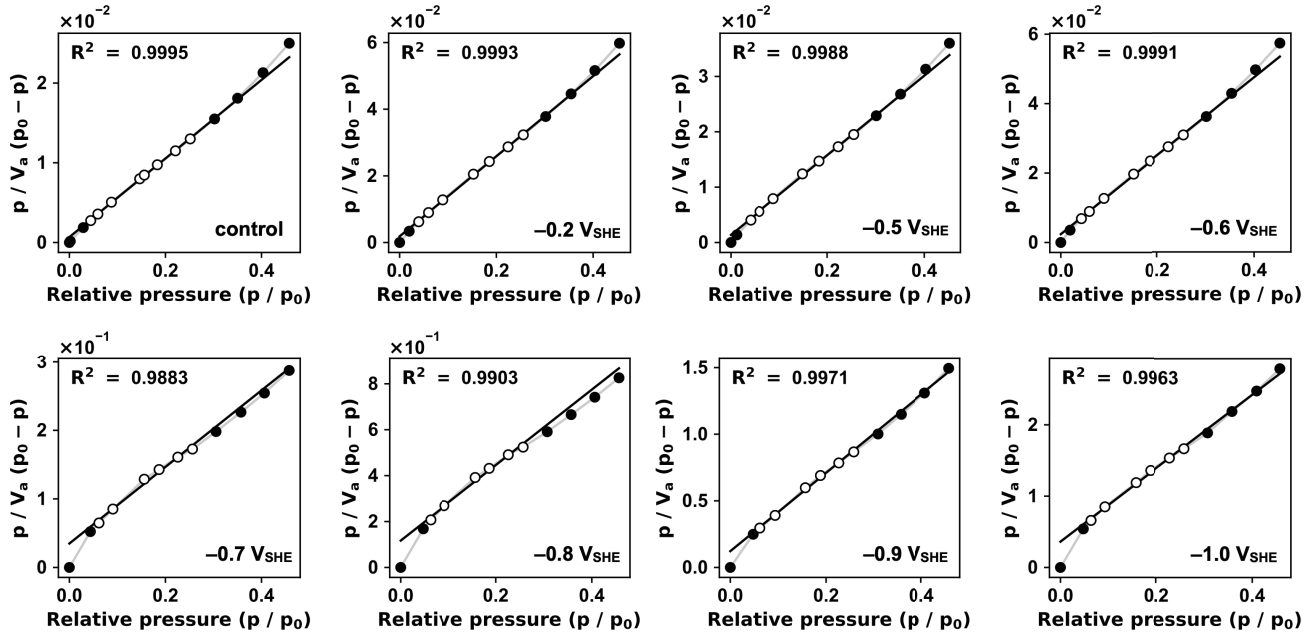

Fig. S8. BET plots for mackinawite calculated from the N_2 adsorption isotherms presented in Fig. S7. The regression lines were obtained using the data shown with open cycle symbols.

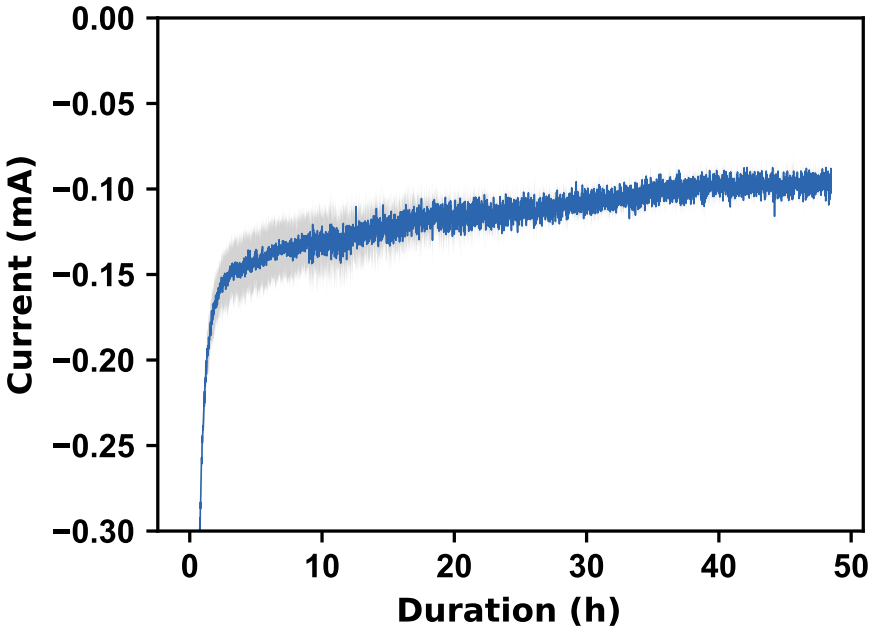

Fig. S9. Change in the current during the ammonia adsorption experiment at $-0.5\,V_{SHE}$. The gray area shows the standard deviation of three independent experiments.

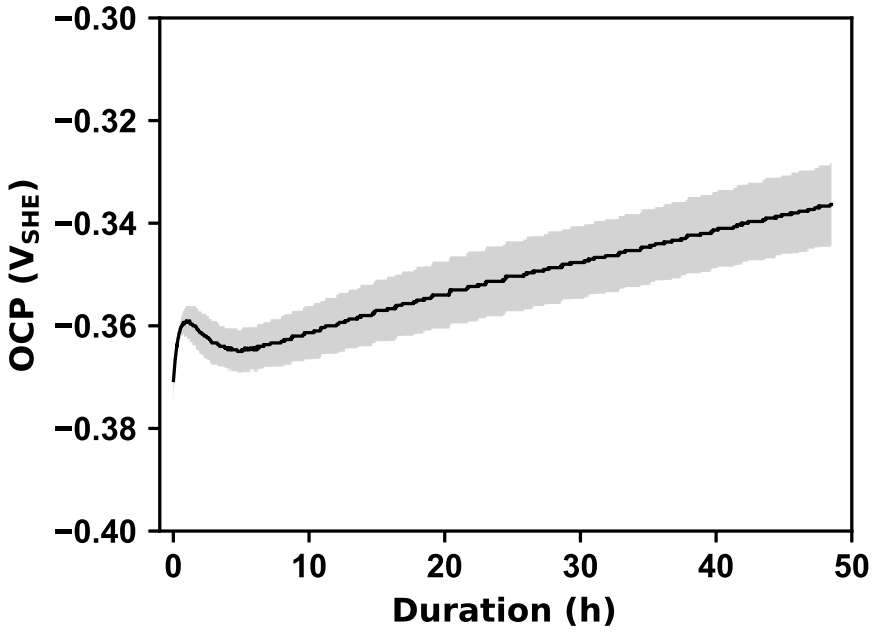

Fig. S10. Change in the open-circuit potential monitored during the control experiment. The gray area shows the standard deviation of three independent experiments.

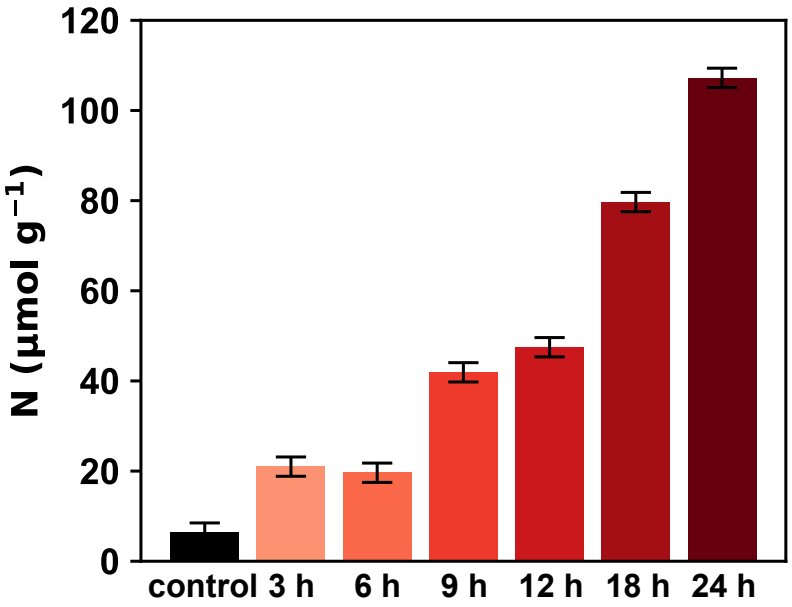

Fig. S11. Amounts of nitrogen stored in mackinawite through the ammonia adsorption experiment at $-0.9\ V_{SHE}$ for different durations. The amounts were determined with an elemental analyzer/isotope ratio mass spectrometer (EA/IRMS) after the vacuum drying of FeS samples (see Materials and Methods).

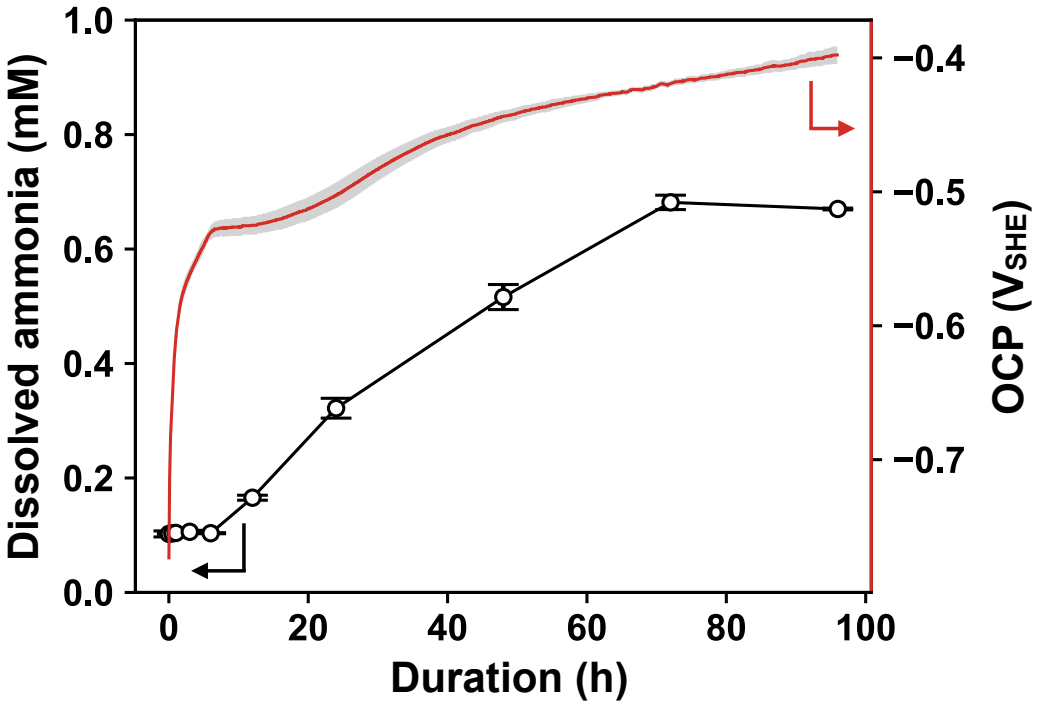

Fig. S12. Changes in the dissolved concentration of ammonia and open-circuit potential (OCP) monitored after the 48 h electrolysis of mackinawite at $-0.9\ V_{SHE}$. During the measurements, no electric potential was applied, whereas the aqueous solution was kept anaerobic by continuous CO_2 bubbling (20 ml min^{-1}). A gray area indicates twice the triplicate experiment's standard error range.

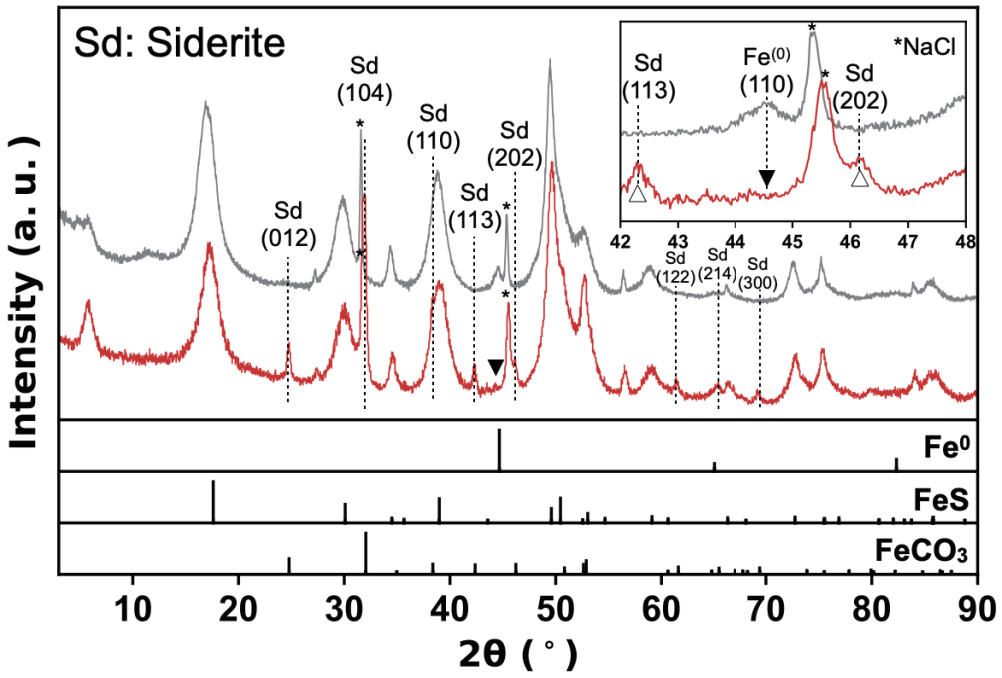

Fig. S13. Oxidation of electrolyzed mackinawite in water. XRD pattern of mackinawite electrolyzed at $-0.9\ V_{SHE}$ for 48 h (gray). The subsequent 48 h exposure in the electrolyte solution without an externally imposed electric potential resulted in the disappearance of the Fe^0 signal and the appearance of siderite ($FeCO_3$) signals (red).

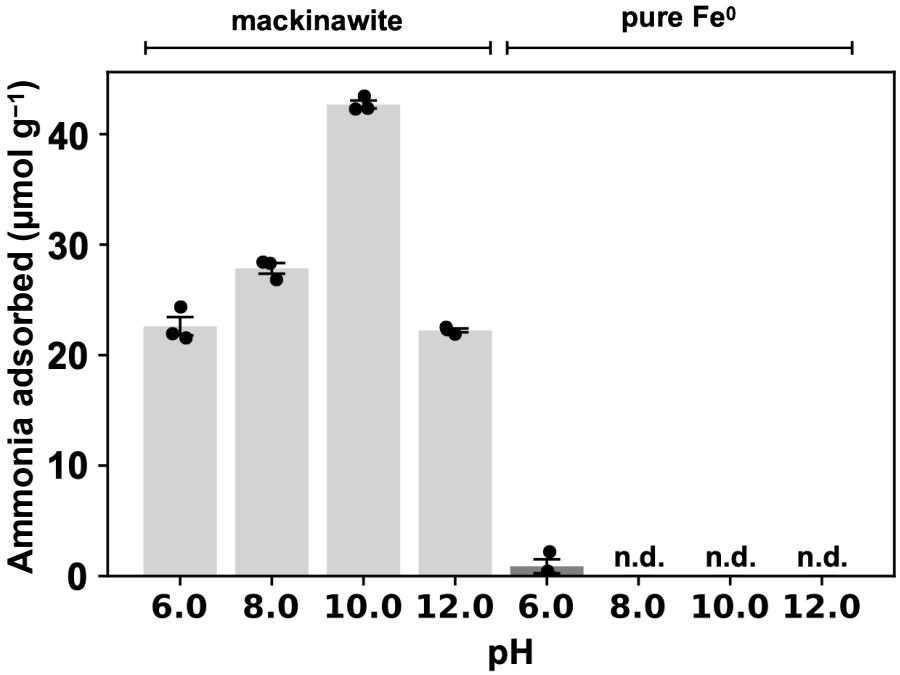

Fig. S14. pH dependence of ammonia adsorption onto mackinawite and pure Fe^0. Experimental procedure: to a serum bottle (13 ml), 50 mg of mackinawite or pure Fe^0 was added with 10 ml of deaerated 1 M NaCl containing 1 mM NH_3 in an aerobic chamber filled with N_2 and H_2 gases (volume ratio = 96:4). The solution pH was adjusted to the desired values (6.0, 8.0, 10.0, or 12.0) with HCl and NaOH prior to the addition. The bottle was then sealed with a butyl rubber cap and an aluminum stopper and was rotated at 60 rpm min^{-1} for 48 h at room temperature (25±2 °C). The resultant ammonia concentration in the sample suspension was measured after filtration. Abbreviation: n.d. = not detected (<0.1 μmol g^{-1}).

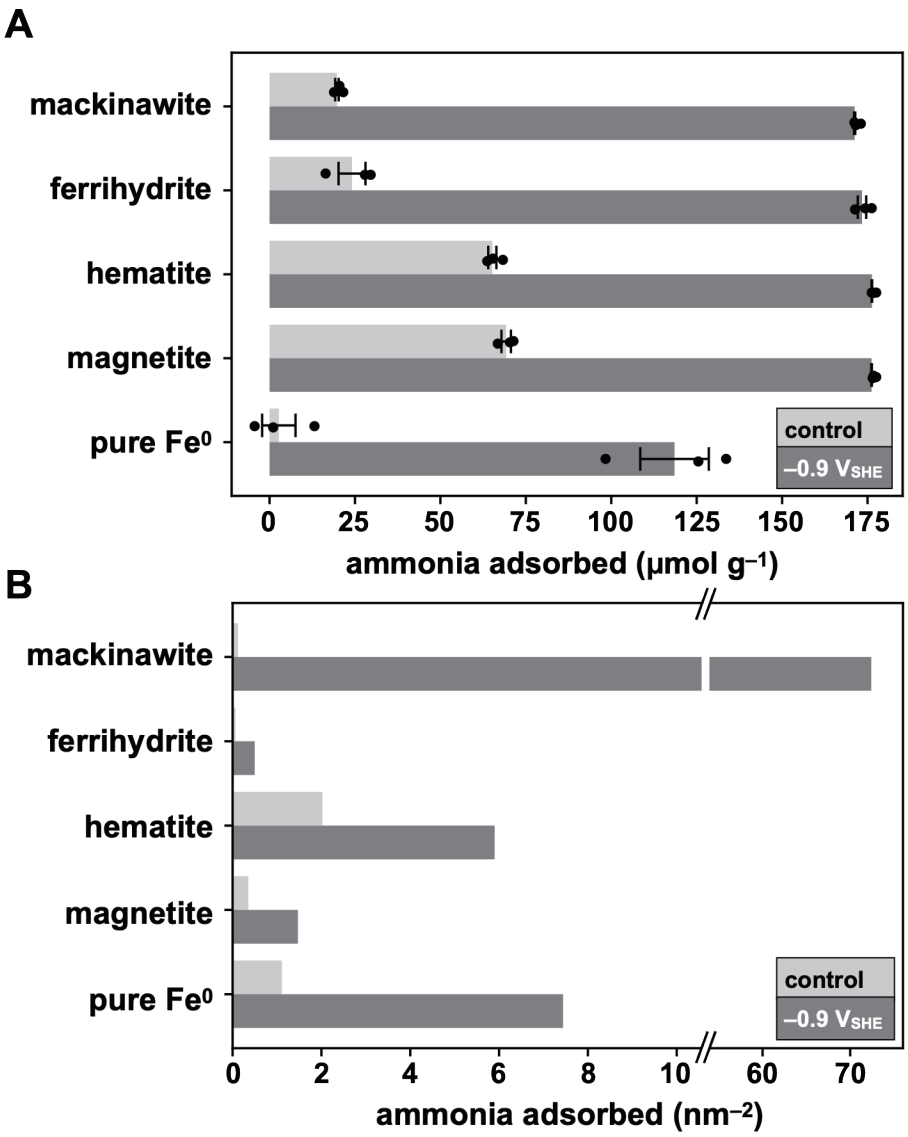

Fig. S15. The mass- (left) and SSA_{BET}-based (right) adsorption amounts of ammonia onto different solid adsorbents. The measurements were carried out after the 48 h electrolysis of adsorbents at $-0.9\ V_{SHE}$, while no electric potential was applied in the control experiment.

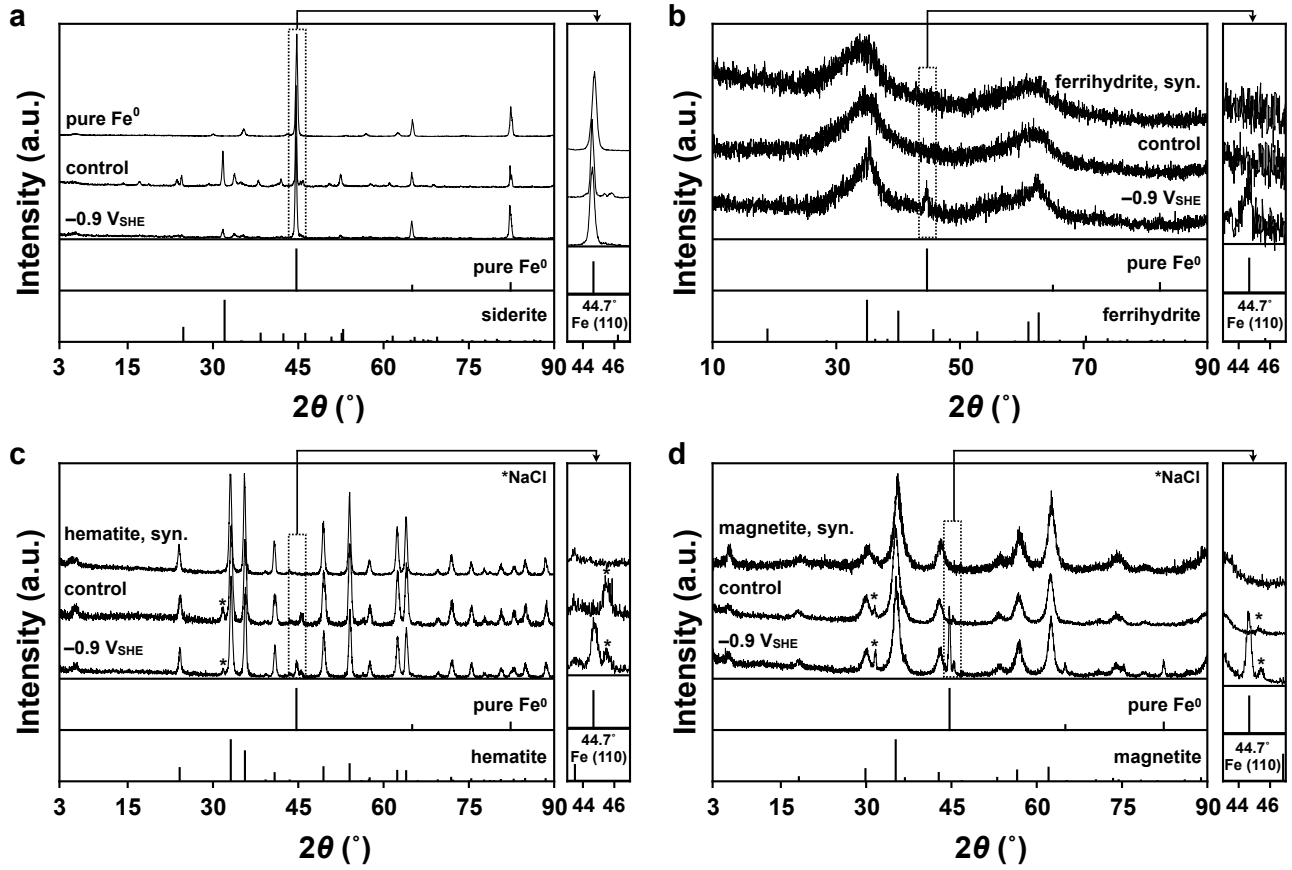

Fig. S16. XRD patterns of (a) pure Fe^0, (b) ferrihydrite, (c) hematite, and (d) magnetite before and after the 48 h electrolysis at $-0.9\ V_{SHE}$. The control experiment was performed in an electrochemical cell (Fig. S1) without an externally imposed electric potential. The asterisks (*) indicate the XRD signals of NaCl.

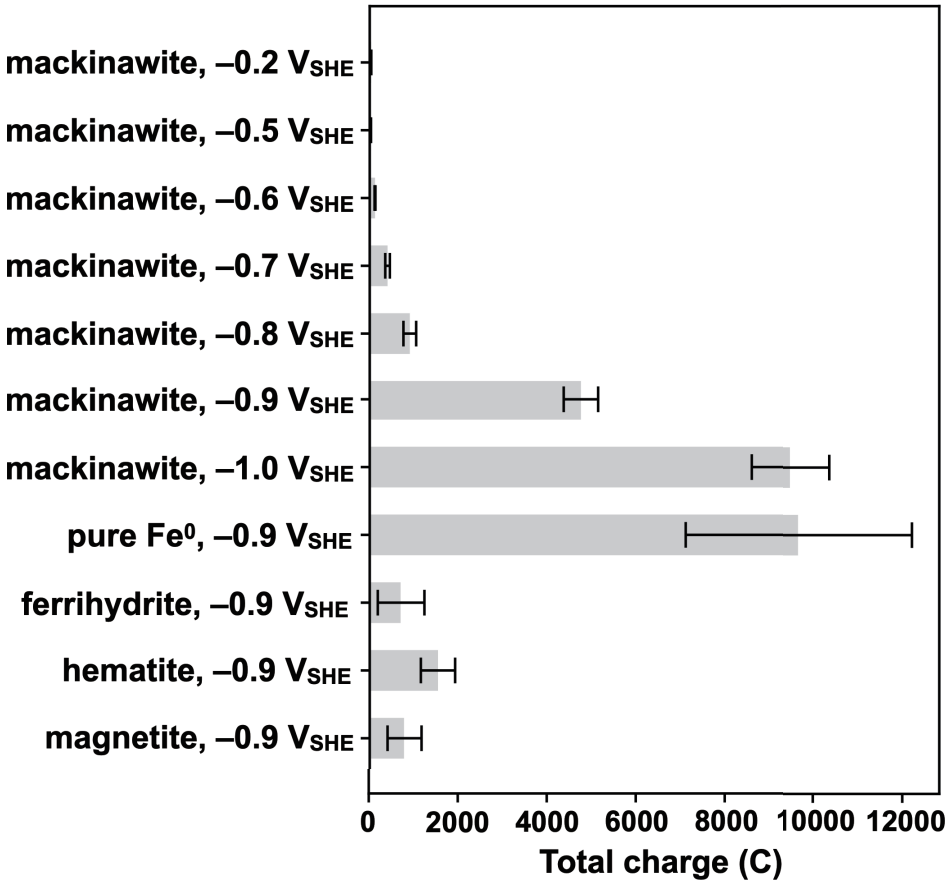

Fig. S17. Total charges built up during the electrolysis.

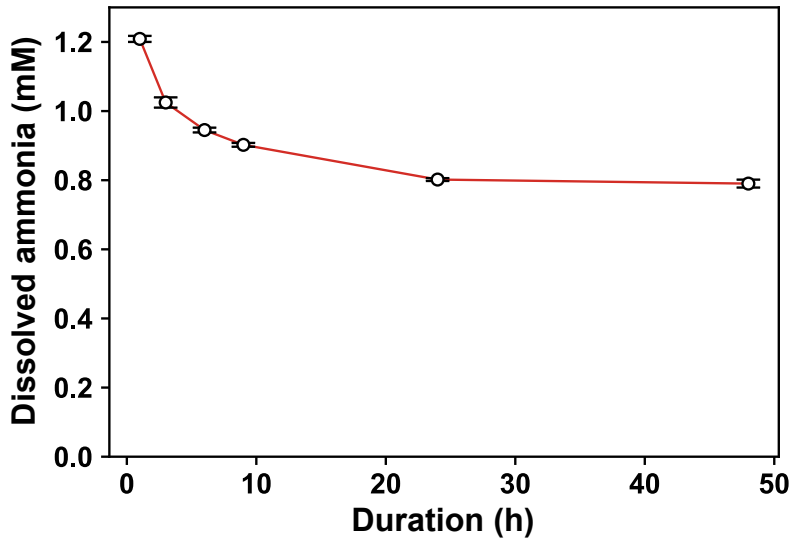

Fig. S18. Change in the dissolved concentration of ammonia in supernatant solution on mackinawite charged at $-0.9\,V_{SHE}$. Prior to the measurement, mackinawite was electrolyzed at $-0.9\,V_{SHE}$ for 48 h in the absence of dissolved ammonia; then, ammonia was added to the supernatant solution to a concentration of 1 mM. The initial data point exhibited a concentration higher than 1 mM, owing to the incomplete dispersion of ammonia at the time of sampling (1 min). Because the sampled volume (1 ml) was much smaller than that of the supernatant solution (60 ml), this excessive extraction of ammonia had negligible influence on the subsequent measurements.

Table S1. Atom percentages of Fe and S and their ratio in mackinawite determined by the EDS analysis.

	Fe L		S K		Fe/S	Fe^0
V_{SHE}	atom%	error	atom%	error		%
control	9.02	1.59	8.81	2.77	1.02±0.03	2.33±1.77
−0.2	7.54	1.62	7.43	2.66	1.01±0.03	1.46±1.75
−0.5	10.05	1.56	10.07	2.85	1.00±0.03	–0.20±1.80
−0.6	10.39	1.56	9.19	2.84	1.13±0.04	11.55±1.69
−0.7	11.81	1.55	10.63	3.01	1.11±0.04	9.99±1.75
−0.8	7.59	1.71	6.64	2.81	1.14±0.04	12.52±1.70
−0.9	8.27	1.58	7.07	2.84	1.17±0.04	14.51±1.67
−1.0	9.47	1.55	7.76	2.98	1.22±0.04	18.06±1.66

Table S2. Brunauer–Emmett–Teller specific surface area (SSA_{BET}) of mackinawite after the ammonia adsorption experiment for 48 h.

Applied potential V_{SHE}	SSA_{BET} m^2g^{-1}
control	87.0
−0.2	35.6
−0.5	59.4
−0.6	37.7
−0.7	7.33
−0.8	2.47
−0.9	1.42
−1.0	0.79

Table S3. Cell dimension and fractional coordinates of 2×2×1 FeS-NH_3.

Cell dimension			
	7.107297	−0.076326	−0.833365
	−0.027296	7.103376	−0.842924
	−0.742211	−0.787853	6.768201

Fractional coordinates			
Fe	0.000000	0.000000	0.000000
Fe	0.971963	0.972752	0.979891
Fe	0.972684	0.472400	0.983352
Fe	0.471731	0.973408	0.983083
Fe	0.473077	0.472900	0.986319
Fe	0.222826	0.222226	0.983208
Fe	0.222181	0.722532	0.979746
Fe	0.722365	0.223669	0.986759
S	0.722015	0.723391	0.983799
S	0.013622	0.262422	0.170594
S	0.013587	0.765419	0.167551
S	0.510798	0.262984	0.173949
S	0.510172	0.765823	0.170501
S	0.183339	0.932255	0.792746
S	0.184718	0.429741	0.796738
S	0.680840	0.933538	0.796783
N	0.682068	0.430988	0.797578
H	0.842747	0.601744	0.496394
H	0.848281	0.745967	0.504103
H	0.980685	0.559581	0.513188

Table S4. Cell dimension and fractional coordinates of 2×2×1 FeS.

Cell dimension			
	7.154386	0.000000	0.000000
	0.000000	7.154386	0.000000
	0.000000	0.000000	4.976529

Fractional coordinates			
Fe	0.000000	0.000000	0.000000
Fe	0.971963	0.972752	0.979891
Fe	0.972684	0.472400	0.983352
Fe	0.471731	0.973408	0.983083
Fe	0.473077	0.472900	0.986319
Fe	0.222826	0.222226	0.983208
Fe	0.222181	0.722532	0.979746
Fe	0.722365	0.223669	0.986759
S	0.722015	0.723391	0.983799
S	0.013622	0.262422	0.170594
S	0.013587	0.765419	0.167551
S	0.510798	0.262984	0.173949
S	0.510172	0.765823	0.170501
S	0.183339	0.932255	0.792746
S	0.184718	0.429741	0.796738
S	0.680840	0.933538	0.796783
N	0.682068	0.430988	0.797578
H	0.842747	0.601744	0.496394
H	0.848281	0.745967	0.504103
H	0.980685	0.559581	0.513188

Table S5. Cell dimension and fractional coordinates of 2×2×1 NH_3 (using FeS cell).

Cell dimension			
	7.107297	−0.076326	−0.833365
	−0.027296	7.103376	−0.842924
	−0.742211	−0.787853	6.768201

Fractional coordinates			
N	0.000000	0.000000	0.000000
H	0.842747	0.601744	0.496394
H	0.848281	0.745967	0.504103
H	0.980685	0.559581	0.513188

Table S6. Cell dimension and fractional coordinates of 2×2×1 reduced FeS-NH_3.

Cell dimension

	7.243760	−0.002509	−0.009048
	0.002767	6.800492	−0.000829
	0.029688	0.010142	4.974539

Fractional coordinates

Fe	0.000000	0.000000	0.000000
Fe	0.974803	0.007533	0.002397
Fe	0.988959	0.507638	0.021976
Fe	0.489718	0.007467	0.002040
Fe	0.475616	0.507698	0.021733
Fe	0.232211	0.252469	0.038780
Fe	0.232201	0.762589	0.039230
Fe	0.732463	0.287791	−0.004301
S	0.732424	0.727005	−0.004252
S	0.971523	0.255841	0.266425
S	0.971464	0.758692	0.266651
S	0.491688	0.255791	0.266001
S	0.491714	0.758718	0.266485
S	0.232829	0.007764	0.773070
S	0.232965	0.507947	0.779373

Table S7. Cell dimension and fractional coordinates of 2×2×1 reduced FeS.

Cell dimension			
	7.154386	0.000000	0.000000
	0.000000	7.154386	0.000000
	0.000000	0.000000	4.976529

Fractional coordinates			
Fe	0.000000	0.000000	0.000000
Fe	−0.001494	0.000000	0.006131
Fe	−0.006138	0.500000	−0.008593
Fe	0.501494	0.000000	0.006131
Fe	0.506138	0.500000	−0.008593
Fe	0.250000	0.251494	0.006131
Fe	0.250000	0.748506	0.006131
Fe	0.750000	0.256138	−0.008593
S	0.750000	0.743862	−0.008593
S	−0.005858	0.255858	0.243274
S	−0.005858	0.744142	0.243274
S	0.505858	0.255858	0.243274
S	0.505858	0.744142	0.243274
S	0.250000	0.000000	0.764371
S	0.250000	0.500000	0.757941

Table S8. Cell dimension and fractional coordinates of 2×2×1 NH_3 (using reduced FeS cell).

Cell dimension			
	7.149766	0.022717	0.380813
	0.024680	6.980119	0.121832
	0.288119	0.092258	5.342456

Fractional coordinates			
N	0.000000	0.000000	0.000000
H	0.646811	0.474034	0.656389
H	0.644062	0.604242	0.562568
H	0.785680	0.437530	0.655207

Table S9. Cell dimension and fractional coordinates of 3×3×1 reduced FeS-NH_3.

Cell dimension			
	10.651442	0.025324	0.147314
	0.021474	10.724394	0.256312
	0.057444	0.121755	5.133879
Fractional coordinates			
Fe	0.000000	0.000000	0.000000
Fe	0.001849	0.995716	0.026856
Fe	0.993767	0.671917	0.031306
Fe	0.666496	0.994031	0.009628
Fe	0.669420	0.666707	0.005844
Fe	0.998704	0.328591	0.004045
Fe	0.668037	0.327395	0.988058
Fe	0.333490	0.995861	0.015971
Fe	0.331653	0.664057	0.000273
Fe	0.332551	0.330698	0.000071
Fe	0.166487	0.163860	0.010386
Fe	0.165569	0.830100	0.022162
Fe	0.834240	0.159915	0.005455
Fe	0.840040	0.830272	0.045715
Fe	0.163381	0.497396	0.999464
Fe	0.836288	0.497854	0.973930
Fe	0.499934	0.162958	0.000306
Fe	0.499995	0.829200	0.008903
S	0.499629	0.496780	0.989284
S	0.996630	0.160264	0.251302
S	0.002352	0.828145	0.282539
S	0.663843	0.158636	0.238703
S	0.662908	0.822705	0.253851
S	0.993561	0.492205	0.234467
S	0.666280	0.490771	0.213412
S	0.331741	0.160189	0.243906
S	0.332153	0.822263	0.250556
S	0.330421	0.492317	0.234005
S	0.169090	0.000823	0.779136
S	0.160271	0.673081	0.777418
S	0.839792	0.992614	0.782841
S	0.167695	0.334046	0.764471
S	0.839095	0.327289	0.754942
S	0.501832	0.999837	0.770191
S	0.503650	0.671910	0.765713
N	0.501172	0.333259	0.756926
H	0.808226	0.609618	0.659025
H	0.788332	0.704802	0.659135
H	0.896864	0.607421	0.570791

Table S10. Cell dimension and fractional coordinates of 3×3×1 reduced FeS.

Cell dimension

10.665771	0.000000	0.000000
0.000000	10.665771	0.000000
−0.000000	−0.000000	4.987747

Fractional coordinates

Fe	0.000000	0.000000	0.000000
Fe	−0.000000	−0.001177	0.002905
Fe	−0.000000	0.666667	−0.010154
Fe	0.665183	−0.002142	0.001753
Fe	0.659532	0.666667	−0.005084
Fe	−0.000000	0.334510	0.002905
Fe	0.665183	0.335475	0.001753
Fe	0.334817	−0.002142	0.001753
Fe	0.340468	0.666667	−0.005084
Fe	0.334817	0.335475	0.001753
Fe	0.167844	0.166667	0.002905
Fe	0.168808	0.831850	0.001753
Fe	0.832156	0.166667	0.002905
Fe	0.831192	0.831850	0.001753
Fe	0.168808	0.501483	0.001753
Fe	0.831192	0.501483	0.001753
Fe	0.500000	0.166667	−0.010154
Fe	0.500000	0.826199	−0.005084
S	0.500000	0.507135	−0.005084
S	−0.000000	0.166667	0.244746
S	−0.000000	0.830281	0.242708
S	0.663615	0.166667	0.242708
S	0.663525	0.830191	0.248144
S	−0.000000	0.503052	0.242708
S	0.663525	0.503142	0.248144
S	0.336385	0.166667	0.242708
S	0.336475	0.830191	0.248144
S	0.336475	0.503142	0.248144
S	0.167265	−0.000599	0.758939
S	0.171880	0.666667	0.753647
S	0.832735	−0.000599	0.758939
S	0.167265	0.333932	0.758939
S	0.832735	0.333932	0.758939
S	0.828120	0.666667	0.753647
S	0.500000	−0.005213	0.753647

Table S11. Cell dimension and fractional coordinates of 3×3×1 NH_3 (using reduced FeS cell).

Cell dimension			
	10.651442	0.025324	0.147314
	0.021474	10.724394	0.256312
	0.057444	0.121755	5.133879

Fractional coordinates			
N	0.000000	0.000000	0.000000
H	0.808226	0.609618	0.659025
H	0.788332	0.704802	0.659135
H	0.896864	0.607421	0.570791

Table S12. Cell dimension and fractional coordinates of 4×4×1 reduced FeS-NH_3.

Cell dimension

14.253583	−0.000000	0.000000
0.000000	14.253583	−0.000000
0.000000	−0.000000	4.976540

Fractional coordinates

Fe	0.000000	0.000000	0.000000	S	0.875426	0.874342	0.000677
Fe	0.001502	−0.000579	0.000505	S	0.001436	0.124176	0.245824
Fe	0.000056	0.500110	0.009593	S	0.000105	0.625911	0.250317
Fe	0.501602	0.000464	−0.000313	S	0.501000	0.126706	0.239222
Fe	0.508983	0.498509	−0.088914	S	0.504066	0.623442	0.225413
Fe	0.001473	0.249725	0.006093	S	0.001314	0.374645	0.251429
Fe	0.000758	0.749685	0.002665	S	0.000700	0.874954	0.244214
Fe	0.502208	0.252056	−0.005001	S	0.501592	0.378869	0.221631
Fe	0.502829	0.748944	−0.003941	S	0.501481	0.874726	0.239290
Fe	0.252394	−0.000229	−0.000080	S	0.252271	0.125648	0.240966
Fe	0.249445	0.500534	0.001704	S	0.252161	0.625068	0.243575
Fe	0.750814	−0.000052	−0.000098	S	0.750058	0.124328	0.245139
Fe	0.751374	0.499062	0.019937	S	0.747230	0.626550	0.245510
Fe	0.252246	0.250773	−0.003247	S	0.252181	0.375410	0.240827
Fe	0.252716	0.748877	−0.002281	S	0.252408	0.874437	0.241663
Fe	0.751081	0.250006	0.005199	S	0.750730	0.372831	0.256998
Fe	0.748990	0.748920	−0.003151	S	0.749270	0.874723	0.241169
Fe	0.127019	0.124858	0.000622	S	0.127352	−0.000657	0.757831
Fe	0.125663	0.625143	0.006249	S	0.124202	0.500215	0.761563
Fe	0.626286	0.125692	−0.003957	S	0.626654	0.000665	0.752943
Fe	0.626420	0.619383	−0.035431	S	0.126196	0.250108	0.758707
Fe	0.125859	0.375060	0.003924	S	0.126548	0.749013	0.759051
Fe	0.127007	0.874359	0.001529	S	0.628682	0.250620	0.754711
Fe	0.629415	0.377259	−0.004651	S	0.627236	0.751126	0.745821
Fe	0.625985	0.875256	−0.007540	S	0.377568	−0.000213	0.753755
Fe	0.377146	0.125891	−0.006288	S	0.367922	0.500874	0.738372
Fe	0.377778	0.622910	−0.005628	S	0.876670	−0.000342	0.758177
Fe	0.876260	0.124565	0.003796	S	0.875621	0.499386	0.767632
Fe	0.874510	0.624898	0.009191	S	0.377013	0.250479	0.750705
Fe	0.376627	0.377595	−0.012726	S	0.377605	0.749001	0.753079
Fe	0.377398	0.874285	−0.005396	S	0.876967	0.250077	0.763351
Fe	0.875797	0.374752	0.011215	N	0.876213	0.748754	0.759532
				H	0.642080	0.493987	0.817969
				H	0.529783	0.585512	0.727306
				H	0.652643	0.491509	0.612935

Table S13. Cell dimension and fractional coordinates of 4×4×1 reduced FeS.

Cell dimension

14.253583	−0.000000	0.000000
0.000000	14.253583	−0.000000
0.000000	−0.000000	4.976540

Fractional coordinates

Fe	0.000000	0.000000	0.000000	S	0.873925	0.874193	0.000290
Fe	−0.000557	0.000000	0.000618	S	−0.000547	0.125547	0.243584
Fe	−0.001422	0.500000	−0.006548	S	−0.000932	0.623484	0.243283
Fe	0.500856	0.000000	0.000879	S	0.501516	0.125932	0.243283
Fe	0.505800	0.500000	−0.003886	S	0.502497	0.622503	0.249799
Fe	−0.000807	0.251075	0.000290	S	−0.000932	0.376516	0.243283
Fe	−0.000807	0.748925	0.000290	S	−0.000547	0.874453	0.243584
Fe	0.501180	0.252312	0.002341	S	0.502497	0.377497	0.249799
Fe	0.501180	0.747688	0.002341	S	0.501516	0.874068	0.243283
Fe	0.250557	0.000000	0.000618	S	0.250547	0.125547	0.243584
Fe	0.251422	0.500000	−0.006548	S	0.250932	0.623484	0.243283
Fe	0.749144	0.000000	0.000879	S	0.748484	0.125932	0.243283
Fe	0.744200	0.500000	−0.003886	S	0.747503	0.622503	0.249799
Fe	0.250807	0.251075	0.000290	S	0.250932	0.376516	0.243283
Fe	0.250807	0.748925	0.000290	S	0.250547	0.874453	0.243584
Fe	0.748820	0.252312	0.002341	S	0.747503	0.377497	0.249799
Fe	0.748820	0.747688	0.002341	S	0.748484	0.874068	0.243283
Fe	0.125000	0.125557	0.000618	S	0.125000	0.000000	0.757083
Fe	0.125000	0.624144	0.000879	S	0.125000	0.500000	0.753023
Fe	0.625000	0.126422	−0.006548	S	0.625000	0.000000	0.753023
Fe	0.625000	0.619200	−0.003886	S	0.125000	0.250889	0.757237
Fe	0.125000	0.375856	0.000879	S	0.125000	0.749111	0.757237
Fe	0.125000	0.874443	0.000618	S	0.625000	0.254531	0.754570
Fe	0.625000	0.380800	−0.003886	S	0.625000	0.745469	0.754570
Fe	0.625000	0.873578	−0.006548	S	0.375889	0.000000	0.757237
Fe	0.376075	0.125807	0.000290	S	0.379531	0.500000	0.754570
Fe	0.377312	0.623820	0.002341	S	0.874111	0.000000	0.757237
Fe	0.873925	0.125807	0.000290	S	0.870469	0.500000	0.754570
Fe	0.872688	0.623820	0.002341	S	0.376051	0.251051	0.757016
Fe	0.377312	0.376180	0.002341	S	0.376051	0.748949	0.757016
Fe	0.376075	0.874193	0.000290	S	0.873949	0.251051	0.757016
Fe	0.872688	0.376180	0.002341				

Table S14. Cell dimension and fractional coordinates of 4×4×1 NH_3 (using reduced FeS cell).

Cell dimension			
	14.306674	0.029652	0.167938
	0.028139	14.263304	0.124753
	0.058488	0.044452	5.049372

Fractional coordinates			
N	0.000000	0.000000	0.000000
H	0.590699	0.479100	0.667169
H	0.599936	0.549347	0.615847
H	0.660409	0.455238	0.649342

Table S15. Intercalation energies ($\triangle E$) of NH_3 in mackinawite determined by first-principles calculations assuming several different mackinawite structures.

	Fe^0 (%)	ΔE (eV)
$2 \times 2 \times 1$ pure mackinawite	0	0.63
$2 \times 2 \times 1$ mackinawite with one S atom removed	33.3	–1.34
$3 \times 3 \times 1$ mackinawite with one S atom removed	12.5	–0.61
$4 \times 4 \times 1$ mackinawite with one S atom removed	6.25	–0.93

References

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