Raman Spectroscopy of Mackinawite FeS in Anodic Iron Sulfide Corrosion Products

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Abstract

Corrosion of iron in H₂S containing solutions is a general problem in crude oil and natural gas production, and is generally referred to as sour corrosion. Aqueous H₂S solutions promote corrosion of steels, but the exact nature and mechanisms of corrosion strongly depend on the reaction conditions. While the process has been widely investigated for pure iron and carbon steels, there is still a lack of understanding of the reaction path and electronic properties of the corrosion products.

The chemistry of the corrosion products formed during H₂S-triggered corrosion is rather complex, as there are many different solids consisting of iron and sulfur. However, mackinawite has been found to be the initial solid, and probably most important corrosion product, of iron in aqueous sulfide solutions as it was observed in reactions carried out over a wide range of pH and temperature. In the field of microbially induced corrosion, sulfate-reducing bacteria are known to transform sulfate compounds into iron sulfides, e.g., mackinawite.

Raman spectroscopy has become an important tool for identification of corrosion products. Some major problems may still occur due to laser heating, fluorescence, or low sensitivity as a consequence of the small cross-sections of Raman scattering. However, the fact that glass and water are both very weak Raman scatterers makes this technique suitable for in situ measurements in aqueous environments. The presence of water has an additional positive effect on the process as it decreases the heating from the laser. The use of (in situ and operando) Raman spectroscopy for study corrosion process studies of iron in sulfide rich environments has been already reported.

In previous work, Raman spectroscopy was used to confirm the nature of iron sulfide films obtained as corrosion products from polarization experiments. Collected spectra showed a good agreement with the database Raman spectrum of mackinawite, but distinct disagreement with data from other authors was found. Due to the lack of availability of a normal mode analysis for mackinawite, no detailed discussion of spectral changes during oxidation of the corrosion products. Furthermore, for oxide thin films it is known that in situ characterization sometimes leads to different results than post mortem analysis.

Experimental

Ex situ investigations.—Samples for the ex situ investigations were prepared in an air tight homebuilt flat bottom PMMA cell of 500 mL electrolyte volume and electrode area A = 0.785 cm². The electrolyte was first de-oxygenated by purging with nitrogen, and then saturated with hydrogen sulfide for at least 30 min. Hydrogen sulfide was maintained throughout the experiments to minimize ingress of oxygen. The conditions used were similar to those reported elsewhere. Polarization and ex situ spectroscopy were conducted at room temperature. No stirring was applied during polarization.

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For ex situ Raman measurements, potentiostatic polarization at 200 mV above the initial corrosion potential was used for the preparation of sulfide films on the surface of the iron sample. The total reaction time was 44 h. For this purpose, a typical three-electrode arrangement and a Gamry PCIV/Series G Family potentiostat (Gamry Instruments Inc.) were used. A carbon rod (Mueller and Roessner, Troisdorf, Germany) acted as the counter electrode, and a commercial Ag/AgCl/3M KCl as reference electrode (Metrohm, Filderstadt, Germany). Using a Luggin capillary arrangement, the reference electrode was positioned very close to the iron sample serving as working electrode.

**In situ experiments.**—For the in situ experiments, the used setup was modified to fit under a confocal Raman microscope, which led to a cell with significantly smaller dimensions (Fig. 1, A = 0.2 cm²). Because of safety concerns, H₂S-prepurged solutions were used for in situ experiments. However, N₂ purging was maintained throughout the experiments to minimize ingress of oxygen. Because of the small size of the cell and the connecting pipes, a lower potential (50 mV above Ecorr) was applied to produce the iron sulfide layers. In this way, excessive formation of bubbles at the counter electrode because of hydrogen evolution and a subsequent plugging of the tubing was avoided. A peristaltic pump was used, thus allowing circulation of the test electrolyte, starting with H₂S-free solution and then switching to H₂S-saturated electrolyte. Continuous flow over the iron was maintained throughout the experiments. In this way, the surface was cooled, preventing a laser-induced heating of the surface. The total reaction time was 30 min. As the size of the in situ Raman cell was small, a modified three-electrode arrangement for the electrochemical experiments was used, with a carbon rod (Mueller and Roessner, Troisdorf, Germany) as the counter electrode, a commercial Ag/AgCl/3M KCl as reference electrode (Metrohm, Filderstadt, Germany), and the iron sample as working electrode. A Gamry PCIV/Series G Family (Gamry Instruments Inc.) potentiostat was used. A Luggin capillary arrangement was used to protect the reference electrode from getting poisoned by sulfide species.

Raman spectra were recorded on an alpha300M confocal Raman microscope (WiTec, Ulm, Germany), with an excitation wavelength of 532.1 nm. Illumination and detection was performed through a microscope objective of 100× magnification, numerical aperture of 0.75 for ex situ, and of 40× magnification, numerical aperture of 0.6 for in situ experiments. Ex situ spectra were recorded in ambient air atmosphere without special protection. The resulting spectra were analyzed using the WiTec Project software.

The identification of the ex situ products using grazing incidence X-ray diffraction (GI-XRD) was conducted on a Bruker D8 Advance diffractometer with Cu Kα radiation and a Sol-X solid-state detector. Diffraction patterns were collected at an angle of incidence α = 3° within a range of the scattering angle 2θ of 10° < 2θ < 75° in steps of 0.05°, and an integration time of 60 s per step. XRD patterns were evaluated using the DIFFRACplus EVA package.

**Results and Discussion**

The coverage of the metal sample with a black precipitate was indicative of the successful growth of corrosion products film containing iron sulfide compounds. The formation of iron sulfides in H₂S-saturated solutions using electrochemical techniques is well known.8,19,21,49,60

Under the conditions used in this work, formation of a black layer of corrosion products on top of the metal surface was already observed after several hours. In Fig. 2, the well-formed FeS layer after a reaction time of 44 h is depicted. (SEM images of similar corrosion product layers are available elsewhere.19) The Raman spectrum of the sample after drying with water/alcohol in a nitrogen stream (Fig. 2b) is in good agreement with literature spectra attributed to the iron sulfide mackinawite, e.g., spectrum (d’) in Fig. 2.52,53 Moreover, XRD measurements showed that mackinawite is the only detectable crystalline compound in the obtained corrosion products (Fig. 3b). After aging the products in air (in this example for 90 days), a change in their color from black to rust-red became visible (Fig. 2c). This is a clear indication for the oxidation of the initial products and has been supported by XRD measurements (Fig. 3c), which confirmed the presence of the iron(III) oxide hydroxide phase akaganeite.

The corresponding Raman spectrum of the oxidized compound (Fig. 2c′) looked, however, almost identical to the spectrum of the non-oxidized compound, mackinawite. Further, the spectrum does not match the one for akaganeite, but rather the one for hematite.50,54,55 A possible explanation for these observations is a transformation of the compound during the Raman measurements, e.g., as a consequence of heating by laser light absorption in the presence of oxygen from air. Hematite was found also in other works as the result of laser heating.54,61 Hematite has an intense spectrum characterized by the strong resonant band at 1310 cm⁻¹ under green excitation.61 Further Raman experiments have been conducted with dry samples. These samples were protected with Capton foil from air. Laser exposure was...
minimized to a power of typically several hundreds of µW, but always below 1 mW (corresponding to ≈ 6 · 10⁻¹⁰ W m⁻² around the focus of the objective). As a result, however, always the same Raman spectrum as shown in Fig. 2c was observed.

In order to identify the reaction products correctly, in situ experiments have been conducted. This approach has been successfully used by other groups.²⁹,⁴⁹ The advantages of in situ techniques are the possibility to monitor the corrosion products in their state of formation,⁶₂ but also to avoid the contact of the sample with oxygen due to post-preparation work, transport, etc. The in situ cell shown in Fig. 1 was used for these experiments. The peristaltic pump allowed circulation of the test solution. The maintaining of the continuous flow over the iron was crucial in order to keep the surface cooled, thus preventing laser-induced heating of the surface. Moreover, due to the purging of the electrolyte with N₂ throughout the in situ experiment, the ingress of oxygen in the cell was reduced to a minimum.

The observed visual changes of the surface during the in situ experiments and the collected Raman spectra are depicted in Fig. 4. The corresponding current time curve recorded during the experiment is shown in Fig. 5, together with the corresponding curve for the preparation of the samples for ex situ experiments (inset). Formation of black corrosion products was observed almost immediately after starting the electrode polarization (Fig. 4c). The only significant Raman bands were observed at 286 cm⁻¹ and 202 cm⁻¹ in the example shown (Fig. 4c), indicating the formation of mackinawite.²⁹,⁴⁹ No additional bands were detected after polarization for up to 30 min and total exposure to the electrolyte of up to 3 h at E⁺corr. After terminating the electrochemical experiment, the position of the sample was shifted to illuminate a different area of the surface. The collected Raman spectra confirmed the uniform coverage of the surface by the iron sulfide mackinawite. However, removing the sample from the cell and drying in a nitrogen stream lead to a change of the spectrum. The detected Raman bands after drying were also in good agreement with those of the iron(III) oxide hematite.⁵⁰,⁶¹ Dominant Raman peaks of the different relevant iron compounds are summarized and compared to literature values in Table I.

Using the information from the in situ measurements, another simpler experiment was developed. For this experiment, the sample was just taken out of the electrochemical cell after a regular polarization experiment, and was carefully washed with distilled water. Care was taken not to remove the thin water layer on top of the reaction products.

Figure 4. Results from in situ Raman experiments. (a), (b) Microscopic images recorded in the same confocal microscope as used for the Raman measurements of the surface before and after introducing the H₂S saturated electrolyte, respectively. (c) Image of substrate surface after starting the electrochemical treatment and (c’) corresponding Raman spectrum. Current time transients during polarization are shown in Fig. 5. (d) Image of surface after termination of the polarization and (d’) corresponding Raman spectrum. (e) Image of corrosion products after removing from in situ cell and drying with nitrogen stream and (e’) corresponding Raman spectrum.

Subsequently, Raman measurements were conducted. Raman spectra obtained in this configuration agree well with spectra of the in situ experiments (Fig. 6). The iron sulfide corrosion products appeared stable and close to their initial structure under the thin water film. During the evaporation of the water layer in ambient atmosphere, further Raman spectra showed transformation of the compound to hematite (as shown in the ex situ experiments above), but with magnetite as an intermediate (Fig. 6).

The different routes of oxidation observed here are summarized in Fig. 7. In the sulfide containing electrolyte, iron was oxidized to FeS (reaction 1). Both Raman and XRD showed the presence of...
tetragonal mackinawite. Peak shifts in the Raman spectrum observed after exposure to oxygen have been interpreted as indication of a partial further oxidation of the initially formed mackinawite to a product containing a fraction of FeIII (reaction 2). From here onward, further oxidation was different depending on whether the process was carried out in the presence or absence of a thin electrolyte film. In the presence of an electrolyte film, the iron(III) oxide hydroxide akaganeite, FeOOH, and below the layers.25,27,64–66 Each sulfur atom is surrounded by four nearest iron atoms, resulting in a square-based pyramid coordination polyhedron. The space group is $Pnma$ with the unit cell containing two formula units of FeS.25,27,64–66

The Raman spectrum of the primary corrosion product mackinawite can be analyzed in detail. This spectrum consists of two peaks in the spectral range investigated here, in line with previous reports.29,63 Tetragonal FeS forms a layer structure in which the iron atoms are arranged in centered squares, and the sulfur atoms lie alternately above and below the layers.25,27,64–66 Each sulfur atom is surrounded by four nearest iron atoms, resulting in a square-based pyramid coordination polyhedron. The space group is $P4mm$ with the unit cell containing two formula units of FeS.25,27,64–66 For a unit cell containing 4 atoms, as in case of mackinawite, 12 vibrations are expected in total. The Fe atoms lie on $D_{4d}$ sites (Wyckoff position 2a) and give rise to two Raman active modes: $B_{1g}$ and $E_g$. The sulfur atoms occupy $C_{2a}$ sites (Wyckoff position 2c) and also give rise to two Raman active vibrations: $A_{2g}$ and $E_g$. Overall, four different modes are Raman active with respect to the above mentioned space group: $A_{2g}$, $B_{1g}$, and 2 $E_g$ modes.53,67–69 For “aged”, polycrystalline mackinawite developed after two months exposure, these have been assigned on the basis of

Table I. Reported Raman peak positions for mackinawite and other relevant iron phases compared to values found in this work.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Position / cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mackinawite</td>
<td>FeS</td>
<td>200, (253), 287</td>
<td>This work, in situ</td>
</tr>
<tr>
<td>Mackinawite</td>
<td>FeS</td>
<td>212, 298</td>
<td>This work, ex situ</td>
</tr>
<tr>
<td>Nanocryst. mackinawite</td>
<td>FeS</td>
<td>208, (256), 283</td>
<td>29</td>
</tr>
<tr>
<td>Cryst. mackinawite</td>
<td>FeS</td>
<td>208, 257, 298</td>
<td>29</td>
</tr>
<tr>
<td>Amorph. mackinawite</td>
<td>FeS</td>
<td>208, 282</td>
<td>49</td>
</tr>
<tr>
<td>Amorph. mackinawite</td>
<td>FeS</td>
<td>214, 282</td>
<td>75</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>218, 285, 401, 1306</td>
<td>This work</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>223, 289, 404, 1310</td>
<td>61,76</td>
</tr>
<tr>
<td>Maghemite</td>
<td>Fe$_2$O$_3$</td>
<td>377, 510, 670, 715</td>
<td>77</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>FeOOH</td>
<td>310, 390, 720</td>
<td>61,76</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>671</td>
<td>This work</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>671</td>
<td>61,76</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td>S$_8$</td>
<td>153, 219, 472</td>
<td>78</td>
</tr>
</tbody>
</table>

Figure 5. Time dependence of current densities during potentiostatically controlled growth of a corrosion product layer in an in situ Raman experiment. Polarization was carried out 50 mV above $E_{corr}$. The recorded Raman spectra are depicted in Fig. 4. Inset: Corresponding current time curves for polarization of samples for ex situ Raman experiments, where polarization was carried out 200 mV above $E_{corr}$. A discussion of current time transients is available elsewhere.19

Figure 6. Results from ex situ Raman experiments of a sample with thin water layer on top. Sample were dried “naturally” by evaporation of water during the recording of spectra. (a) The Raman bands at 209 cm$^{-1}$ and 296 cm$^{-1}$ show the presence of FeS (mackinawite) of the wet sample. (b) An additional band at 253 cm$^{-1}$ arose when water layer became thinner. (c) A strong band at 671 cm$^{-1}$ indicates the transformation of the initial corrosion product mackinawite to maghemite, Fe$_3$O$_4$. (d) The final transformation product hematite (219 cm$^{-1}$, 285 cm$^{-1}$, 396 cm$^{-1}$, 1306 cm$^{-1}$) was detected when sample was completely dry, similar to results of ex situ experiments.

Figure 7. Scheme summarizing the observed chemical transformations. During exposure to H$_2$S-containing electrolyte (1), iron transformed into mackinawite FeS. Partial oxidation (2) led to a mixed sulfide. Different further oxidation was observed depending on whether the process was carried out in presence of water (3, 4) or in absence of macroscopic amounts of water (5, 6). $\Delta T$ indicates heating, in this particular case as a consequence of exposure to a laser source.
DFT calculation as 388 cm$^{-1}$, 225 cm$^{-1}$, 243 cm$^{-1}$, and 396 cm$^{-1}$, respectively. On the other hand, the observation in this work is that XRD already shows a typically crystalline mackinawite diffraction pattern, even though the Raman spectrum is similar to the spectrum that other sources assigned to a special nanocrystalline “initial” form of mackinawite. It is not directly obvious why a nanocrystalline mackinawite should have a Raman spectrum that is so qualitatively different from the spectrum of the crystalline product. The fact remains that the observed Raman spectra for the “initial” mackinawite contains only two of the four modes expected (Table I). The two missing modes may be below the accessible wavenumber range. At lower wavenumbers, the spectrum of water complicates the analysis. However, compared to the spectra of “aged” mackinawite, the modes should actually be in the spectral range investigated here.

For an interpretation of the Raman spectrum of “initial” mackinawite, a comparison with other compounds in spacegroup $P4/nmnm$ is instructive, in addition to a comparison to the calculated spectrum for “aged” mackinawite. Raman studies of thin films of SnO$_2$ and single crystals of both FeTe and FeSe show the absence of the $E_g$ modes because of crystal orientation. (On the other hand, the $E_g$ modes were detected e.g. in PbO and FeS in appropriate experiments.) Layers of mackinawite corrosion products are often strongly textured in (001) direction as well. We therefore conclude that the $E_g$ modes are absent here as well due to texturing, so that the dominant modes at 200–215 cm$^{-1}$ and 285–300 cm$^{-1}$ must be $A_{1g}$ and $B_{1g}$ modes. The small peak at 258 cm$^{-1}$ visible in the spectra in Figs. 6a and 6b may originate from one of the $E_g$ modes, as these films are not single crystalline. Such an assignment agrees with DFT calculations. In “aged” mackinawite, as well as in iron compounds that crystallize in the same space group, FeTe$^{20}$, FeSe$^{21}$, and both LaFeAsO and SmFeAsO$_x$ $B_{1g}$ modes of the Fe sublattice at the Wyckoff position 2a are observed between 190 and 230 cm$^{-1}$, which agrees with one of the peaks observed for the “initial” mackinawite investigated in this study. We therefore reason that the peak at 200–215 cm$^{-1}$ corresponds to the $B_{1g}$ mode of the Fe sublattice in “initial” mackinawite FeS. Consequently, the mode at 286 cm$^{-1}$ should be the $A_{1g}$ mode of the S sublattice. This assignment is not in agreement with the assignment based on DFT calculations for “aged” mackinawite, which reports the $A_{1g}$ mode of the S sublattice around 380 cm$^{-1}$. (Aged mackinawite shows no peak around 286 cm$^{-1}$.) Both assignments are reasonable when compared to the modes of the chalcogenide sublattices in FeTe (159 cm$^{-1}$)$^{79}$ and FeSe (180 cm$^{-1}$)$^{72}$ which follow the expected trends based on the atomic masses of Te, Se, and S.

The evolution of the spectrum of mackinawite and mackinawite-like corrosion products with time, together with the assignments as far as they agree between “initial” and “aged” mackinawite, may serve as a starting point to discuss in more detail the structural evolution of mackinawite corrosion products. “Aged” mackinawite is polycrystalline and shows both $E_g$ modes. These modes are absent in the strongly textured “initial” mackinawite. The characteristic $B_{1g}$ mode of the Fe sublattice changes slightly in position, which may be attributed to partial oxidation with time.$^{29,51,52}$ If the reasoning in the previous paragraph is correct, strong restructuring occurs in the S sublattice of mackinawite over time.

It is known from other compounds, e.g. ZnO, that point defects, e.g. vacancies, can significantly alter the Raman spectrum. It is known from other compounds, e.g. ZnO, that point defects, e.g. vacancies, can significantly alter the Raman spectrum. It is known from other compounds, e.g. ZnO, that point defects, e.g. vacancies, can significantly alter the Raman spectrum. It is known from other compounds, e.g. ZnO, that point defects, e.g. vacancies, can significantly alter the Raman spectrum. If the mackinawite-based corrosion products are exposed to sulfide-containing media, point defects can significantly alter the Raman spectrum.

Conclusions

In ambient atmosphere, iron sulfide corrosion products underwent oxidation to iron oxides and subsequently suffered the heat induced transformations known from Raman spectroscopy of iron oxides (Fig. 7). Apparently, some spectra reported in the literature and in reference databases were affected by this problem and present therefore mixed spectra including iron oxide peaks. Consequently, different sources report different Raman spectra for the same compound, in this case mackinawite FeS. Even reported reference spectra need to be treated carefully. Because the peaks of $A_{1g}$ and one $E_g$ mode of hematite are very close to the $B_{1g}$ and $A_{1g}$ modes of “initial” mackinawite, hematite may be wrongly identified as mackinawite. Oxidation and subsequent transformation can be avoided either by in situ experiments, or by a simple wetting of the sample with water, and ensuring a thin water film remains present during the Raman measurement.

Comparing results from this work to literature data shows that the spectrum of mackinawite itself significantly changes with time if the mackinawite-based corrosion products are exposed to sulfide-containing media. The different spectra observed over time in the literature may be explained by restructuring, defect healing and defect formation within the sulfur sublattice, possibly caused by minor oxidation of a fraction of the Fe$^{3+}$ in mackinawite. The observed aging clearly does imply structural changes on the local level. Overall, this work serves as an example that post mortem analysis of corrosion products is sometimes not sufficient for a full understanding of the corrosion process.

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References
