![ESRF logo] **ESRF**	**Experiment title:** *In situ* SMS study of Fe/Fe$_2$O$_3$ redox cycles for energy storage	**Experiment number**: MA-5770
Beamline: ID18	**Date of experiment**: from: 12.04.2023　　　　　　to: 17.04.2023	**Date of report**: 10.07.2023
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Report:

Investigations of this beamtime were performed for the Clean Circles project of TU Darmstadt, that targets iron as carrier of energy from renewable sources. Iron should be used in a circular network wherein energy release is achieved by iron powder oxidation and energy storage by reduction of the previously oxidized powder. Phase composition data for development of kinetic models and their calibration is needed to set up the network. The goal of this beamtime was thus to investigate *in situ* the oxidation and reduction behavior of iron powder during repeated oxidation and reduction cycles at elevated temperatures on small timescales (few minutes per spectrum) aiming to extract phase composition data.

To achieve the best possible time resolution, partially enriched iron oxide powder was synthesized for the experiments and loadings were calculated according to ideal loading approximations by Long et al.. [1],[2] The Fe$_2$O$_3$ powder was mixed with boron nitride (BN) to ensure a homogeneous distribution of particles throughout the probed volume and to prevent sintering.

Fig. 1a shows the experimental set-up. The samples were loaded in quartz glass capillaries (o. d. 1.5 mm, wall thickness 0.01 mm) to allow gas flow through the sample, which was set to 50 mL/min and controlled by mass flow controllers (MFCs). Gases used were a) synthetic air for oxidation (20.5 % O$_2$/N$_2$: pure and with 1 ppm H$_2$S and 50 ppm methane as model substances for impurities expected during realistic technical applications), b) 5% H$_2$/N$_2$ for reduction and c) N$_2$ as inert. Exhaust gas was analysed by a Pfeiffer Vacuum ThermoStar GSD320 mass spectrometer. Heat was supplied via a hot air blower (Leister LE mini kit).

The proposal features a variation of particle size, where natural iron powder should be used. However, pre-experiments at ESRF showed, that time resolution is not sufficient for SMS measurements of natural iron powder (> 30 min per spectrum). The variation of particle size was thus changed to a temperature variation series in the range of 500 to 650 °C. Below 570 °C one iron phase (wustite) is thermodynamically unstable, which leads to a change in reaction mechanism and makes it interesting to compare low and high temperature

oxidation/reduction. Above 680 °C, fitting of Mössbauer spectra becomes complicated due to the collapse of magnetic hyperfine fields of Fe_3O_4 and Fe_2O_3, which is the reason for 650 °C as upper temperature limit for the experiments.
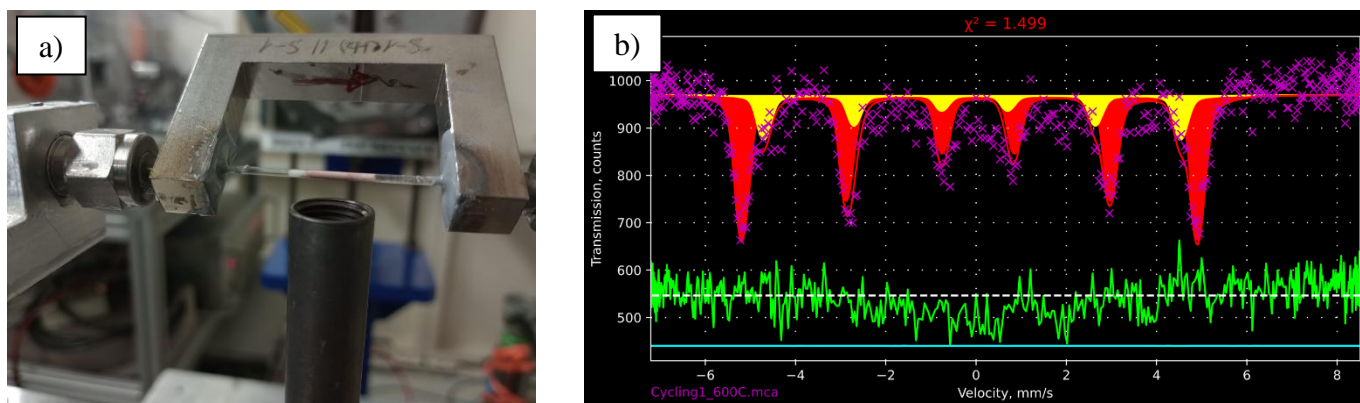

Fig. 1: Fe_2O_3-sample prepared in a quartz glass capillary and glued in a holder above the hot air blower (a) and a spectrum recorded during a reduction cycle at 600 °C (b). For the fitted spectrum shown, measurement time was **2 min** and different expected iron species are already clearly distinguishable.

A typical protocol for oxidation-reduction cycles was as follows: Heating up the starting α-Fe_2O_3 sample in 5% H_2/N_2 from RT to 800 °C, holding for 15 min to ensure complete reduction, cooling down to cycling temperature, then switching gas atmosphere to synthetic air, holding for 1h, switching to 5% H_2/N_2 for 1 h, and so on. Alternating between synthetic air and 5% H_2/N_2 was performed 6 times in total to result in three full oxidation – reduction cycles. Additionally, reduction experiments under constant heating were performed to support a QEXAFS/XRD study from the group of Prof. Grunwaldt/KIT (DESY, P64) performed on the same samples using the same setup.

The following experiments were performed:

1. Reduction during constant heating
   a. One sample, heated with 2 K/min from RT to 800 °C in 5% H_2/N_2
   b. Two samples, heated with 15 K/min from RT to 800 °C in 5% H_2/N_2
2. Cycling at constant temperatures
   a. Two samples, 650 °C, three full cycles
   b. Two samples, 600 °C, three full cycles
   c. Two samples, 500 °C, three full cycles
3. Cycling with impurities at constant temperatures
   a. Two sample, 600 °C, three full cycles
   b. One sample, 550 °C, three full cycles
   c. One sample, 500 °C, only oxidation

Fig. 1b shows that it is possible to resolve different iron phases under reaction conditions with measurement times of as low as **2 min**, allowing for detailed insights into the oxidation and reduction mechanism of the iron oxide powder under investigation. This time resolution is exceptional for Mössbauer measurements, usually only giving decent spectra for measurement times of > 30 min to hours.

Repetition of most samples was performed for 1) a reproducibility check and 2) to further increase the time resolution, achieved by summing up spectra of equal reaction times and conditions to double the statistics.
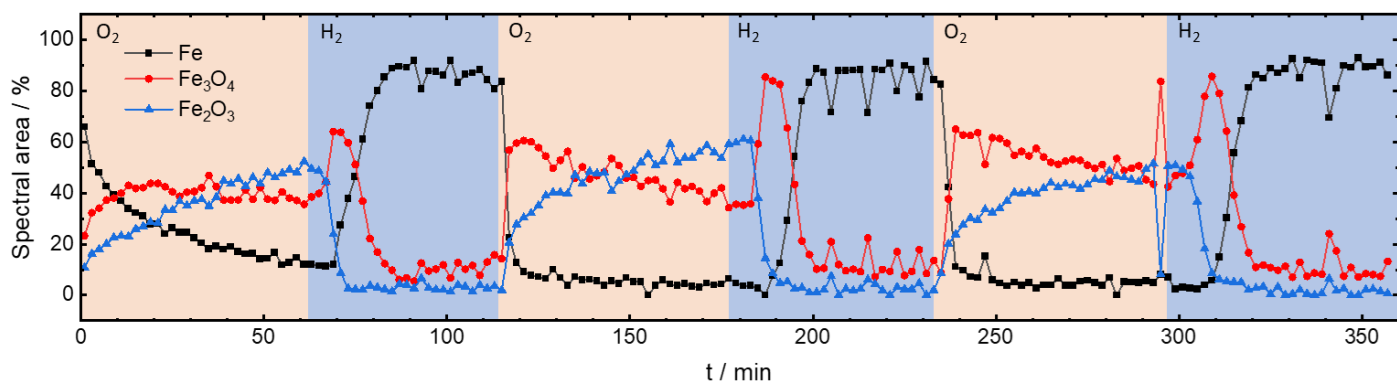
Fig. 2: Spectral area development of oxides present during cycling in pure synthetic air and H_2/N_2 at 500 °C. Plotted is the average composition for 2 min each, during which the spectrum was recorded. The dots represent the obtained values, the line is only a guide for the eye.

Fig. 2 shows an example analysis of cycling data (here for cycling at 500 °C). Data analysis was performed with SyncMoss [3] (by S. Yaroslavtsev, ESRF), an analysis software for Mössbauer data that also allows for convenient batch processing of synchrotron based Mössbauer data. For the analysis spectra of 2 min measurement duration were used. The data points in fig. 2 thus represent average values of composition and are plotted at their average time value (e.g. spectrum recorded from 0 to 2 min, data point plotted at 1 min, and so on). The line should only help to guide the eye.

There are several interesting facts to point out related to the cycling:

1. Oxidation starts fast and continues slow, as compared to reduction, that starts slow and continues fast.
2. During the first oxidation step, Fe content decreases slower as in the following steps, which could be interpreted as an acceleration of the initial reaction due to an increasing porosity of the particle.
3. The oxidation steps never fully reach Fe_2O_3 (full oxidation, target oxide). While Fe gets fully consumed during oxidation step 2 and 3, an increasing layer of Fe_2O_3 seems to hinder or slow down further oxidation. This finding is in accordance with literature on bulk iron oxidation, [4] indicating similarities in oxidation properties that are important for later kinetic model development and calibration. The particles are composed of Fe_3O_4 and Fe_2O_3 in about equal amounts at the end of each oxidation step.
4. Reduction, on the other hand, proceeds via intermediate Fe_3O_4 formation fully to Fe. Remaining contributions of Fe_3O_4 or Fe_2O_3 to the particle composition found during the plateau phase of the reduction are most likely artifacts of an unoptimized fitting model. Evaluating the spectra by eye leads to the believe, that pure Fe is reached during the reduction steps.

In the next steps, the fitting model for 500 °C will be further developed, as well as those for different temperatures and conditions. After careful comparison of measurements under equal conditions, the above-described addition of spectra will be performed to further increase the accuracy of the fits. Data from temperature controller and mass spectrometer will also be included in the analysis.

One publication is currently being prepared from the results of the beamtime and a second one is planned. We will properly acknowledge the ESRF and the contribution of the beamline scientists to this work in the publications.

References:
[1]   F. Grandjean and G.J. Long, *Chem. Mater.,* **2021**, 33(11), 3878.
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[4]   R.Y. Chen, *Oxid Met*, **2003**, 59(5/6), 433.