**Readme File**

Dates of data collection:

July 2016 - January 2017

Key words used to describe the data topic:

water-gas shift, chemical looping, reverse flow, OCM, perovskite, hydrogen, water, carbon monoxide, carbon dioxide, mole fraction, conversion, oxygen content, oxygen partial pressure, XRD

Processed data used in figures

The files in the folder named “Processed data used in figures” contain the data used to directly plot the graphs in the Main Text, Extended Data and Supplementary Information. Each file is named for the figure that it corresponds to.

Figure 2: in this file there are data of the conversion of carbon monoxide, water, and *K\** measured for each cycle and hydrogen, water, carbon monoxide, carbon dioxide mole fraction for three cycles used in the corresponding figure in the manuscript.

Figure 3: in this file there are data of the XRD for the data marked 1 and 2 and the relative oxygen content versus position used in the corresponding figure in the manuscript.

Figure S3: in this file there are data of XRD of scan 001 and corresponding Rietveld fit used in Supplementary Information Fig. 3.

Figure S5: in this file there are data of oxygen content and oxygen partial pressure for the three regions used in Supplementary Information Fig. 5

Figure S6: in this file there are data of oxygen content and oxygen partial pressure for the three thermodynamic constants used in Supplementary Information Fig. 6.

Figure S7a: in this file there are data of the conversion of carbon monoxide, water, and *K\** measured for each cycle used in Supplementary Information Fig. 7a.

Figure S7b: in this file there are data of the mole fraction of hydrogen, water, carbon monoxide and carbon dioxide measured for the six cycles used in Supplementary Information Fig. 7b.

Figure S9a: in this file there are data of the conversion of reducing gas, oxidising gas, and *K\** measured for each cycle used in Supplementary Information Fig. 9a.

Figure S9b: in this file there are data of the mole fraction of hydrogen, water, carbon monoxide and carbon dioxide measured for the four cycles used in Supplementary Information Fig. 9b.

Figure S10a: in this file there are data of the mole fraction of hydrogen, water, carbon monoxide and carbon dioxide used in Supplementary Information Fig. 10a.

Figure S10b: in this file there are data of the mole fraction of hydrogen, water, carbon monoxide and carbon dioxide measured for the four cycles used in Supplementary Information Fig. 10b.

The following information, below, can be used in aid interpretation of the data files.

Figure 2:

Cycle: the corresponding cycle for that data (units; unitless)

CO conversion: carbon monoxide conversion (units: unitless)

H2O conversion: water conversion (units: unitless)

K\* (units: unitless)

Time: the elapsed time for the corresponding cycle (units: seconds)

H2: the hydrogen mole fraction (units: unitless)

H2O: the water mole fraction (units: unitless)

CO: the carbon monoxide mole fraction (units: unitless)

CO2: the carbon dioxide mole fraction (units: unitless)

Figure 3:

2-theta: two-theta angle (units: degrees)

Scan 1: observed XRD intensity at given 2-theta angle for data marked scan 1 in Figure (units: arbitrary units)

Scan 2: observed XRD intensity at given 2-theta angle for data marked scan 2 in Figure (units: arbitrary units)

x: position in reactor bed, measured from CO feed-end (units: millimetres, mm)

y after CO: relative oxygen content after CO feed for corresponding position in the reactor bed (units: unitless)

y after H2O: relative oxygen content after H2O feed for corresponding position in the reactor bed (units: unitless)

Figure S3:

2-theta: two-theta angle (units: degrees)

yo: observed XRD intensity for scan 001 at corresponding two-theta angle (unit: arbitrary units)

yc: calculated XRD intensity for scan 001 from Rietveld refinement at corresponding two-theta angle (units: arbitrary units)

diff/esd: difference between observed and calculated intensity normalized with the standard error at corresponding two-theta angle (units: unitless)

Figure S5:

x: position in reactor bed, measured from CO feed-end (units: millimetres, mm)

y after CO: corresponding relative oxygen content or oxygen partial pressure after CO feed for corresponding position in the reactor bed (units: unitless)

y after H2O: corresponding relative oxygen content or oxygen partial pressure after H2O feed for corresponding position in the reactor bed (units: unitless)

Figure S6:

x: position in reactor bed, measured from CO feed-end (units: millimetres, mm)

y after CO: corresponding relative oxygen content or oxygen partial pressure after CO feed for corresponding position in the reactor bed (units: unitless)

y after H2O: corresponding relative oxygen content or oxygen partial pressure after H2O feed for corresponding position in the reactor bed (units: unitless)

Figure S7a:

Cycle: the corresponding cycle for that data (units; unitless)

CO conversion: carbon monoxide conversion (units: unitless)

H2O conversion: water conversion (units: unitless)

K\* (units: unitless)

Figure S7b:

Time: the elapsed time for the corresponding cycle (units: seconds)

H2: the hydrogen mole fraction (units: unitless)

H2O: the water mole fraction (units: unitless)

CO: the carbon monoxide mole fraction (units: unitless)

CO2: the carbon dioxide mole fraction (units: unitless)

Figure S9a:

Cycle: the corresponding cycle for that data (units; unitless)

Reducing gas conversion: carbon monoxide conversion (units: unitless)

Oxidising gas conversion: water conversion (units: unitless)

K\* (units: unitless)

Figure S9b:

Time: the elapsed time for the corresponding cycle (units: seconds)

H2: the hydrogen mole fraction (units: unitless)

H2O: the water mole fraction (units: unitless)

CO: the carbon monoxide mole fraction (units: unitless)

CO2: the carbon dioxide mole fraction (units: unitless)

Figure S10a:

Time: the elapsed time for the corresponding cycle (units: seconds)

H2: the hydrogen mole fraction (units: unitless)

H2O: the water mole fraction (units: unitless)

CO: the carbon monoxide mole fraction (units: unitless)

CO2: the carbon dioxide mole fraction (units: unitless)

Figure S10b:

Time: the elapsed time for the corresponding cycle (units: seconds)

H2: the hydrogen mole fraction (units: unitless)

H2O: the water mole fraction (units: unitless)

CO: the carbon monoxide mole fraction (units: unitless)

CO2: the carbon dioxide mole fraction (units: unitless)

Unprocessed exhaust gas data

In the folder titled “Unprocessedexhaustgasdata’ there are the raw mass spectrometer current readings for the main experiment (*operando* data) and the reference experiments. Note that for the reverse water gas shift experiment the initial cycles using the water gas shift are in a separate file to the reverse water gas shift data.

Outletgasmasspeccurrent\_inoperandodata: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized species for the *operando* experiment and its associated calibration points.

Outletgasmasspeccurrent\_coccurentflow: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized species for the WGS reaction and its associated calibration points.

Outletgasmasspeccurrent\_emptytube: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized species for the empty reactor with unmixed reactants experiment and its associated calibration points.

Outletgasmasspeccurrent\_300cycles: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized for the long term stability test and its associated calibration points.

Outletgasmasspeccurrent\_RWGSintialcycles: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized species for the initial cycles of the RWGS experiment when the reactor was operated as a WGS reactor and its associated calibration points.

Outletgasmasspeccurrent\_RWGS: In this file there are data of the current readings associated with a given mass to charge ratio of an ionized species for the RWGS experiment and its associated calibration points.

To convert the current readings in these files into the mole fractions and conversions used in the figures the methodology detailed below was used.

To account for the splitting of molecules, such as CO2 and H2O, into fragments on other mass to charge ratios being measured in this experiment, a fragmentation correction was applied to the currents. For the gases present in this system the following conversions were applied. The proportion of the current measured with mass to charge ratio 28, corresponding to CO, was equal to the total current for mass to charge ratio 28 minus 0.07 of the current for mass to charge ratio 44. The proportion of the current measured with mass to charge ratio 2, corresponding to H2, was equal to the total current for mass to charge ratio 2 minus 0.007 of the current for mass to charge ratio 18. Additionally, the mass spectrometer also produced a constant background current for each mass to charge ratio when it was not being fed with a gas with that ratio. A zero point reading was taken where only the balance gas was fed, Ar. This was then subtracted from the current to get a true current. A calibration factor was then applied to take into account that the ionization efficiency and the mass to charge ratio filtering in the quadrupole was not equivalent for all gas species measured in this experiment. In order to convert the calibrated currents into the molar percentages, they were divided by the total calibrated current. This meant the molar percentages were then calculated using Equations 1 to 4 below.

eq. 1

eq. 2

eq. 3

eq. 4

In Equations 1-4 *x* denotes the molar percentage of each gas and *Ij* denotes the current for a given mass to charge ratio *j*. The subscript ‘zero value’ denotes the background current *Ij* recorded when that mass to charge ratio was not present in the mass spectrometer. The noise on the background current for the mass spectrometer led to an effective lower detection limit for a mole fraction of 100 ppm.

The calibration values drifted throughout the experiment. To ensure accurate results full calibrations were carried out before and after each experiment. Additionally every 15 duty cycles a known mole fraction of a key gas and of water was feed to the mass spec directly for 900 s. Therefore calibrations for each gas occurred every 45 cycles. Linear interpolation was then used to determine the calibration factor as a function of time. The calibration gases are of known mole fractions however for water, a chilled-mirror hygrometer (Alpha Moisture Systems, CMH-1), was used obtain the inlet mole fraction. The largest drift in the calibration value during the experiment was that of hydrogen, which had a total drift of 3.5% over 19 hours.

To calculate the conversions of hydrogen and the carbon dioxide for each cycle, Equations 5 and 6 below, were used.

eq. 5

eq. 6

Each of the variables in equations 1 to 6 have an associated uncertainty. As the values for the zero points and calibration factors for CO, CO2, H2 and H2O are calculated as part of the data analysis by taking the average of values when feed with gasses of known mole fractions. The standard error can then be found as part of the calculation. For the other variables in the equation the precision is used as a measure of the uncertainty.

The uncertainty is then propagated through the system using the following equations assuming that the covariance is zero:

eq. 7

+ eq.8

eq. 9

eq. 10

By applying equations 7 to 10 to equations 1 to 6 to get an equation for the uncertainty for the molar mole fractions. In order to obtain the uncertainty for the conversions the integration in equations 5 and 6 was repeated twice with every value increased by one standard deviation and decreased by one standard deviation to give uncertainty bounds.

Unprocessed XRD data

In the folder titled “UnprocessedXRDdata’ there are the raw XRD patterns for the main experiment (*operando* data). In order to understand the naming convention you must understand the spacing of the points studied inside the packed bed.

The LSF641 powder was packed into a bed that had a diameter of 4 mm and was contained in quartz tubes with 2 mm thick walls. The bed was 11.45 cm long, as defined as the points on the top and bottom where the 9.5 degree peak of our material yielded counts of 400-600, which would go to 2000 or higher into the bulk of the bed, but stayed around a high background noise of 150 when in the quartz wool. The exact definition of the top of the bed is hard to define with a 1 mm x 1 mm x-ray beam probing the transition from the powder into the quartz wool plugs used to secure the bed. From those defined end points, scans were took in four clusters spread along the length of the bed with one cluster closely spaced at the top of the bed, one closely spaced at the bottom, and the remaining two clusters coarsely spaced about evenly along the rest of the bed.

The cluster of positions at the top and bottom of the beds consisted of a scan at the defined end point, another scan 2 mm into the bed, and then three more scans spaced a further 2mm into the bed from the previous point, for a total of 5 scans. The cluster of positions at the top of the bed was Cluster A, the cluster at the bottom was Cluster D. Cluster B consisted of 4 scans that were 23 mm, 33 mm, 43 mm, and 53 mm in from the top of the bed. Cluster C consisted of 4 scans that were 63 mm, 73 mm, 83 mm, and 93 mm in from the top of the bed.

In summary, the table below has all the positions that were scanned within the four clusters listed below. Please note that positions pos6 in Cluster D and pos1 in Cluster A are absent as originally there were more scans in the script for those clusters, but they were removed to shorten the inert hold between reactive gas feeds.

**Table 1:** The 18 different locations in the bed that were scanned

|  |  |  |  |
| --- | --- | --- | --- |
| **Cluster** | **Position** | **Distance from the top of the bed (mm)** | **Absolute position of the table (mm)** |
| A | pos6 | 0 | 147.5 |
| pos5 | 2 | 149.5 |
| pos4 | 4 | 151.5 |
| pos3 | 6 | 153.5 |
| pos2 | 8 | 155.5 |
| B | pos4 | 23 | 170.5 |
| pos3 | 33 | 180.5 |
| pos2 | 43 | 190.5 |
| pos1 | 53 | 200.5 |
| C | pos4 | 63 | 210.5 |
| pos3 | 73 | 220.5 |
| pos2 | 83 | 230.5 |
| pos1 | 93 | 240.5 |
| D | pos5 | 106.5 | 254.0 |
| pos4 | 108.5 | 256.0 |
| pos3 | 110.5 | 258.0 |
| pos2 | 112.5 | 260.0 |
| pos1 | 114.5 | 262.0 |

A single cluster of scans was run during the four minute hold in inert argon that separated the reactive gas feeds (H2O and CO). To better understand the sequencing, it is best to start by defining a chemical looping cycle. A full chemical looping cycle consisted a flow of H2O (fed into the top of the bed) for 1 minute that followed an inert hold, which was followed by 4 minutes of Ar, then a flow of CO (fed into the bottom of the bed) for 1 minute, which again was followed by 4 minutes of Ar. This cycle was then repeated in groups of 15, and set to end on a hold in Ar while reactive gases flower to the mass spectrometers, bypassing the bed, for calibrations. During this time, it was possible to then enter the hutch and set up the next batch of 15 cycles and then start the next XRD script.

Therefore, with 15 full chemical looping cycles, there was time for 31 clusters to be run, including the time before the first cycle and after the 15th. The order of the 31 clusters, as well as the direction within the cluster between the scans is shown in the table below. The z-positioner speed was quite slow, and it was required to reverse the direction of the scans between the clusters to have enough time to get the sample in the correct position for the next cluster. The 1 minute during which the reactive gases were fed was used to reposition the sample in anticipation of the next cluster to be run.

**Table 2**: Order of scans performed over 15 chemical looping cycles, to be read left to right, then top to bottom. This order of scans is repeated for each 15 cycles.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Set** | **Cluster** | **Scan direction** | **1st Scan** | **2nd Scan** | **3rd Scan** | **4th Scan** | **5th Scan** |
| 01 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |
| 02 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 03 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |
| 04 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 05 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |
| 06 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 07 | D | up | Misnamed | pos2 | pos3 | pos4 | pos5 |
| 08 | C | up | pos1 | pos2 | pos3 | pos4 |  |
| 09 | C | down | pos4 | pos3 | pos2 | pos1 |  |
| 10 | C | up | pos1 | pos2 | pos3 | pos4 |  |
| 11 | B | up | pos1 | pos2 | pos3 | pos4 |  |
| 12 | B | down | pos4 | pos3 | pos2 | pos1 |  |
| 13 | B | up | pos1 | pos2 | pos3 | pos4 |  |
| 14 | A | up | pos2 | pos3 | pos4 | pos5 | pos6 |
| 15 | A | down | pos6 | pos5 | pos4 | pos3 | pos2 |
| 16 | A | up | pos2 | pos3 | pos4 | pos5 | pos6 |
| 17 | A | down | pos6 | pos5 | pos4 | pos3 | pos2 |
| 18 | A | up | pos2 | pos3 | pos4 | pos5 | pos6 |
| 19 | A | down | pos6 | pos5 | pos4 | pos3 | pos2 |
| 20 | B | down | pos4 | pos3 | pos2 | pos1 |  |
| 21 | B | up | pos1 | pos2 | pos3 | pos4 |  |
| 22 | B | down | pos4 | pos3 | pos2 | pos1 |  |
| 23 | C | down | pos4 | pos3 | pos2 | pos1 |  |
| 24 | C | up | pos1 | pos2 | pos3 | pos4 |  |
| 25 | C | down | pos4 | pos3 | pos2 | pos1 |  |
| 26 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 27 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |
| 28 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 29 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |
| 30 | D | down | pos5 | pos4 | pos3 | pos2 | pos1 |
| 31 | D | up | pos1 | pos2 | pos3 | pos4 | pos5 |

There were 143 scans per 15 chemical looping cycles. Pos1 from scan D07 was misnamed in the script file, so there are only 142. Of these 22 were at the edge of the bed so the pattern was dominated by the quartz wool used to hold the bed in place so were excluded from further analysis.

Cell parameters for the XRD scans taken within the reactor bed during the operando x-ray diffraction study, 120 each from Cycles 16-30 (Region B), Cycles 31-45 (Region C) and Cycles 46-60 (Region D), in Table S2 of the Supplementary Information, were extracted using the Rietveld method and Topas Academic software., an example script has been included with the readme file named ‘Example\_topas\_file.inp’. The fitting was performed over 4 to 19.2 degrees (2θ), excluding the data collected from the fifth analyser crystal, 11.0 to 13.2 degrees, due to anomalous noise. An instrumental peak shape and the experimental wavelength, 0.3262711 Å, were determined using a silicon standard and subsequently kept constant. For each data set the cubic cell parameter, an instrumental zero point, parameters to describe a size and strain Lorentzian contribution to the peak shape, and a polynomial to describe the instrumental background were refined. The local lattice parameters, Rwp, and the goodness of fit, gof, are shown in Tables S3-5 of the Supplementary Information for Regions B, C, and D respectively. The standard uncertainty derived from the Rietveld least squares fitting procedure for the lattice constant was 0.00002 Å or less for all the refinements. It was noted that there are no noticeable asymmetries in the XRD peaks that would suggest that gradients in the lattice parameter (and thus degree of oxygen non-stoichiometry) exist within the observable bulk of the OCM particles. A representative refinement is shown in Extended Data Fig. 3.

The naming convention can be exemplified by looking at the name of file ‘ma2914\_cycles\_01-15\_bed6\_SCAN\_A14\_up\_pos2.xye’. This file contains a scan that occurred during the first 15 cycles (Region A of Table S2 in the Supplementary Information). Bed6 refers to the particular packed bed that was analysed; all data for this paper uses bed6. The point in the bed studied was pos2 of Cluster A and this was during the 14th set of scans which corresponds to the scans that occurred immediately before the 14th half cycle or the reducing half cycle of Cycle 7 (the first half cycle of Cycle 1 involved oxidation). The beam was moving up the bed.

Scans are also referred to using a scan number in the Supplementary Information which is the order in which the scans were carried out excluding those scans at the edge of the bed (A position 6 and D position 1), after the first 15 cycles which were used to reach steady cycling, with the first scan being 001 (16-30 cycles, set 01 Cluster D pos2) then 002 (16-30cycles, set 01 Cluster D pos2) and so on.

The methodology for the conversion of unit cell parameter into the degree of non-stoichiometry of the material is detailed in Supplementary Information using equations S5-S17. The excel file used to perform these operations is available online with the readme file and named ‘ESRF bed 6 analysis’. The temperature profile of the bed was found by linearly interpolating between the points recorded in ‘Temperature profile of operando reactor’ and in the excel file used to perform the operations.