**Readme File**

Dates of data collection:

May 2017 - September 2018

Key words used to describe the data topic:

chemical looping, OCM, perovskite, 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 and Supplementary Information. Each file is named for the figure that it corresponds to.

XRD patterns

In the folder titled “XRD patterns’ there are the raw XRD patterns used for the XRD data

The excel spread sheet ‘esrf\_june2017\_experimental\_logbook.xlsx’ contain a list of the temperature and gas conditions for each scan with experiment number corresponding to the file name.

Masspec outlet files

In the folder titled “Masspec outletfile’ there are the raw mass spectrometer current readings for the different experiments carried out

LSF641andYittiracyclesbufferandbuffercycles.csv contains the raw mass spectrometer current readings for the experiments carried out on the vertical reactor used in the XRD experiments

1000\_cycles\_rawmasspec.csv contains the raw mass spectrometer current readings for the experiments using 1000 cycles.

Effectoftemperature\_ rawmasspec.csv contains the raw mass spectrometer current readings for the experiments using the different reactor temperatures.

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.