

Ferrite-YSZ composites for solar thermochemical production of synthetic fuels: In operando characterization of CO₂ reduction

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Supplementary Information

Equilibrium composition of iron oxides as a function of temperature

Figure S1 shows the iron oxide phases calculated to be in equilibrium with one another as a function of temperature in air. At low temperatures, Fe₂O₃ is the only phase present. At approximately 700 °C, Fe₃O₄ begins to form, and FeO is observed at temperatures exceeding 1100 °C. These results are calculated from known thermodynamic properties of the various phases present using the commercial HSC Chemistry 5.11 software (reference), and show only the phase distribution expected under equilibrium conditions; no kinetic information should be inferred.

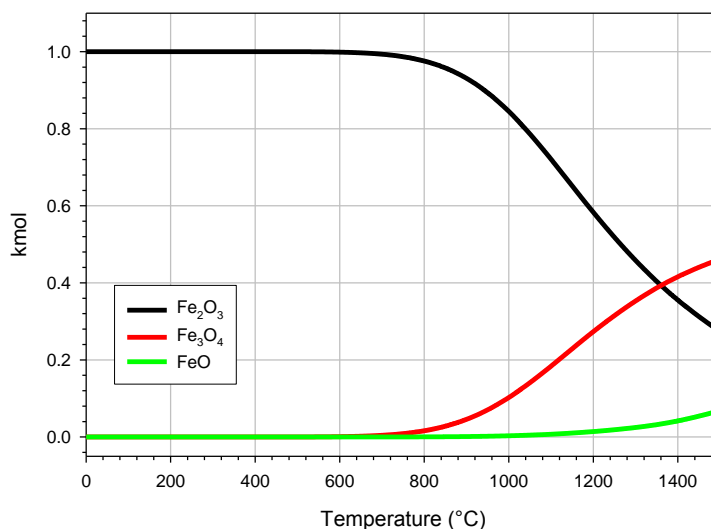


Figure S1. Equilibrium composition of iron oxides as a function of temperature. Input to the calculation consisted of Fe₂O₃ (1 kmol), N₂ (79 kmol), and O₂ (21 kmol).

Oxygen evolution during thermal reduction in the HT-XRD set-up

The data in Figure S2 illustrates oxygen evolution from a sample of iron oxide/8YSZ containing 27.6 mol-% Fe during three thermal reduction cycles in the HT-XRD apparatus. The amount of O₂ evolved decreased dramatically for each subsequent cycle, indicating that the majority of the reduction occurred during the first thermal cycle, although some reduction was still occurring during the third cycle. Oxygen evolution appeared to be maximal between 1200 and 1300 °C during the first cycle, whereas O₂-levels peaked at 1400 °C for the 2nd and 3rd cycles. The oxygen analyzer reached full scale output at 20 ppm O₂. The temperature readings are given purely as a guide, since changes in sample colour during cycling result in differences in measured temperature due to emissivity changes. The pyrometer does not register temperatures below ~ 800 °C.

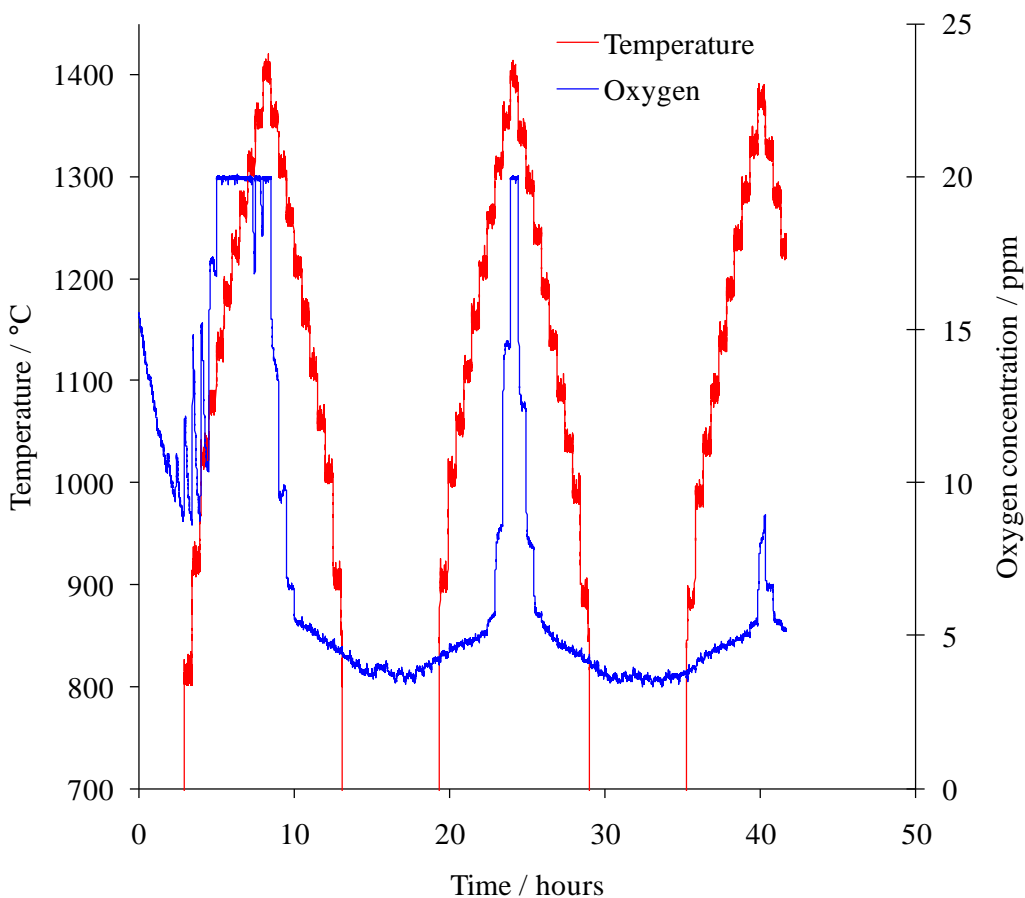


Figure S2. Sample temperature as read by pyrometer, and oxygen concentration measured downstream of the heated sample cell recorded during three HT-XRD cycles on a pressed and sintered disc of iron oxide/8YSZ containing 27.6 mol-% Fe.

Lattice spacing variations during multiple cycles on a 14.5 mol-% Fe sample

A freshly air-calcined (1375 °C/48hrs; 1500 °C/2hrs) sample of iron oxide/8YSZ containing 14.5 mol-% Fe was subjected to three consecutive thermal reduction cycles under helium. The results (Figure S3) indicated that during the first cycle, a large unit cell expansion occurred (i.e., Fe migrated out of 8YSZ); during the second cycle, a smaller cell expansion was observed, while the third cycle saw no overall expansion of the lattice after cooling, implying that after the second cycle, the Fe distribution had reached steady state. The variation in the 8YSZ (220) lattice parameter is shown as a function of temperature for the three cycles in Figure S3. The d-spacings for the 8YSZ (220) peak at the beginning of the three runs were 1.8064(±0.0002), 1.8132(±0.0002), and 1.8139(±0.0002) Å, the final d-spacing measured at the end of the third cycle was identical to that at the beginning of the third cycle, indicating that a steady-state had been reached with respect to Fe dissolved in 8YSZ. The phase evolution of Fe/8YSZ species for the first of the three cycles was similar to that described in the paper (Figure 6), except that FeO formed during the first cycle and was observed to disappear, while Fe₃O₄ and Fe metal were detected during the later stages of the second cycle and during the 3rd cycle. This follows the disproportionation reaction of FeO (i.e., $4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$) which is thermodynamically favoured at lower temperatures. The 8YSZ lattice parameters did not appear to be influenced by the occurrence of disproportionation in cycles 2 and 3, thus the Fe species dissolved in the 8YSZ do not appear to participate in the transformations exhibited by the non-substituted iron species. The fact that disproportionation was not observed during the first cycle may be due to either a gradual decrease in the partial pressure of oxygen over the course of the three cycles, altering the phase stabilities, or due to size effects related to particle sintering.

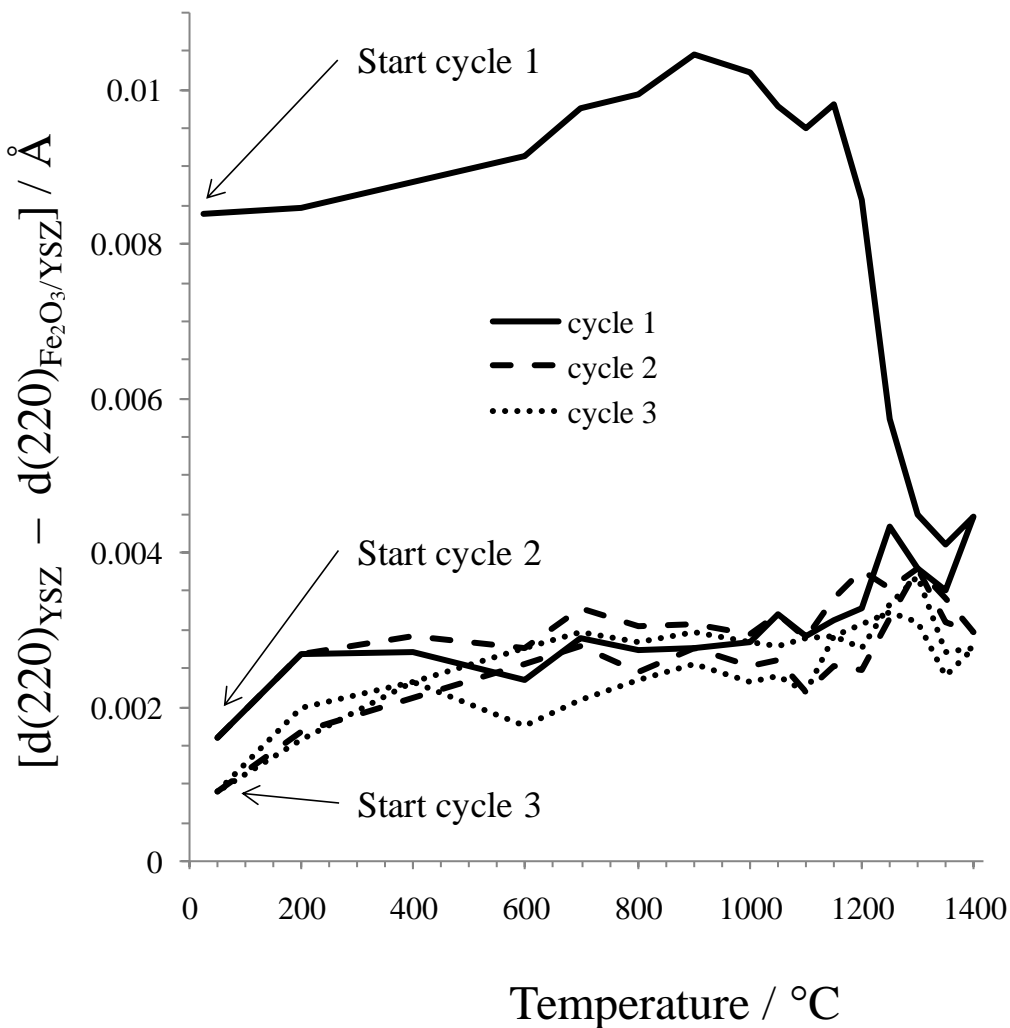


Figure S3. Variation in 8YSZ (220) lattice constant during three consecutive heating and cooling cycles of iron oxide/8YSZ containing 14.5 mol-% Fe under helium, plotted as the difference between measured d(220) for iron oxide/8YSZ and d(220) measured for 8YSZ alone.

CO evolution during CDS

The evolution of carbon monoxide during CO₂-exposure of a reduced sample of iron oxide/8YSZ containing 27.6 mol-% Fe is shown in Figure S4. Exposure to CO₂ began at time 0, but gas dispersion effects (displacement of He by CO₂/CO) delayed CO detection by 4 minutes. This CO evolution profile is a typical result, and was not observed to differ with number of cycles.

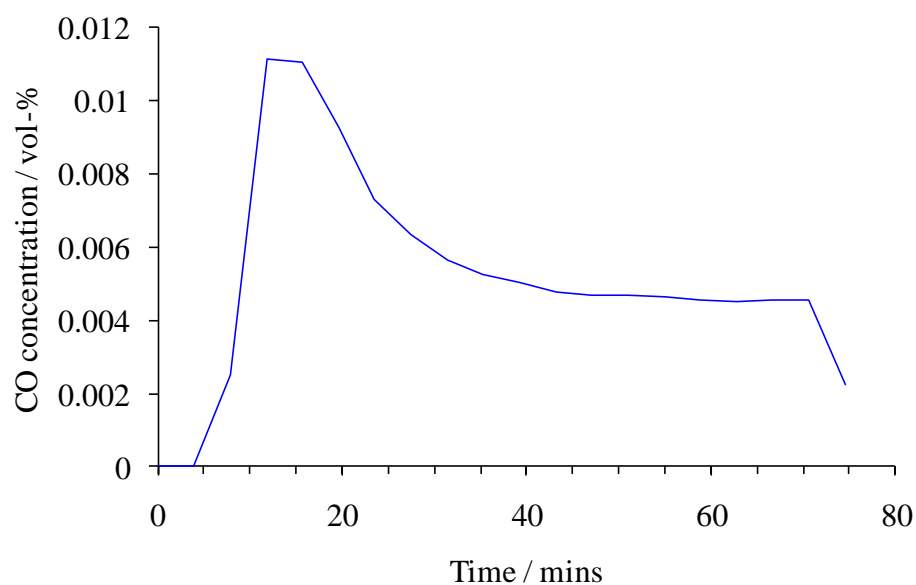


Figure S4. Carbon monoxide concentration measured by micro-gas chromatograph downstream of the heated sample cell during CO₂ exposure at 1100 °C of a pre-reduced (1400 °C, He) pressed and sintered disc of iron oxide/8YSZ containing 27.6 mol-% Fe.