Development and Testing of the Labyrinth Reactor for Thermochemical Water/CO_2 Splitting

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1. Introduction

Decades of research, by teams worldwide, have identified numerous characteristics that promising reactor designs for thermochemical water and CO_2 splitting must satisfy.[1-6] For example, countercurrent flows of solid and gas have been understood to maximize the utilization of the material chemical potential.[7] Building on this knowledge base, including recent theoretical understanding for operating near reversibility (and therefore maximizing efficiency) in thermochemical cycles, we report on the design and testing of our *Labyrinth Reactor* (LR), a next-generation concept for thermochemical water and CO_2 splitting.

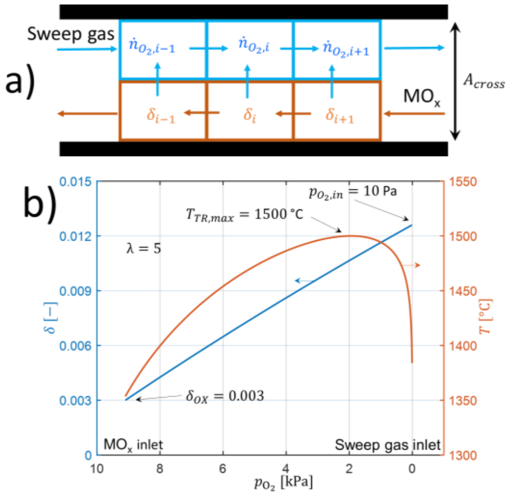

Figure 1. (a) Oxygen mass balance discretization in a counter-current reactor. (b) $T - p_{O_2} - \delta$ example at equilibrium in a countercurrent flow reactor.

2. Theoretical, Experiment, and Results

The LR allows cycle operation close to a reversible path, to maximize efficiency.[6] Approaching this ideal reversible path is possible if reactions occur at a specific, reaction coordinate- and material-dependent temperature such that $\Delta G \rightarrow 0$, with mass conservation for oxygen exchange between solid and gas phases at each infinitesimal point along the reacting paths. For example, the thermal reduction step of the cycle, in an inert gas swept reactor with a single inert gas inlet (**Figure 1a**), $\Delta G = 0$ requires a variable temperature profile as a function of the reaction coordinate (**Figure 1b**). Well-understood features necessary in thermochemical reactor designs, such as solid-solid heat recovery, temperature and gas species separation, and matching reactor operation with chemical kinetics, remain.

The LR prototype, shown in **Figure 2,** builds on the strengths (and drawbacks) of two of our previous designs, the CR5 [1,2], and the Cascading Pressure Reactor [5,6], as well as on designs from other groups, especially [3,4]. To simplify construction and testing, the LR uses internal radiant heaters [8] to achieve the necessary reaction temperatures in a small volume. In addition to having a high power density, these in-house developed heaters are also low-cost, highly resistant to transients and thermal shock, and we expect them to be compatible with poorly conditioned electrical input. In the LR, the redox active metal oxide (ceria) traces a narrow path through an insulating cavity with three main zones: (1) thermal reduction (TR), (2) solid-solid heat recovery (HR), and (3) water/CO_2 splitting (WS/CDS). The reactor absolute pressure is near uniform, and near-ambient in the prototype.

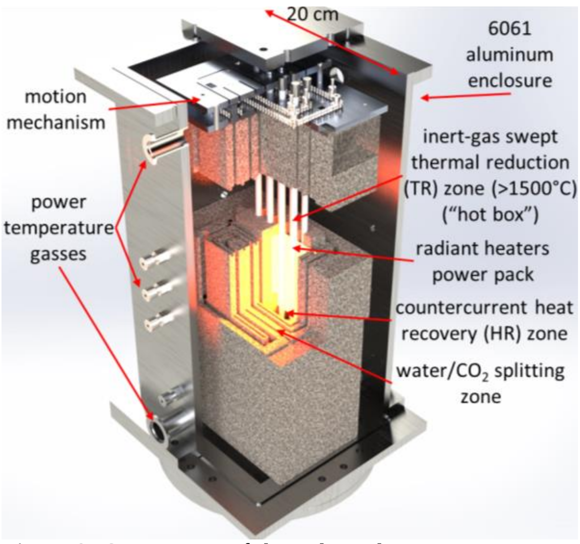

Figure 2. Cutout view of the Labyrinth Reactor prototype, constructed of low-cost, insulating firebrick elements, which have shown outstanding mechanical stability and failure tolerance in numerous heat/cool cycles.

In the TR zone, ceria reduces while heating in an inert sweep gas flowing countercurrent to the moving ceria, which serves to remove the evolved O_2 from the reactor. The temperature in the TR zone is intended to follow a profile (**Figure 3**), such that the TR step operates near the chemical equilibrium path, i.e., maximizing reversibility. The TR zone physical length is set to match residence time with inherent chemical kinetics.

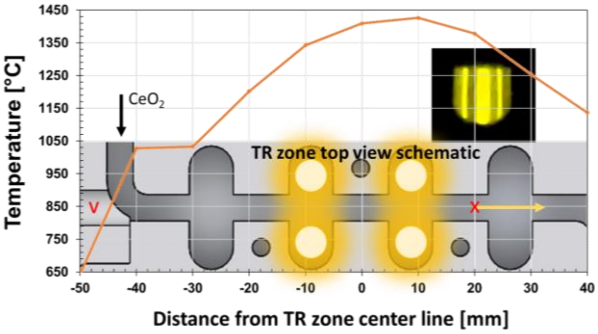

Figure 3. TR zone temperature profile with a partial heater set. Inset: having passed through the TR zone, a ceria "car" at location 'x', imaged through port 'v', is brightly incandescent.

In the HR zone, metal oxide flows from the TR and WS/CDS zones move past each other in opposite directions, exchanging heat, but not gases, through an innovative IR-transparent window. Because the length of the HR zone can be independently set, a desired heat recovery effectiveness can be targeted. Equally important, the length and meandering geometry of the HR zone help minimize unwanted gas flow between the TR and WS/CDS zones.

In the WS/CDS zone gas-phase steam/CO_2 flows countercurrent to the solid, re-oxidizing the metal oxide and producing H_2 and/or CO. Similar to the HR zone, the WS zone length (residence time) can be set independently of the other two zones, to achieve the desired extent of the re-oxidation reaction. A temperature profile and thermal management can also be engineered in this zone, e.g., by steam temperature, to again minimize irreversibility and maximize reaction extent.

For the reactor to function properly, we must isolate the gas flows by zone (HR zone and WS zone) and prevent them from mixing. To that end, we have designed an innovative system that includes multiple gas inlets and outlets, including two buffer gas inlets. This system has been successfully tested on a test bench.

Because the reaction zones weave through the cavity, a comparatively long path fits in a small reactor volume, a benefit in terms of productivity per unit reactor size, as well as to minimize heat losses. A simple horizontal chain drive creates the necessary countercurrent motion of the vertical ceria rods through the reactor (Figure 2).

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