

# Summary

To address the challenges of the climate crisis and to achieve full sustainability in the societies of the near future, humankind will increasingly rely on renewable energy sources, among which abundant and accessible solar energy will play a role of dominant importance. Notably, its efficient conversion into renewable chemicals and fuels is currently considered a promising route. In this context, this dissertation advances the field of thermochemical fuel production *via* chemical looping (CL), typically assumed to be effectively driven by solar-derived high-temperature heat. The research reported here is twofold. Firstly, detailed multiphysics reactor modeling is addressed, together with advancements in the implementation and simulation of novel perovskite-based oxygen carrier materials for two-step thermochemical splitting (TCS) redox cycles. Secondly, a novel oxygen carrier, specifically a double perovskite with composition  $\text{Sr}_2\text{FeMo}_{0.6}\text{Ni}_{0.4}\text{O}_{6-\delta}$  (SFMN), is investigated for the first time in the reverse water-gas shift chemical looping (RWGS-CL) process, demonstrating outstanding performance in terms of CO yield and long-term stability, correlated to exsolution-promoted morphological and structural transformations.

Concerning the first piece of work on TCS, a comprehensive simulation framework was developed to describe the full two-step thermochemical redox cycle in porous reactors operating under indirect and diffuse irradiation, representative of the Reactor Train System (RTS) architecture. The model includes radiative heat transfer, porous media gas flow, solid-gas redox chemistry, and refined oxidation kinetics treatment, offering a realistic prediction tool for reactor performance. Simulation results for a benchmark, non-optimized ceria-based reactor design revealed limited solar-to-fuel efficiencies in the range 2 – 3% when heat recovery to the lower-temperature heat sink is also included, and a redox volume-based power density in the range 12 – 15  $\text{kW}/\text{m}^3_{\text{porous}}$ , reflecting the intrinsic limitations of the baseline concept on one hand, and the crucial need to integrate countercurrent radiative heat recovery between multiple reactors on the other hand, in order to reduce the massive sensible heat fraction going into the solid parts. Despite these modest values, the model proves highly valuable as a comparative and design-guiding tool, enabling the identification of operational strategies to enhance fuel productivity in this new class of reactors. Increasing the heat source temperature and reducing the oxygen partial pressure during the reduction step, either through moderate vacuum or inert sweeping, can

significantly improve the cycle efficiency. Additionally, a parametric study on the porous medium morphology was performed, revealing that nonuniform porosity combinations can be beneficial in terms of heat transfer, temperature distribution and hotspots mitigation, gas flow and oxygen removal, and improved uniformity in redox material reactivity. The oxidation step simulations demonstrate a relationship between steam flow rates and conversion extent, with lower flow rates favouring higher steam-to-hydrogen conversions, but increasing the time needed to reach full reoxidation. The novel oxidation kinetic model resolves the physical gap developing between the actual local nonstoichiometry and the equilibrium state counterpart, with direct implications on the reaction rate, highlighting the importance of simulating the reaction chemistry accurately.

Beyond reactor modeling, the second piece of work explored in this dissertation focuses on material innovation through the synthesis and characterization of the exsolution-promoted SFMN perovskite for RWGS-CL process aimed at CO<sub>2</sub> valorisation. Thermogravimetric analysis, structural characterization, high-resolution microscopy, and long-term microreactor tests confirm SFMN's exceptional redox performance: stable CO yields of approximately 1500  $\mu\text{molCO/g}$  were achieved at 850 °C after more than 320 isothermal cycles, with diminishing and negligible degradation after an initial stabilization phase. The *in-situ* exsolution of Ni-Fe alloy nanoparticles from the host perovskite matrix, combined with the unprecedented observation of a core-shell structure formation on the exsolved particles, proved crucial for enhancing both the reduction and oxidation steps, while sustaining catalytic activity and structural stability under the investigated cycling conditions, ultimately promoting remarkable durability and activity retention.

Collectively, the results of this work demonstrate the critical importance of detailed multiphysics modeling for understanding complex reactor behaviour and guiding future optimization efforts. Moreover, they highlight the promise of engineered perovskite oxides for next-generation thermochemical fuel production, particularly in CL processes operable at more moderate temperatures than conventional TCS. The modeling platform developed herein will serve as a foundation for scaling up reactor designs, implementing heat recovery strategies, and systematically exploring advanced architectures with improved efficiencies. Meanwhile, the successful demonstration of durable, exsolution-stabilized perovskite materials opens new pathways for integrating CL into practical solar fuel systems. These findings contribute to bridging fundamental research and technological deployment, supporting the global transition toward a carbon-neutral energy future.