

# Theoretical Design of CeO<sub>2</sub>-Based Materials for Enhanced RWGS-CL Performance

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# Significance and Relevance

Reverse water gas shift reaction via chemical looping (RWGS-CL) enables efficient CO<sub>2</sub> utilization through materials with high oxygen storage capacity. Through theoretical calculations, we predicted enhanced oxygen release capability in Pr-doped CeO<sub>2</sub>, which achieving a higher reduction rate and increased redox capacity (>99% CO<sub>2</sub> conversion at 773 K) experimentally. *In-situ* XAFS measurements and theoretical calculations revealed that Ce-O-Pr interactions tune Ce valence states, leading to enhanced RWGS-CL performance. This study demonstrates the successful theory-driven development of Ce<sub>0.67</sub>Pr<sub>0.33</sub>O<sub>2</sub>, achieving enhanced RWGS-CL performance.

# Introduction and Motivations

CO<sub>2</sub> utilization under moderate conditions is essential for addressing environmental challenges. Among various approaches, the reverse water gas shift (RWGS) reaction has attracted widely<sup>1</sup>. The RWGS reaction is the equilibrium process that produces CO from  $CO_2$  and  $H_2$ , as shown in equation (1).

 $CO_2 + H_2 \rightarrow CO + H_2O, \ \Delta H^{\circ}_{298 K} = 42.1 \ kJ \ mol^{-1}$ (1)However, the RWGS reaction faces several challenges. Due to its endothermic nature, it requires higher temperatures to achieve high CO<sub>2</sub> conversion. Additionally, equilibrium limitations, methanation side reactions, and product separation costs pose significant constraints.

To overcome these challenges, we focus on RWGS reaction via chemical looping (RWGS-CL)<sup>2</sup>, which can separate the whole redox reaction into oxidation and reduction steps using the lattice oxygen from metal oxides  $(MO_x)$ , as described in equation (2) and (3).

$$\begin{array}{l} MO_x + \delta H_2 \to MO_{x-\delta} + \delta H_2 O \\ MO_{x-\delta} + \delta CO_2 \to MO_x + \delta CO \end{array}$$

$$(2)$$

$$(3)$$

$$IO_{x-\delta} + \delta CO_2 \to MO_x + \delta CO \tag{3}$$

By separation of reaction gas, RWGS-CL emerges as a promising process for CO<sub>2</sub> utilization under moderate conditions. Previous studies have investigated suitable materials for RWGS-CL, focusing on lattice oxygen release and refill capabilities in perovskite and spinel oxides. However, these materials still require temperatures exceeding 823 K<sup>3,4</sup>. Thus, developing materials with high oxygen storage capacity at lower temperatures is crucial for enhancing RWGS-CL performance.

In this study, we conducted the theory-driven screening of suitable material for RWGS-CL focusing on CeO<sub>2</sub>-based materials. Also, we evaluated the experimental CO<sub>2</sub> conversion performance and uncovered the dominant factors through surface analysis, combining theoretical calculations with spectroscopic investigations. Our results demonstrate that material design based on theoretical calculations can provide valuable insights for developing novel oxygen carrier materials.

### **Materials and Methods**

The theoretical material screening and other evaluations were carried out with Matlantis<sup>5</sup>, an atomistic simulator of density functional theory calculations. All calculations used v4.0.0 of the PFP neural network potential<sup>6</sup> based on GGA-PBE functional. For material screening, CeO<sub>2</sub> (111) surface models with various cations (Ce<sub>0.67</sub>M<sub>0.33</sub>O<sub>2</sub>: M=V, Cr, Mn, Y, Zr, Mo, Pr, Nd, Sm, Gd), which consists of (6×6) supercell with six O-Ce-O tri layers, were constructed and optimized. Dopant positions were determined by minimizing formation energies. Since oxygen vacancy formation ability significantly influences the reaction, each doped surface model with a lattice oxygen vacancy was also prepared, and their oxygen vacancy formation energies were evaluated. Moreover, Ce<sub>0.67</sub>M<sub>0.33</sub>O<sub>2</sub> (M=Cr, Mn, Y, Zr, Pr, Nd, Sm, Gd) samples were synthesized by citric acid complex polymerization, with calcination at 823 K for 10 h. The redox behavior was evaluated through isothermal RWGS-CL tests at 773 K using a thermogravimetric analyzer (TGA-50; Shimadzu Corp.), under 10vol% H<sub>2</sub> and 10vol% CO<sub>2</sub> flow for



reduction and oxidation steps. Additionally, XPS and XAFS measurement and Bader charge analysis were performed for uncovering the dominant factors of RWGS-CL using CeO<sub>2</sub>-based materials.

#### **Results and Discussion**

From the theoretical material screening, we discovered that Pr-doped CeO<sub>2</sub> exhibits the lowest formation energy of oxygen vacancy among various dopants, indicating facilitated lattice oxygen release. Isothermal RWGS-CL tests validated our theoretical predictions, with Ce<sub>0.67</sub>Pr<sub>0.33</sub>O<sub>2</sub> achieving both the highest redox amount and 99% CO<sub>2</sub> conversion to CO (Fig. 1(a)). The Pr doping ratio change tests revealed that the oxygen vacancy formation energy decreases and the redox amount increases as the Pr doping ratio was increased (Fig. 1(b)). While these materials with larger doping ratios display some structural distortion in XRD measurements, they retain the fluorite structure of the pure CeO<sub>2</sub> throughout the reaction, which brings high stability across 10 RWGS-CL cycles.

To elucidate the redox mechanisms of  $Ce_{0.67}Pr_{0.33}O_2$ , theoretical charge analysis and *in-situ* XAFS measurement were conducted. Bader charge analysis result (Fig. 2(a)) revealed that two key trends: first, Ce atom charge intensifies with increasing Pr doping ratios; second, this charge diminishes during oxygen release, with  $Ce_{0.67}Pr_{0.33}O_2$  demonstrating a more substantial decrease compared to pure CeO<sub>2</sub>. Moreover, linear combination fitting of *in-situ* XAFS data (Fig. 2(b)) confirmed that more pronounced changes in Ce<sup>3+</sup> fraction for Ce<sub>0.67</sub>Pr<sub>0.33</sub>O<sub>2</sub> relative to pure CeO<sub>2</sub>, supporting our theoretical charge analysis findings. These analyses established that Pr doping enhances Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycling throughout reaction steps. To distinguish between structural and electronic effects of Pr doping, we prepared a theoretical model replacing Pr with Ce while preserving the Pr-induced structural distortion. Notably, oxygen vacancy formation energy of prepared calculation model becomes the similar to that of the pure CeO<sub>2</sub>, confirming that electronic structure modification through Pr doping, rather than structural distortion, predominantly drives the enhanced RWGS-CL performance of Ce<sub>0.67</sub>Pr<sub>0.33</sub>O<sub>2</sub>.



In conclusion, our theoretical screening identified Pr-doped CeO<sub>2</sub> as an optimal RWGS-CL material, demonstrating minimal oxygen vacancy formation energy and superior redox capacity. Bader charge analysis and *in-situ* XAFS revealed that Pr doping promotes Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycle because of tuning the electronic structure by Ce-O-Pr interactions. These findings establish electronic structure control by compositional engineering as a design strategy for optimizing RWGS-CL and related redox reactions.

#### References

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