



# Computational screening of perovskite redox materials for solar thermochemical ammonia synthesis from N<sub>2</sub> and H<sub>2</sub>O



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## ABSTRACT

To circumvent the scaling relations of activation energies and adsorption energies at catalytic surfaces limiting their catalytic activity, perovskites are investigated for a solar-driven production of ammonia (NH<sub>3</sub>) from N<sub>2</sub> and H<sub>2</sub>O via a two-step redox cycle. The cycle consists of an endothermic reduction of N<sub>2</sub> at 1400 °C using solar process heat, followed by an exothermic hydrolysis forming NH<sub>3</sub> at 400 °C. Both steps are carried out at ambient pressure. Electronic structure computations are employed to assess the stability and surface activity of oxygen vacancies and lattice nitrogen at the (001) facet of nitrogen-doped perovskites. The results are compared to the activities of Mo<sub>2</sub>N(100), Mo<sub>2</sub>N(111), and Mn<sub>2</sub>N(0001) reference models. We find producing oxygen vacancies at high temperature that are active in N<sub>2</sub> reduction is the energetically limiting reaction step of the redox cycle. The redox energetics can be tuned by the perovskite composition and are most sensitive to the type of transition metal at the B site terminating the surface. Promising perovskites contain Co or Mn at the surface and Co doped with Mo or W in the bulk, such as CaCoO<sub>3</sub>-terminated La<sub>0.5</sub>Ca<sub>0.5</sub>Mo<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub>, SrCoO<sub>3</sub>-terminated Sr<sub>0.5</sub>La<sub>0.5</sub>Co<sub>0.5</sub>W<sub>0.5</sub>O<sub>3</sub>, and CaMnO<sub>3</sub>-terminated Sr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub>. Trade-offs in the redox energetics are quantified to guide future experimental work.

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## 1. Introduction

Thermochemical redox cycles facilitate the production of renewable chemical fuels using the entire spectrum of concentrated sunlight as the source of high-temperature process heat [1,2]. A promising example is splitting of CO<sub>2</sub> and H<sub>2</sub>O with a two-step metal oxide redox cycle into separate streams of CO, H<sub>2</sub> (syngas) and O<sub>2</sub>. Syngas can be further processed into liquid hydrocarbon fuels, e.g. kerosene [3] or methanol [4], via commercial catalytic technology.

Concentrated solar process heat can also be used for the sustainable production of energy-intensive chemical commodities that are currently derived using finite and polluting fossil resources. One such example is the synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub> via the catalytic Haber-Bosch process at up to 300 bar and 400–500 °C [5,6]. The industrial implementation of this reaction consumes 28–166 GJ ton<sup>-1</sup> NH<sub>3</sub> [5,7], mainly supplied by natural gas, coal, or naphtha [7], at a global scale equivalent to 1–2% of the world's annual energy production [8]. A major fraction of it is consumed for the production of the two elemental precursors, i.e. H<sub>2</sub> – typically by

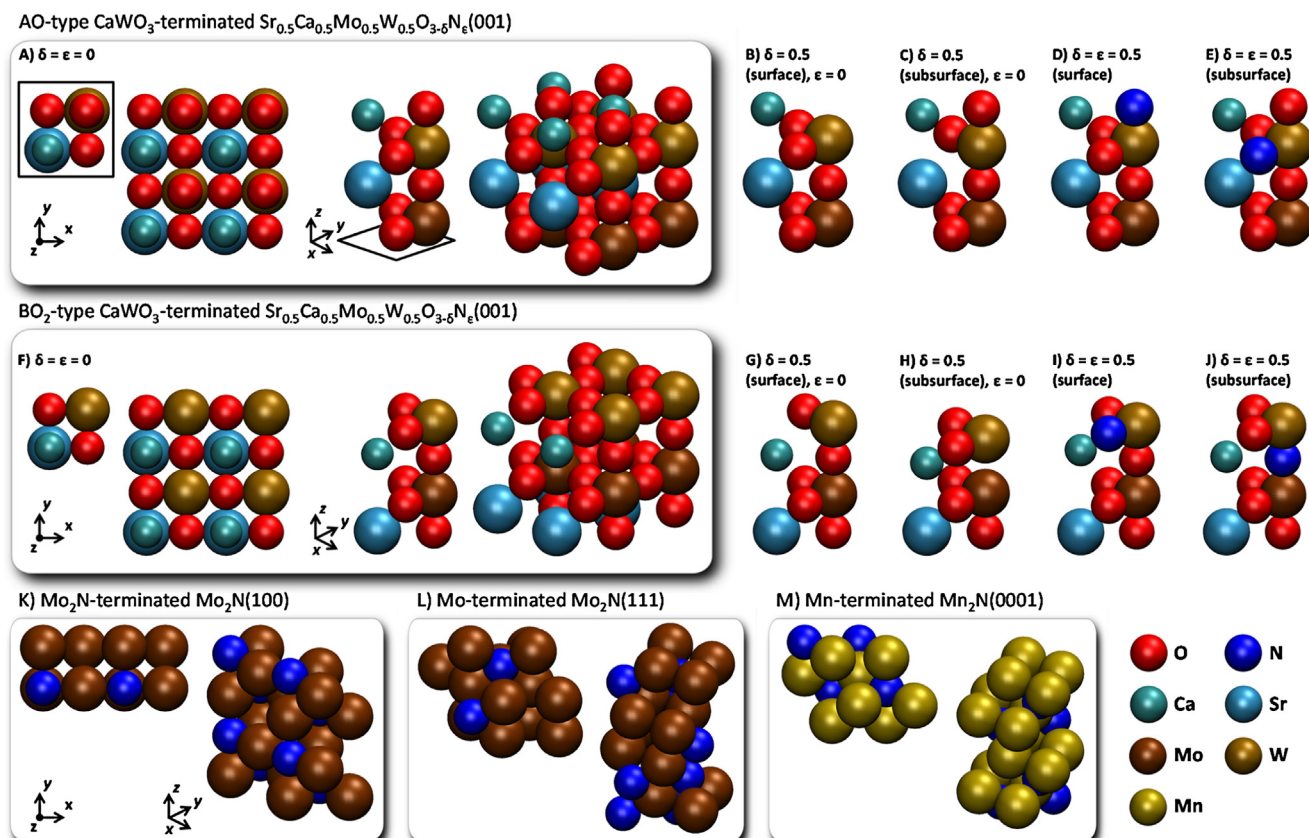
steam-reforming of natural gas – and N<sub>2</sub> – typically by cryogenic separation from air [7]. While renewable H<sub>2</sub> and electricity may be employed for the Haber-Bosch process [9], an economic NH<sub>3</sub> production from renewable resources remains challenging as about 15% of the net energy requirements of the industrially implemented Haber-Bosch process are consumed for cyclic heating/cooling and recompression to form NH<sub>3</sub> and separate it from unconverted N<sub>2</sub> and H<sub>2</sub> [7]. Furthermore, the limited activity of the catalysts [7,10,11], calls for high-pressure high-temperature machinery that limit economical production to large-scale centralized plants with a capacity exceeding 1000 t NH<sub>3</sub> day<sup>-1</sup> [7,12].

Current research focuses on alternative routes to produce renewable NH<sub>3</sub>, such as electrochemical [13–15], and low-pressure catalytic synthesis [16–18]. For example, certain metal nitrides are currently investigated for a catalytic NH<sub>3</sub> synthesis at moderate process conditions [16], while other metal nitrides are studied for a two-step NH<sub>3</sub> synthesis via separate N<sub>2</sub> reduction and hydrogenation with H<sub>2</sub> [17,19]. Density functional theory (DFT) suggests that materials such as Co<sub>3</sub>Mo<sub>3</sub>N may yield NH<sub>3</sub> via a Mars-van Krevelen mechanism, where the lattice nitrogen partakes in the reaction [18].

The severe process conditions of the Haber-Bosch process are rationalized with the scaling of the activation energy for the N<sub>2</sub> dissociation and the adsorption energy of nitrogen at catalytic surfaces

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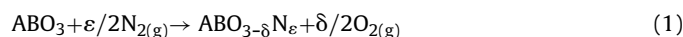


**Fig. 1.** Optimized surface geometries for a representative perovskite (panels A to J),  $\text{Mo}_2\text{N}(100)$ ,  $\text{Mo}_2\text{N}(111)$  and  $\text{Mn}_2\text{N}(0001)$  (panels K to M). Perovskite surface conditions are shown representatively for  $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_{3-\delta}\text{N}_\epsilon(001)$  terminated by a  $\text{CaWO}_3$  layer and with AO- (panels A to E) and  $\text{BO}_2$ -surface geometry (panels F to J). The second and fourth image (counting starting from the left) of panels A and F show the periodicity of the models parallel to the surface. Introduction of oxygen vacancies ( $\delta > 0$ ) and lattice nitrogen ( $\epsilon > 0$ ) is shown with panels B to E and panels G to J for both surface terminations. As guide to the eye, solid lines around two atomic geometries in panel A show the boundaries of the periodic unit cell.

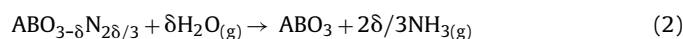
[20]. To circumvent these scaling relations, this paper investigates redox materials for production of  $\text{NH}_3$  from  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and sunlight at ambient pressure via a two-step thermochemical redox cycle [21]. Separating the catalytic ammonia synthesis by use of a redox material into two reaction steps generally increases the degree of freedom when designing catalysts with desirable activation and adsorption energies [19]. Ammonia synthesis with redox materials has been demonstrated successfully by  $\text{AlN}$  hydrolysis at  $900\text{--}1200^\circ\text{C}$  to produce  $\text{NH}_3$ , followed by carbothermic reduction of the formed  $\text{Al}_2\text{O}_3$  with  $\text{N}_2$  using a biogenic reducing agent such as wood charcoal at  $1500\text{--}1700^\circ\text{C}$  [22–24]. Due to a trade-off in the redox energetics [25,26], materials that can be recycled more easily yield less  $\text{NH}_3$ , such as  $\text{Cr}_2\text{O}_3$  which can be recycled with gasified biomass below  $1500^\circ\text{C}$  into chromium nitrides [27]. The economic prospect of producing  $\text{NH}_3$  overall from air, water, and sunlight, with on-site solar-driven  $\text{H}_2\text{O}$  splitting to produce  $\text{H}_2$  as reducing agent, have been assessed previously and indicate that a major fraction of the required capital investment is due to the need for the  $\text{H}_2$  reducing agent [21].

Here, we explore the possibility of entirely eliminating the need for a reducing agent to facilitate the conversion of  $\text{N}_2$  and  $\text{H}_2\text{O}$  into  $\text{NH}_3$  and  $\text{O}_2$  using perovskites with  $\text{ABO}_3$  stoichiometry, where A and B are metal cations in twelve- and six-coordinated interstices of the metal oxide. Due to their stable crystal phase, tuneable oxygen vacancy concentrations, and high oxygen vacancy conductivities, perovskites are attractive materials for fuel cells and high-temperature oxygen separation [28–30], as well as for solar-driven thermochemical splitting of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and solar-driven reforming of  $\text{CH}_4$  [31–33]. Conceptually, using concentrated solar

energy at high temperature and low  $\text{O}_2$  partial pressure a perovskite is reduced endothermically to form oxygen vacancies for  $\text{N}_2$  reduction:



where  $\delta$  is the oxygen non-stoichiometry and  $\epsilon \leq \delta$  is the amount of nitrogen incorporated into the crystal lattice. Assuming for simplicity that two thirds of the oxygen vacancies are active in  $\text{N}_2$  reduction,  $\text{NH}_3$  is formed exothermically in a second hydrolysis step at ambient pressure and lower temperature:



In general, if  $\epsilon > 2\delta/3$  some of the lattice nitrogen will yield  $\text{N}_2$ , while excess  $\text{H}_2$  will be formed if  $\epsilon < 2\delta/3$ .

The thermodynamic activity of perovskites in these reactions is assessed here with electronic structure calculations. Section 3.1 computes the energy required for the  $\text{O}_2$  evolution reaction (OER) and the activity of oxygen vacancies in the  $\text{N}_2$  reduction reaction (NRR), described with Eq. (1). Section 3.2 quantifies the stability of oxygen vacancies and lattice nitrogen at the surface. Section 3.3 assess the energetics of the  $\text{H}_2\text{O}$  splitting reaction (WSR) and  $\text{NH}_3$  evolution reaction (AER), described with Eq. (2).

## 2. Computational methods

### 2.1. Electronic structure computations

The thermochemical activity of 60 cubic  $\text{A}_{0.5}\text{A}'_{0.5}\text{B}_{0.5}\text{B}'_{0.5}\text{O}_{3-\delta}\text{N}_\epsilon$  ( $\text{A}$ ,  $\text{A}' = \text{Ca}$ ,  $\text{Sr}$ ,  $\text{La}$ ; and  $\text{B}$ ,  $\text{B}' = \text{Mn}$ ,  $\text{Co}$ ,  $\text{Mo}$ ,  $\text{W}$ ) perovskites and of

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