Ammonia recently has gained increasing attention as a carrier for the efficient and safe usage of hydrogen to further advance the hydrogen economy. However, there is a pressing need to develop new ammonia synthesis techniques to overcome the problem of intense energy consumption associated with the widely used Haber–Bosch process. Chemical looping ammonia synthesis (CLAS) is a promising approach to tackle this problem, but the ideal redox materials to drive these chemical looping processes are yet to be discovered. Here, by mining the well-established MP database, the reaction free energies for CLAS involving 1699 bicationic inorganic redox pairs are screened to comprehensively investigate their potentials as efficient redox materials in four different CLAS schemes. A state-of-the-art machine learning strategy is further deployed to significantly widen the chemical space for discovering the promising redox materials from more than half a million candidates. Most importantly, using the three-step H$_2$O-CL as an example, a new metric is introduced to determine bicationic redox pairs that are “cooperatively enhanced” compared to their corresponding monocationic counterparts. It is found that bicationic compounds containing a combination of alkali/alkaline-earth metals and transition metal (TM)/post-TM/metalloid elements are compounds that are particularly promising in this respect.

1. Introduction

Ammonia is a crucial industrial material that acts as a precursor for large-scale manufacturing of products that are essential to sustain basic human life, including agricultural fertilizers, pharmaceutical drugs, explosives, and many others.[1–6] Recently, it is also considered as a promising medium to facilitate the global energy dispatch for hydrogen economy due to its easily liquefiable and less-explosive nature. This is further stimulated by the existence of complete transport and storage infrastructures that have been developed for the ammonia industry over the past few decades.[7–9]

Currently, the most well-established approach for manufacturing ammonia in industrial scale is the Haber–Bosch process, which catalytically converts nitrogen and hydrogen into ammonia at an elevated pressure (100–350 atm) and temperature (400–500 °C).[10] This century-old process is heavy in both energy consumption and greenhouse gas emissions, particularly when the energies are sourced from the combustion of fossil fuels. Therefore, significant efforts have been devoted to search for alternative green approaches in ammonia synthesis.[11–24] Within these approaches, chemical looping ammonia synthesis (CLAS) is particularly attractive as it enables the synthetic process to be separately manipulated in sequential steps, providing more freedoms in selecting the most suitable redox materials to drive the chemical reactions.

The state-of-the-art CLAS approaches can be categorized into four schemes where their looping mechanisms are depicted in Figure 1.[31] All CLAS processes involve the interconversions between active materials enabled by reacting them with different feedstocks. H$_2$ is the most sustainable reducing agent to be used in CLAS for its low carbon footprint, especially when it is produced from renewable resources.[12,23] Figure 1a demonstrates a conventional two-step chemical looping (CL) process that drives the NH$_3$ formation through interconverting between a metal oxide and nitride redox pair (M$_x$O$_y$/M$_a$N$_b$). In this approach, N$_2$ is fixed by M$_y$O$_x$ under the H$_2$ environment (Rxn I) at high temperature (>1000 °C). NH$_3$ then is generated from the subsequent hydrolysis of M$_x$N$_y$ (Rxn II, thus denoted as H$_2$O-CL).[34,35] Depending on the thermodynamic equilibria of the sub-reactions, a three-step variant (Figure 1b) of the H$_2$O-CL can be derived by splitting the nitrogen fixation step into an oxide reduction (Rxn I) and a metal nitridation (Rxn II) step.[26,36,37] In this way, the formation of metallic intermediate could help to reduce the thermodynamic barrier for converting the oxide to nitride, thus improves the cyclic efficiency. In contrast to the previous two chemical loops, the H$_2$-CL (Figure 1c) purely loops between two nitrides with different nitrogen contents at a lower temperature (>500 °C). In H$_2$-CL, NH$_3$ is generated from reacting H$_2$, with the phase consisting of higher nitrogen content (M$_x$N$_y$) in Rxn I.[25,38] The reduced nitrogen-deficient compound (M$_a$N$_b$, 0 < γ < β) can then

Jiaxin Fan, Wenxian Li, Sean Li, and Jack Yang*

Ammonia recently has gained increasing attention as a carrier for the efficient and safe usage of hydrogen to further advance the hydrogen economy. However, there is a pressing need to develop new ammonia synthesis techniques to overcome the problem of intense energy consumption associated with the widely used Haber–Bosch process. Chemical looping ammonia synthesis (CLAS) is a promising approach to tackle this problem, but the ideal redox materials to drive these chemical looping processes are yet to be discovered. Here, by mining the well-established MP database, the reaction free energies for CLAS involving 1699 bicationic inorganic redox pairs are screened to comprehensively investigate their potentials as efficient redox materials in four different CLAS schemes. A state-of-the-art machine learning strategy is further deployed to significantly widen the chemical space for discovering the promising redox materials from more than half a million candidates. Most importantly, using the three-step H$_2$O-CL as an example, a new metric is introduced to determine bicationic redox pairs that are “cooperatively enhanced” compared to their corresponding monocationic counterparts. It is found that bicationic compounds containing a combination of alkali/alkaline-earth metals and transition metal (TM)/post-TM/metalloid elements are compounds that are particularly promising in this respect.

1. Introduction

Ammonia is a crucial industrial material that acts as a precursor for large-scale manufacturing of products that are essential to sustain basic human life, including agricultural fertilizers, pharmaceutical drugs, explosives, and many others.[1–6] Recently, it is also considered as a promising medium to facilitate the global energy dispatch for hydrogen economy due to its easily liquefiable and less-explosive nature. This is further stimulated by the existence of complete transport and storage infrastructures that have been developed for the ammonia industry over the past few decades.[7–9]

Currently, the most well-established approach for manufacturing ammonia in industrial scale is the Haber–Bosch process, which catalytically converts nitrogen and hydrogen into ammonia at an elevated pressure (100–350 atm) and temperature (400–500 °C).[10] This century-old process is heavy in both energy consumption and greenhouse gas emissions, particularly when the energies are sourced from the combustion of fossil fuels. Therefore, significant efforts have been devoted to search for alternative green approaches in ammonia synthesis.[11–24] Within these approaches, chemical looping ammonia synthesis (CLAS) is particularly attractive as it enables the synthetic process to be separately manipulated in sequential steps, providing more freedoms in selecting the most suitable redox materials to drive the chemical reactions.

The state-of-the-art CLAS approaches can be categorized into four schemes where their looping mechanisms are depicted in Figure 1.[31] All CLAS processes involve the interconversions between active materials enabled by reacting them with different feedstocks. H$_2$ is the most sustainable reducing agent to be used in CLAS for its low carbon footprint, especially when it is produced from renewable resources.[12,23] Figure 1a demonstrates a conventional two-step chemical looping (CL) process that drives the NH$_3$ formation through interconverting between a metal oxide and nitride redox pair (M$_x$O$_y$/M$_a$N$_b$). In this approach, N$_2$ is fixed by M$_y$O$_x$ under the H$_2$ environment (Rxn I) at high temperature (>1000 °C). NH$_3$ then is generated from the subsequent hydrolysis of M$_x$N$_y$ (Rxn II, thus denoted as H$_2$O-CL).[34,35] Depending on the thermodynamic equilibria of the sub-reactions, a three-step variant (Figure 1b) of the H$_2$O-CL can be derived by splitting the nitrogen fixation step into an oxide reduction (Rxn I) and a metal nitridation (Rxn II) step.[26,36,37] In this way, the formation of metallic intermediate could help to reduce the thermodynamic barrier for converting the oxide to nitride, thus improves the cyclic efficiency. In contrast to the previous two chemical loops, the H$_2$-CL (Figure 1c) purely loops between two nitrides with different nitrogen contents at a lower temperature (>500 °C). In H$_2$-CL, NH$_3$ is generated from reacting H$_2$, with the phase consisting of higher nitrogen content (M$_x$N$_y$) in Rxn I.[25,38] The reduced nitrogen-deficient compound (M$_a$N$_b$, 0 < γ < β) can then...
Figure 1. Schematic illustration of the state-of-the-art CLAS mechanisms that involve the monocationic compounds (M–X) as the redox materials. a) two-step and b) three-step H₂O-CL. In these two chemical looping (CL) processes, metal nitrides are used as the nitrogen carriers, which are formed during the nitrogen harvest process (Rxn I in the two-step loop and Rxn II in the three-step loop, respectively). NH₃ is generated when the nitrides are subsequently reacted with steam and simultaneously converted back to the corresponding oxides. c) H₂-CL, which is driven by either the conversion between two different nitrides or the formation and recovery of nitrogen vacancy (also known as the Mars-van Krevelen mechanism[29,30]). A nitrogen-rich (N_rich) metal nitride (M₂N₂) possessing cation in the high oxidation state is first reduced in H₂ environment to generate NH₃ (Rxn I). The nitrogen-poor (N_poore) nitride (M₁N₂, 0 < γ < β) formed from the last step is then converted back to the corresponding N_rich phase by putting it in contact with N₂ (Rxn II). d) MH-CL, which has a similar looping mechanism as the H₂-CL loop. The main difference is in the redox materials, which MH-CL involves the transformation between metal hydrides (M–H) and nitride-hydrides (M–N–H). The sub-reactions that involve H₂ as reactant are labeled as Rxn I in all four CLs (a–d). More detailed chemical equations can be found in Section S1, Supporting Information.

To date, the majority of studies on CLAS have been focusing on using monocationic compounds, that is, looping materials sharing one common cation (M–X), as the active redox materials. However, various challenges have been identified in association with the usage of this material system, including high reaction temperatures, sluggish kinetics, and low NH₃ production rates.[5] Recently, a few experimental attempts have been reported on the investigations of the bicationic compounds (with a general formula of M₁–M₂–X) as the active materials in CLAS.[42–44] This sparks the search for suitable redox materials among compounds with more complex chemical compositions, as well as all different possible CLAS processes in which these materials may be applied. However, increasing the chemical complexity will also dramatically increase the number of candidate compounds, making the search with the traditional trial-and-error approach grossly inefficient. In this regard, high-throughput computational material screenings have emerged to be an invaluable alternative in helping the community to expedite the process of property-driven material development.[25,45–48]

In light of this, hereby, we extend the search of new redox materials for CLAS into a wider chemical space of bicationic compounds. In particular, the fast enumeration of the temperature-dependent Gibbs reaction energies ΔG_r(T) that involve 1699 M₁–M₂–X and 1647 M–X pairs are enabled by the usage of a machine-learned Gibbs energy descriptor[49] on materials recorded in the Materials Project (MP) database.[50] Statistically, we have seen many more bicationic redox pairs that are energetically viable in driving three-step H₂O-CL compared to two-step H₂O-CL and H₂-CL with stronger thermodynamic driving forces. However, with only the compounds extracted from the MP database are not sufficient to complete all four different CLAS cycles. As such, using MH-CL process as the example, we adopt the strategy of elemental substitution to generate 526,396 hypothetical compounds. Using a recently developed machine learning framework, their formation energies can be quickly predicted with almost negligible computational cost. With the further usage of convex hull stabilities as filtering criteria, additional 4698 potentially synthesizable redox pair candidates are attained to assess their potential for driving this particular process. The ability to predict and screen such a large set of hypothetical crystal structures, as a component of a single study, already represents a significant leap forward in what is achievable in modern crystal structure predictions.[51–54]

Most importantly, to our best knowledge, no prior studies have been devoted to understand the possible thermodynamic
advantages of using compounds with complex compositions in CLAS compared to those with simpler compositions. We will gain some critical insights to this question by considering a cooperativity metric calculated from the reaction energetics of three-step H2O-CL that are driven by the bicationic oxide/nitride redox pairs (M1–M2–O/N) with those driven by the monocationic redox pairs (M–O/N). More specifically, we reveal the possible “cooperative enhancement effect” being the key thermodynamic driving forces which favor M1–M2–O/N to be used as the redox materials. This is reflected by the reaction free energy of using M1–M–O/N being even lower compared to the case of using a simple mixture of M1–O/N and M–O/N. Such a cooperative effect is observable within certain groups of bicationic compounds, such as those composed with alkali/alkaline-earth metals and first-row transition metals. In principle, the cooperativity metric put forward in this work can also be used with reaction thermochemical data extracted from the MP database and is limited by the stoichiometric constraint imposed in the chemical reactions (Equations (1)–(6) in Experimental Section). For example, CoMoO4 can only be paired with Co3MoO4 but not with Co2MoO4 or CoMo2O4 in the H2O-CL. The most extreme case is the H2O-CL, whereby only one pair of redox materials (Li2MgH4 and Li2Mg(NH)2) was found to be able to satisfy the corresponding stoichiometric constraint. As such, in this section, we will focus our discussions on the temperature-dependent reaction thermodynamics for CL processes a–c shown in Figure 1. The limitations in analyzing the MH-CL process will be overcome by generating more hypothetical bicationic hydrides (M1–M2–H) and nitride-hydrides (M1–M2–N–H), which will be discussed with more details in the later section.

Based on the redox pairs collated from the materials existing in the MP database, we first compare the temperature-dependent Gibbs formation energies (ΔGf(T)) between the compounds in each redox pair, which is an important property that will determine the suitability for the redox pairs to drive specific CL reactions. Figure 2a compares the ΔGf(T) for M1–M2–O/N and M–O/N calculated using the Gibbs energy descriptor (Equations 7–9). The ΔGf(T) are calculated up to 1800 K to cover the high operation temperature for reducing oxides in H2O-CL. As temperature increases, ΔGf(T) for both the monocationic and bicationic compounds increase correspondingly, which implies a general decrease in thermal stability. Within this temperature range, ΔGf(T) of the vast majority of oxides are more negative than the corresponding nitrides in both bicationic and monocationic pairs. This is predominantly owing to the greatest scale of nitride metastability among all inorganic compounds. The kinetic density distributions have also shown that the ΔGf(T) for bicationic compounds are generally more negative than those for the monocationic ones. It indicates that both the bicationic oxides and nitrides are statistically more stable than their monocationic counterparts.

Figure 2b compares the ΔGf(T) of nitrogen rich (Nrich) and poor (Npoor) nitride pairs in H2O-CL. A maximum temperature of 1200 K is considered because of the generally lower temperature required for H2O-CL experiment. The trend of ΔGf(T) change with respect to increasing temperature is consistent with oxide/nitride pairs. However unlike the clear tendency of ΔGf<oxides < ΔGf<nitrides observed for the vast majority of the nitride/oxide pairs, the ΔGf values for both the Nrich and Npoor metal nitrides are similar to each other. Statistically, 47.8% of the M–Nrich/Npoor and 61.3% of the M1–M2–Nrich/Npoor prefer the Nrich phase at 0 K (ΔGf,Nrich < ΔGf,Npoor), and these numbers reduce to 35.9% and 48.0% at 1200 K respectively. It suggests that the increasing temperature would have larger impact on destabilizing the Nrich nitride for both groups. Also since Rxn II (nitrogen fixation) in H2O-CL only involves the conversion between these two nitrides, the differences in the ΔGf between these two phases would directly determine the energetics of this reaction.

2. Results and Discussions

2.1. Analysis of Temperature-Dependent Thermodynamics of CLAS

2.1.1. Construction of the Redox Pairs

As shown in Table 1, the total numbers of bicationic compounds extracted from the MP database are significantly larger than the monocationic ones, particularly for oxides and nitrides. (Details of materials selection can be found in Section S2, Supporting Information) This seemingly suggests that it is likely to find much more viable redox pairs from compounds with complex chemical compositions. However, the number of redox pairs that can be formed among the available compounds are significantly less than the number of compounds that have been extracted from the MP database, which is limited by the stoichiometric constraint imposed in the chemical reactions (Equations (1)–(6) in Experimental Section). For example, CoMoO4 can only be paired with CoMoO4 but not with Co2MoO4 or CoMo2O4 in the H2O-CL. The most extreme case is the MH-CL, whereby only one pair of redox materials (Li2MgH4 and Li2Mg(NH)2) was found to be able to satisfy the corresponding stoichiometric constraint. As such, in this section, we will focus our discussions on the temperature-dependent reaction thermodynamics for CL processes a–c shown in Figure 1. The limitations in analyzing the MH-CL process will be overcome by generating more hypothetical bicationic hydrides (M1–M2–H) and nitride-hydrides (M1–M2–N–H), which will be discussed with more details in the later section.

Table 1. Numbers of crystalline solids in Materials Project database categorized by the anion groups as well as the constructed redox pairs based on the looping mechanisms demonstrated in Figure 1.

| System | Number of compounds | Number of pairs |
|--------|---------------------|-----------------|
| Oxide  | Nitride  | Hydride | Nitride-hydride | H2O-CL | H2-CL | MH-CL |
| M–X    | 461  | 244  | 175  | 65  | 1174 | 473  | 136  |
| M1–M2–X | 9087 | 2378 | 394  | 111 | 1526 | 173  | 1    |

Based on the redox pairs collated from the materials existing in the MP database, we first compare the temperature-dependent Gibbs formation energies (ΔGf(T)) between the compounds in each redox pair, which is an important property that will determine the suitability for the redox pairs to drive specific CL reactions. Figure 2a compares the ΔGf(T) for M1–M2–O/N and M–O/N calculated using the Gibbs energy descriptor (Equations 7–9). The ΔGf(T) are calculated up to 1800 K to cover the high operation temperature for reducing oxides in H2O-CL. As temperature increases, ΔGf(T) for both the monocationic and bicationic compounds increase correspondingly, which implies a general decrease in thermal stability. Within this temperature range, ΔGf(T) of the vast majority of oxides are more negative than the corresponding nitrides in both bicationic and monocationic pairs. This is predominantly owing to the greatest scale of nitride metastability among all inorganic compounds. The kinetic density distributions have also shown that the ΔGf(T) for bicationic compounds are generally more negative than those for the monocationic ones. It indicates that both the bicationic oxides and nitrides are statistically more stable than their monocationic counterparts.

Figure 2b compares the ΔGf(T) of nitrogen rich (Nrich) and poor (Npoor) nitride pairs in H2O-CL. A maximum temperature of 1200 K is considered because of the generally lower temperature required for H2-CL experiment. The trend of ΔGf(T) change with respect to increasing temperature is consistent with oxide/nitride pairs. However unlike the clear tendency of ΔGf<oxides < ΔGf<nitrides observed for the vast majority of the nitride/oxide pairs, the ΔGf values for both the Nrich and Npoor metal nitrides are similar to each other. Statistically, 47.8% of the M–Nrich/Npoor and 61.3% of the M1–M2–Nrich/Npoor prefer the Nrich phase at 0 K (ΔGf,Nrich < ΔGf,Npoor), and these numbers reduce to 35.9% and 48.0% at 1200 K respectively. It suggests that the increasing temperature would have larger impact on destabilizing the Nrich nitride for both groups. Also since Rxn II (nitrogen fixation) in H2O-CL only involves the conversion between these two nitrides, the differences in the ΔGf between these two phases would directly determine the energetics of this reaction.

2.1.2. Gibbs Reaction Energies of Sub-Reactions

With the determinations of the ΔGf values for different compounds to be used as the redox pairs, the Gibbs reaction energies (ΔGf) for each constituent chemical reactions can be subsequently calculated based on Equation (10). The proportions of the spontaneous chemical reactions being identified (i.e., those with ΔGf < 0) are plotted in Figure 3 as a function of the reaction temperature, whereas more detailed mappings of ΔGf for each redox pair are shown in Figures S1–S3, Supporting Information. It can be seen from Figure 3 that, most of the chemical reactions tend to proceed spontaneously at lower reaction temperatures, which is a desirable feature for the industrial development of ammonia synthesis with lower energy consumption. However, exceptions to this trend can be found for the reduction process that involves M1–M–O and M–O in the three-step H2O-CL (Rxn I, Figure 3a), where the equilibria are shifted toward the product formations at
Figure 2. Comparison of the Gibbs formation energies ($\Delta G_f(T)$) of $M$–$X$ and $M_1$–$M_2$–$X$ pairs with respect to rising temperature. a) $X = O$ and $N$, b) $X = N_{rich}$ and $N_{poor}$, which correspond to metal nitrides with higher/lower nitrogen contents, respectively. Redox pairs that are made from monocation/bicationic compounds are colored in blue/orange markers respectively. The yellow-shaded areas indicate that both solids in the active pair have negative Gibbs formation energies meaning they are more stable and less likely to be decomposed at the temperature(s) considered.

Figure 3a shows that for Rxn I in three-step $H_2$O-CL (reduction of oxides), less bicationic oxides $M_1$–$M_2$–$O$ are likely to be spontaneously reduced to the corresponding metals compared to monocationic oxides $M$–$O$ (the blue solid line is below the blue dashed line). However in subsequent Rxn II (nitridation, colored as magenta) and Rxn III (hydrolysis, colored as yellow), many more reactions driven by the bicationic redox pairs $M_1$–$M_2$–$O/N$ are likely to proceed compared to those driven by the monocationic ones. Statistically, 21.8% and 51.4% of $M_1$–$M_2$–$O$ and $M$–$O$ can undergo spontaneous oxidation at 300 K, respectively. Although significantly more oxides can be reduced at a higher temperature of 1800 K, it remains easier to reduce the $M$–$O$ (66.8%) compared to $M_1$–$M_2$–$O$ (38.8%). On the other hand, 80.2% and 76.7% of the bicationic systems can undergo spontaneous nitridation and hydrolysis reactions at 300 K, which are higher than the percentages of the same chemical reactions involving the monocationic ones (65.3% and 45.1% respectively). This shows that the bicationic pairs $M_1$–$M_2$–$O/N$ are clearly preferred in both two steps at low temperature. However, the numbers of spontaneous reactions decrease drastically with the rising temperature, especially in the nitridation process. At extremely high temperature of 1800 K, we see no advantage in the nitridation of bicationic nitrides $M_1$–$M_2$–$N$ compared to the monocationic nitrides $M$–$N$, as indicated by 29.0% and 29.8% of all the reactions that may proceed spontaneously. The trends observed above can be mainly attributed to the change of $\Delta G_f$ for $M_1$–$M_2$–$N$ and $M$–$N$ in Figure 2a. As the stabilities of bicationic nitrides decrease, it then becomes more difficult for the nitridation reactions to proceed.

Figure 3b analyzes the percentages of sub-reactions with negative $\Delta G_f$ in the two-step $H_2$O-CL. In this process, the nitrogen fixation is carried out by purging the mixed gases of $H_2$ and $N_2$ simultaneously into the reactor to directly convert the oxide into the corresponding nitride (Rxn I). The ratios of Rxn I that can proceed spontaneously are nearly insensitive to the temperature variation, which remain at around 55% and 23% for $M$–$O/N$ and $M_1$–$M_2$–$O/N$. The degree of spontaneous reactions decreases for both $M$–$O/N$ and $M_1$–$M_2$–$O/N$ with an increasing temperature, which is consistent with the trends observed in Figure 3a.
Figure 3. Percentages of redox pairs that possess spontaneous sub-reaction ($\Delta G_r < 0$) at different temperatures that can practically be reached in different CLAS processes: a) three-step H2O-CL, b) two-step H2O-CL, and c) H2-CL. The solid lines correspond to CLs using bicationic compounds $M_1–M_2–X$ as the active materials, whereas the dashed lines correspond to those using monocationic compounds $M–X$ as the active materials. The blue, magenta, and orange colors are used to distinguish the sub-reactions shown in Figure 1. Rxn II in the two-step H2O-CL (magenta lines) are identical to the Rxn III (orange lines) in the three-step H2O-CL, because they both correspond to the same chemical reaction of hydrolyzing the nitrides back to the oxides.

For H2-CL (Figure 3c), our analysis shows that $M–N$ rich can react with H2 easier to form NH3 (Rxn I, 54.1% for monocationic nitrides compared to 39.2% for bicationic ones at 300 K), whereas $M_1–M_2–N$ rich are slightly more stable (cf., Figure 2b), such that more nitrogen fixation reactions (Rxn II, 51.2% and 65.9% for mono- and bicationic nitrides at 300 K, respectively) occur spontaneously in this case. It shows that whilst $M_1–M_2–N$ systems may have stronger propensity to capture the atmospheric N2 and form the nitrogen-rich phase, it is harder to dissociate the metal–nitrogen bonds to form NH3 compared to the monocationic nitrides.

2.1.3. Assessment of Limiting Energies and Reactions

In order to cross-compare different CLAS processes that each consists of multiple sub-reactions, thus facilitating the identification of the best redox pairs, we calculated the limiting energies ($\Delta G_{r,\text{lim}}$) for all loops carried out by either monocationic or bicationic redox pairs using Equation (12). We note that, a limiting reaction is the sub-reaction in a specific CL process that contributes to the limiting energy ($\Delta G_{r,\text{lim}}$), in the temperature range considered. As such, $\Delta G_{r,\text{lim}} < 0$ would imply that all steps within the reaction cycle will proceed spontaneously at given temperatures, and redox pairs that will contribute to negative $\Delta G_{r,\text{lim}}$ are highly desirable. Nevertheless, it should be noted that having negative $\Delta G_{r,\text{lim}}$ is a necessary but insufficient thermodynamic requirement for solid-state CLAS to proceed. This is because the chemical reactivity can inevitably be affected by many other factors, such as reaction barrier heights, phase transition, dimensions (e.g., surface effects), and so on. The considerations of these influencing factors are beyond the scope of the present investigation.

In Figure 4, we plot the $\Delta G_{r,\text{lim}}$ for CLs involving bicationic redox pairs with respect to either the formation enthalpies $\Delta H_f$ of the active oxides (Figure 4a), or the differences in the $\Delta H_f$ (i.e., $\Delta \Delta H_f$, Figure 4b,c) between the redox pairs, in order to reveal how $\Delta G_{r,\text{lim}}$ for different sub-reactions are fundamentally determined by $\Delta H_f$. Similar plots for the monocationic systems can be found in Figure S4, Supporting Information.) This gives rise to the so-called “volcano plots,” and the choice of presenting $\Delta G_{r,\text{lim}}$ with respect to either $\Delta H_f$ or $\Delta \Delta H_f$ depends on whether both the reduced and oxidized forms of the redox pair are coexisting in all sub-reactions. More detailed explanation on these choices can be found in Section S3 and Figure S5, Supporting Information.

Figure 4a shows the $\Delta G_{r,\text{lim}}$ of three-step H2O-CL against $\Delta H_{f,\text{oxd}}$ (i.e., the formation enthalpies for the bicationic oxides). Statistically, we found that the limiting reactions for more than 60% (936 out of 1526) of the three-step H2O-CL are coming from the reduction step (Rxn I), whereas only 351 and 239 CL processes are limited by the hydrolysis (Rxn III) and the nitridation (Rxn II), respectively. Similar statistical trend for the monocationic redox pairs can also be observed in Figure S4a, Supporting Information. This shows that, for the three-step H2O-CL, the reduction of metal oxides to metals is the most difficult part to proceed in the entire loop.

Focusing on redox pairs that are able to drive spontaneous three-step H2O-CL (i.e., those possess negative $\Delta G_{r,\text{lim}}$), Figure 4a shows that, the $\Delta H_{f,\text{oxd}}$ for these pairs predominantly fall into a narrow region between $-1.33$ and $-2.09$ eV atom$^{-1}$. When the oxides are too stable ($\Delta H_{f,\text{oxd}} < -2.09$ eV atom$^{-1}$), they...
Figure 4. Volcano plots of the limiting energies using bicationic redox materials (M₁–M₂–X) in a) three-step H₂O-CL, b) two-step H₂O-CL, and c) H₂-CL. ΔGᵣ,lim for the candidates with the most negative values are also plotted for each CL (FeMoO₄/Fe₃Mo₃N for three-step H₂O-CL, Mn₃ZnO₇/Mn₃ZnN for two-step H₂O-CL, and TaMoN₃/TaMoN₃ for H₂-CL) with respect to the reaction temperatures in the looping processes. The limiting reactions are marked as blue, green, and red for Rxn I, II, and III in the three-step H₂O-CL and as blue and red for Rxn I and Rxn II in the rest two-step processes respectively (b and c).

become very difficult to be reduced in Rxn I, resulting in the increase of ΔGᵣ,lim with Rxn I as the limiting reaction. On the other hand, when the ΔHᵣ,oxd is larger than −1.33 eV atom⁻¹, Rxn II or III now becomes the limiting reaction. The scenario for Rxn II being the limiting reaction can be attributed to the correlated ΔGᵣ between oxides and nitrides seen in Figure 2. When the oxides are less stable, the stabilities of the complementary nitrides would also decrease in most cases, which makes their formations more difficult from directly reacting the metals with N₂ and therefore leads to the Rxn II becoming the limiting reaction. Similarly, when both the oxides and nitrides have ΔHᵣ that are too large, the energy released from the conversion of nitride back to the oxide will not be sufficient to drive the endothermic reaction that converts H₂O to NH₃ (At 300 K, ΔGᵣ,H₂O = −2.37eV atom⁻¹ and ΔGᵣ,NH₃ = −0.17eV atom⁻¹[57]), which can also turn the hydrolysis reaction (Rxn III) into the limiting reaction.

Statistically, 97 three-step H₂O-CL that are driven by the bicationic redox pairs could proceed spontaneously, which are 26% more than those driven by the monocationic ones. Among all viable candidates, FeMoO₄/Fe₃Mo₃N gives the lowest ΔGᵣ,lim of −1.01 eV with Rxn I as the limiting reaction. To illustrate how this limiting reaction and the corresponding reaction free energy are determined, the right hand side of Figure 4a shows a plot of ΔGᵣ,lim as a function of the three sub-reaction temperatures. It is immediately clear that the lowest ΔGᵣ,lim is reached when Rxn I is set at the highest reaction temperature of 1800 K while the temperatures for Rxn II and III are fixed at the lowest 300 K. The high (low) temperatures required for Rxn I (II/III) revealed...
in Figure 4a are also consistent with the trends observed in the Figure 3a for three-step H$_2$O-CL. Moreover, it is also seen from the temperature-dependency of $\Delta G_{r,\text{lim}}$ that there exist a range of temperatures in which $\Delta G_{r,\text{lim}}$ are negative. For example, the temperature for the oxide reduction (Rxn I) may be further lowered to 1400 K, at which the reaction can still proceed spontaneously, albeit with potentially slower reaction kinetics. It shows that this information is particularly useful to guide the optimization of the reaction conditions in a CL process.

Further examinations on the chemical constituents for all 97 lead candidates of the M$_1$–M$_2$–O/N redox pairs reveal many of them contain one or both cations of which corresponding monocationic counterparts (M–O/N) are not viable candidates, such as MgCoO$_3$/MgCoN, CaAgO$_2$/CaAgN, ZnCrO$_3$/ZnCrN$_2$, CoWO$_4$/Co,$_2$W$_3$N, etc. This further demonstrates the existence of new chemical bonding interactions in compounds with complex compositions plays a significant role in changing materials’ thermodynamic stabilities, enabling them to become promising active materials that do not exist in the chemical space of simpler compounds.

The left hand side of Figure 4b shows the volcano plot for the two-step H$_2$O-CL constructed for the bicationic redox pairs. It shows that the $\Delta G_{r,\text{lim}}$ are most negative when the oxides are $\pm 1.5$ eV atom$^{-1}$ enthalpically more stable that the corresponding nitrides. Statistically, the numbers of viable redox pairs for the two-step process are 44 and 54 for M$_1$–M$_2$–O/N and M–O/N (see also Figure S4b, Supporting Information), which are less than those for the three-step cycle. Notably the number of bicationic redox pairs has been halved indicating that there is no significant benefit in using bicationic compounds to drive the two-step CL processes. Meanwhile, the $\Delta G_{r,\text{lim}}$ values for many redox pairs that are negative in the three-step cycle have increased significantly in the two-step process. For instance, $\Delta G_{r,\text{lim}}$ using KSe$_2$/K$_2$SeN as the active materials increases from $-0.96$ eV atom$^{-1}$ in the three-step cycle to $0.99$ eV atom$^{-1}$ calculated for the two-step one. It shows thermodynamically, the direct conversion of oxides to their corresponding nitrides without the formation of the metallic intermediates could be challenging to proceed. Within these candidates in the two-step process, MnN$_2$/ZnO$_2$/Mn$_2$ZnN has the most negative $\Delta G_{r,\text{lim}}$ of $-0.62$ eV atom$^{-1}$, where its temperature dependence is shown in the contour plot in Figure 4b (right panel). The applicable temperatures of Rxn I have a particularly wide range from 600 to 1800 K to deliver $\Delta G_r < 0$. In contrast, Rxn II is exothermic only when the hydrosilization temperature is below 500 K.

Finally, Figure 4c demonstrates that the reaction spontaneity for the H$_2$-CL is also largely dependent upon the differences in the formation enthalpies between the N$_\text{rich}$ and N$_\text{poor}$ phases of the metal nitrides. Unlike the trends observed in the previous two CL processes, the two nitride phases should have comparable formation enthalpies in order to lower the overall $\Delta G_r$. This is because H$_2$O, as being thermodynamically very stable, is not involved in this particular CL process. When the N$_\text{rich}$ phase is more stable than the N$_\text{poor}$ phase, that is, $\Delta H_{f,N_{\text{rich}}} - \Delta H_{f,N_{\text{poor}}} < 0$, the main energy barrier for the entire CL process is contributed by the Rxn I. This implies the difficulty of releasing chemically bonded nitrogen from the crystalline lattice to combine with H$_2$ in the environment to form NH$_3$. In contrast, nitrogen fixation in Rxn II will become difficult to proceed when the N$_\text{poor}$ compound is energetically more stable as indicated by $\Delta H_{f,N_{\text{poor}}} > 0$. More specifically, only nine bicationic nitride pairs are found to possess negative $\Delta G_{r,\text{lim}}$, whereas for monocationic nitride pairs, this number is 28 (Figure S4c, Supporting Information). This is mainly due to the fact that the number of bicationic nitrides that can be extracted from the MP database is only one third of the monocationic nitrides.

Overall, our screening results show that the thermodynamic driving force of H$_2$-CL is much lower than the other two CL processes with $\Delta G_{r,\text{lim}} < -0.1$ eV for all viable monocationic and bicationic redox pairs. This leads to a much narrower temperature range in which the CL process might proceed spontaneously, as demonstrated by the temperature-dependent contour plots for TaMoN$_3$/TaMoN$_3$ (right panel in Figure 4c) and CaN$_2$/Ca$_3$N$_2$ (right panel in Figure S4c, Supporting Information). The low reactivation temperatures could potentially lead to sluggish kinetics, therefore further hinder the yield of NH$_3$.

### 2.2. Diversifying the Chemical Space to Discover Redox Pairs for MH-CL

As previously shown in Table 1, the MP database does not contain enough number of compounds that will enable us to achieve a thorough screening of redox pairs suitable for MH-CL. To overcome this problem, we applied the strategy using elemental substitution of the existing materials in the MP database, in order to expand the chemical space.

The workflow is illustrated in Figure 5. We first constructed 1532 prototypical redox pairs from 185/82 unique bicationic hydrides/nitride-hydrides extracted from the MP database. Then the cations in the prototypical bicationic redox pairs were both replaced by 53 different chemical elements consisting of alkali/alkaline-earth metals, transition metals (TM), post-transition metals (post-TM), and metalloids, that are prior to the element Po. Such a strategy provided us with more than half a million structures to be screened. However, to obtain their $\Delta H_f$ values requires the crystal structures to be first optimized with first-principles calculations, which is computationally unfeasible for a study in this scale. Instead, the Bayesian optimization with symmetry relaxation (BOND$^+$) algorithm was used that allowed us to optimize the crystal structures of the hypothetical compounds at a negligible cost. Then, $\Delta H_f$ of these optimized structures were predicted by a graph network (MEGNet$^+$) trained on the DFT formation energies for compounds existing in the MP database. The benchmarking results and parameters used for predicting the $\Delta H_f$ of the hypothetical materials in this work are discussed in Figure S6, Supporting Information. With this, $\Delta H_f$ for 523 640 structures were successfully obtained.

Three energy metrics were then applied to hierarchically filter out the viable candidates for the subsequent screening of the reaction thermodynamics. First, only the most stable polymorph with the lowest $\Delta H_f$ was retained for a given compound. Second, the decomposition enthalpy ($\Delta H_d$) was calculated for the lowest energy polymorphs and those with $\Delta H_d <$ 70 meV atom$^{-1}$ were chosen for the subsequent reaction thermodynamic screenings. The threshold set for $\Delta H_d$ is to ensure the hypothetical bicationic hydrides and nitride-hydrides to be (meta)stable in competing with other compounds in the
corresponding chemical space. From the consideration of practicality, it indicates that the filtered candidates are most likely to be experimentally synthesizable.[63,64] Finally, similar to the proceeding analysis of H₂O-CL and H₂-CL, ΔG_{r,lim} was calculated to assess the cyclic spontaneity of the MH-CL under elevated temperatures.

To illustrate how ΔH_{f} and ΔH_{d} affect each other. Figure 6a shows plots of ΔH_{d} against ΔH_{f} for a subset of bicationic metal M₁–M₂–H (left panel) and M₁–M₂–N–H (right panel), respectively, with at least one cation being alkali metal. Most of the compounds screened here contain at least one TM element as cation, which is because the majority of cation candidates used for the initial model generation are TMs. While ΔH_{d} depicts the energy difference between the compound and its constituent elements only, ΔH_{f}, by definition, represents the relative stability of a specific phase to its competing phases. Therefore, ΔH_{d} is often considered as a more rigorous criterion for judging the synthesizability of a hypothetical material.[65] 70% of M₁–M₂–H and 79% of M₁–M₂–N–H are with ΔH_{f} < 0. In contrast, only around 7% of M₁–M₂–H and 9% of M₁–M₂–N–H are found to possess ΔH_{d} < 0. Nevertheless, it was found that the metastable phases of many materials (as characterized by a positive ΔH_{d}) could also be synthesized.[66,67] As such, it is necessary to slightly relax the threshold of the ΔH_{d} filter. Here, by setting ΔH_{d} < 70 meV atom⁻¹, 3,914 M₁–M₂–H, and 5,187 M₁–M₂–N–H are retained.

In Figure 6b, the distributions of ΔH_{d} for bicationic compounds with different combinations of metal cations are summarized, which further demonstrates that around 20% (metastable) structures for each subgroup of compounds are included with the applied filtering criterion based on ΔH_{d}. It is also clear from Figure 6b that, the nitride-hydrides are generally more stable than the pure hydrides, which would significantly influence the reaction energies that convert between these two types of compounds.

Focusing more on the chemical trends of the stable compounds (Figure S7, Supporting Information), it is found that the combination of alkali metal and post-TM has the highest probability (24.9%) of forming (meta)stable M₁–M₂–N–H. This is closely followed by a group of materials composed by alkali metal and TM (23.9%), of which the experimental success on MH-CL has been recently reported.[68] For M₁–M₂–H, 22.0% of those that contain one alkali-earth metal and one TM are (metastable), which is the most preferred cation combination that involves a TM. Although M₁–M₂–N–H are more stable than the M₁–M₂–H, we do observe exception where intermixing two alkali metals gives more stable hydrides (24.9%) in comparison to their nitride-hydride counterparts (22.2%).

Moving on to examine how the phase stabilities of bicationic metal hydrides/nitride-hydrides affect the reaction thermodynamics of MH-CL, Figure 6c demonstrates the volcano plot that correlates ΔG_{r,lim} with ΔH_{f,nit-hyd} = ΔH_{f,hyd} of (meta)stable M₁–M₂–N–H/M₁–M₂–H that may be used for MH-CL. 90.5% of the limiting reactions are found to be the hydrogenation of M₁–M₂–N–H (Rxn I) to form NH₃. It is due to the higher phase stability of nitride-hydrides that makes the formation of the pure hydrides become less favored. Amongst 45,467 hypothetical redox pairs that have been constructed, only 10% of them have negative ΔG_{r,lim} within the formation energy window of ΔH_{f,nit-hyd} = ΔH_{f,hyd} ∈ [−0.40, 0.70] eV atom⁻¹. It shows that spontaneous conversion through MH-CL is only possible when the metal hydrides and their corresponding nitride-hydrides have comparable formation enthalpies.

Figure 6d visualizes the occurrence of cations in these viable redox pairs to reveal the preferred chemical compositions of redox pairs for MH-CL. The most frequently occurring cations are from the TMs, especially precious metals Ir, Pt, Rh, Pd, Os, and Ru. Furthermore, many systems containing alkali (K, Na, Li, and Rb) and alkaline-earth metals (Ca, Sr, and Ba) also occur frequently. Examining what cation combinations could lead to negative ΔG_{r,lim}, similar patterns can also be observed in Figure S8a, Supporting Information. After excluding precious metals and toxic/radioactive elements (e.g., As, Hg, Tc, etc.), more cost-effective and sustainable bicationic pairs can be found in Figure S8b, Supporting Information. In these candidates, experimental successes of redox materials involving Ni/Mn/Mo and alkali/alkaline-earth metals have been reported in recent studies.[31,68] More significantly, new cation combinations containing In–Mo, Fe–Mn, and In–W (in the families of TM/post-TM and TM/TM) have also shown promising potentials to be applied for MH-CL, with suitable phase stabilities and limiting reaction free energies.
2.3. Exploring the Cooperative Effects in Bicationic Redox Pairs Using Three-Step H₂O-CL as an Example

So far, we have successfully screened the reaction thermodynamics for the four chosen CL processes using both monocationic and bicationic redox pairs, from which the viable pairs for each process have been identified. However, it does not provide us with the information to judge whether the unique interactions between two heterocations in bicationic redox pairs M₁–M₂–X could indeed enhance the performance of chemical looping compared to the two corresponding monocationic counterparts, that is, M₁–X and M₂–X.

Hereby, we attempt to shed light on this question by analyzing the differences in ΔGₘₙₚₑₙ for chemical looping processes that are enabled by M₁–M₂–X to those facilitated by the corresponding monocationic counterparts Mᵢ–X (i = 1, 2).
For this, we define a measuring metric \( \lambda = \frac{\Delta G_{\text{lim}} + \Delta G_{\text{lim}}}{|\Delta G_{\text{lim}} - \Delta G_{\text{lim}}|} \)

where \( \Delta G_{\text{lim}} \) is the difference in the limiting reaction free energies between CLs that are driven by \( M_1-M_2-X \) and \( M_1-X \). With this definition, we categorize the thermodynamics of three-step \( H_2O-CLs \) that are driven by the bicationic redox pairs as being: 1) Cooperatively enhanced \( (\lambda < -1) \), occurs when \( \Delta G_{\text{lim}} \) of \( M_1-X \) < \( \min(\Delta G_{\text{lim}} M_1X, \Delta G_{\text{lim}} M_1X) \), which means the intermixing of two different cations in a single bicationic compound creates new bonding states that are beneficial in facilitating the \( NH_3 \) formations in three-step \( H_2O-CL \). 2) Additive effects \( (\lambda \in [-1, 1]) \), meaning that from the thermodynamic perspective, the performances of the \( M_1-M_2-X \) are comparable to the \( M_1-X \) \((\lambda = 1, 2) \). And 3) anti-cooperative \( (\lambda > 1) \), occurs when \( \Delta G_{\text{lim}} \) of \( M_1-X \) > \( \max(\Delta G_{\text{lim}} M_1X, \Delta G_{\text{lim}} M_1X) \), which corresponds to a situation where the looping performances of using a bicationic compound as the active material are worsened compared to using either one of the two corresponding monocationic redox materials. A more detailed explanation of the correlation between \( \lambda \) and the limiting energies of \( M_1-M_2-X \) and \( M_1-X \) can be found in Figure S9, Supporting Information.

Here, we focus our analysis of \( \lambda \) using three-step \( H_2O-CL \) as an example, due to the long-lasting interest of applying this looping mechanism in the research community of ammonia synthesis. The results are presented in the matrix plot shown in Figure 7. The matrix plot is symmetrical about its diagonal because the cations \( M_1 \) and \( M_2 \) in the chemical formulas are treated equivalently. Each block of the matrix plot is color-coded according to the \( \lambda \) calculated for that particular combination of cations.

Overall, as revealed in the heat map, most bicationic redox pairs (46.3%) are showing an anti-cooperative effect \((\lambda > 1) \). It implies that for the majority of the three-step \( H_2O-CL \), using the bicationic redox pair as the active material makes the limiting reaction less likely to proceed spontaneously, compared to the case where either one of the corresponding monocationic redox pairs is used. It also indicates that compounds with more complex chemical compositions do not necessarily make them better active materials for thermal ammonia synthesis, which may also explain why most of the prior studies were focusing on the monocationic systems. 36.9% cases show additive effect \((-1 \leq \lambda \leq 1) \), which means performance-wise, using the bicationic active materials is equivalent to the usage of a simple mixture of the two monocationic compounds. It also indicates that mixing two cations in a single compound did not create different chemical bondings that will fundamentally change the thermodynamic behaviors of the bicationic compounds. In stark contrast, only 93 (16.8%) CLs show cooperatively enhanced spontaneity for the limiting reaction when the bicationic redox pair is used as indicated by \( \lambda < -1 \). This occurs for a few groups of bicationic compounds scattered across the map shown in Figure 7.

To enable a better judgement on the deviation of \( \Delta G_{\text{lim}} M_1X \) from the \( \Delta G_{\text{lim}} \) of the monocationic counterparts, we also map out the limiting energy differences defined as \( \Delta G_{\text{lim}} = \max(\Delta G_{\text{lim}} M_1X, \Delta G_{\text{lim}} M_1X) \) in Figure S10, Supporting Information.
Figure 7. Heatmap of $\lambda$ between bicationic and monocationic redox pairs for three-step $\text{H}_2\text{O}$-CL. Blue color indicates both monocationic pairs are more favorable than the bicationic ones ($\lambda > 1$). Green color indicates the bicationic pairs are merely showing additive effect from the constituent cations ($-1 < \lambda < 1$). Most importantly, red color highlights the bicationic pairs with cooperative enhancement ($\lambda < -1$). The elements are grouped by their positions in the periodic table, that is, s-block (alkali/alkaline-earth metals), d-block (transition metals), p-block (post-transition metals, metalloids, and nonmetals), and 4f-block. 3d-transition metals are further separated because of their highest rate of cooperative enhancement, convex hull (meta)stability, and looping spontaneity. Viable pairs with negative limiting energies are labeled by black squares. (Meta)stable bicationic pairs of which redox materials have decomposition energies both smaller than 70 eV atom$^{-1}$ are marked by black dots. An interactive version of this map can be found in Supporting Information.
the reaction thermodynamics may be affected by the increase of the chemical complexity of the redox materials. With the usage of a machine-learned Gibbs free energy descriptor, the reaction free energies for H2O-CLs and H2-CL that involves 1528 M1-M2-O/N and 173 M1-M2-Nrich/Npoor active materials were systematically screened. From the volcano relationships that correlate the limiting reaction free energies with the formation enthalpies of the active redox materials, we discovered that CLs driven by the bicationic active materials tend to be thermodynamically limited by a different sub-reaction. More importantly, the number of viable bicationic redox pairs and their corresponding chemical diversity increased significantly for the three-step H2O-CL, whereby 97 pairs have been predicted to be capable of driving the chemical loop spontaneously with novel cations that are absent in the workable monocationic counterparts.

Moreover, to overcome the scarcity of redox pairs extracted from the MP database that may be suitable for driving the MH-CL process, we combined the strategies of cation substitutions and data-driven ultrafast structural optimization, to significantly expand the chemical space of bicationic hydrides and nitride-hydrides. This enables us to further identify 4698 candidates that may potentially be able to drive the MH-CL process. In particular, we discovered that bicationic system with alkali/alkaline-earth metals and TM/post-TM elements are particularly promising candidates.

Last, by analyzing the differences in the $\Delta G_{\text{lim}}$ between M1-M2-O/N and the complementary monocationic redox pairs in three-step H2O-CL, we are able to further discover which bicationic redox materials can significantly lower the limiting reaction free energies compared to the cases where a simple mixture of two monocationic redox materials is used as the active materials. Among these candidates, LiCoO2/LiCoN, Li3FeO4/Li3FeN2, FeMoO4/Fe3Mo3N, and ZnGeO3/ZnGeN2 are pairs that show significant "cooperative enhancement" effect while possess low decomposition energies and ideal looping spontaneity.

Notably, many other important factors that could affect the chemical reaction outcomes of ammonia synthesis have not been considered in the current work, such as pressure, reaction kinetics, as well as the possible existence of the competing reactions. Most of the chemical reactions between solid materials and gaseous environment occur on surfaces, on which the reaction thermochimistries can differ considerably compared to the usage of the active materials in bulk form. Such effect is also not accounted for in the current theoretical model. For the lead candidates identified from our screening study, surface models of different crystallographic planes can be built, on which detailed reaction pathway calculations for gas dissociation (for N2, H2, or H2O) and ammonia formation can be performed using DFT. From here, the reaction energy barriers can be extracted for kinetic Monte Carlo simulations to model the reaction kinetics and yields. This will inevitably come at much higher computational costs than those employed in our present study. In light of this, we also note that some recent works have proposed new machine-learning approaches to expedite the prediction of reaction pathways, which bring promise to study the catalytic reactions that involve more complex systems. How the cooperative enhancements in bicationic redox materials are affected by their unique electronic structures will also need to be further examined with detailed DFT calculations. Finally, to compete the cycle of theory-driven material designs, the synthesizability of the lead bicationic compounds and their chemical looping performances under realistic experimental conditions should also be investigated. These will be the subjects of our future studies.

4. Experimental Section

**Expanding Redox Materials from Monocaticonic to Bicationic Compounds:**

In the conventional chemical looping processes that involved two sub-reactions (Figure 1a,c,d), completion of the chemical loop was accompanied with the yield of the product (NH3, in this case) and reoxidation of the reduced material back to its original state. For instance, in a two-step H2O-CL, considering a generic binary metal oxide M1Ox and nitride M2Ny pair, the chemical cycle can be represented by the following two equilibrium reactions (given as per mole of NH3 synthesized per cycle):

I. Nitrogen fixation

\[
\frac{\varepsilon}{\beta} M_1 O_x + \frac{\beta}{\varepsilon} H_2 + \frac{1}{2} N_2 \rightarrow \frac{\varepsilon}{\beta} M_1 N_y + \frac{\beta}{\varepsilon} H_2 O
\]  

II. Hydrolysis

\[
\frac{1}{\beta} M_1 N_y + \frac{\beta}{\varepsilon} H_2 O \rightarrow \frac{\varepsilon}{\beta} M_1 O_x + \frac{\beta}{\varepsilon} H_2 + \frac{1}{2} N_2 + \frac{\beta}{\varepsilon} H_2 O
\]

Here, the metal oxide was first placed in the environment of mixed N2 and H2 where it can be reduced and nitridated to form the corresponding nitride. Then the nitride was put in contact with water vapor to yield ammonia and regenerated the oxide thus completing the loop. Analogously, for using a generic ternary pair M1M2′Ox/M1M2′Ny as the active materials, the same chemical reactions can be rewritten as

I. Nitrogen fixation

\[
\frac{\varepsilon}{\beta} M_1 M_2′ O_x + \frac{\beta}{\varepsilon} H_2 + \frac{1}{2} N_2 \rightarrow \frac{\varepsilon}{\beta} M_1 M_2′ N_y + \frac{\beta}{\varepsilon} H_2 O
\]

II. Hydrolysis

\[
\frac{1}{\beta} M_1 M_2′ N_y + \frac{\beta}{\varepsilon} H_2 O \rightarrow \frac{\varepsilon}{\beta} M_1 M_2′ O_x + \frac{\beta}{\varepsilon} H_2 + \frac{1}{2} N_2 + \frac{\beta}{\varepsilon} H_2 O
\]
It was clear that Equation (3) can be obtained by summing Equations (5) and (6) together. Here the products were constrained in the reduction step to be two pure metals to avoid the complexity of binary metal alloy formation with different possible stoichiometries.[60] As a result, the subsequent nitridation step was the formation reaction of ternary nitride from its constituent elements. The rest of the chemical equations for both bicationic and monocationic redox pairs applied in studied CLs can be found in Section S1, Supporting Information.

**Machine Learning Approaches for Fast Free Energy Calculations: Gibbs Free Energy Descriptor:** The Gibbs free energy was the fundamental variable that governed the thermodynamics of CLAS reactions, which enables to determine the likelihood for a given chemical reaction to proceed under a specific thermodynamic condition. However the experimental Gibbs free energies were only available for a small fraction of known inorganic solids.[57] Conventional computational approach for determining the temperature-dependent Gibbs free energies for solids involved calculating the phonon density-of-states for each material, which will not be feasible for conducting high-throughput material screenings.[81] To tackle this problem, recently, a new regression relationship that related the temperature-dependent Gibbs free energies with basic atomic properties in a solid was established via machine-learning,[49] enabling the ultrafast estimation of the Gibbs free energy. In its essence, the temperature-dependent Gibbs free energies can be determined from the following equations:

\[ \Delta G_f(0 K) = \Delta H_f(0 K) \]  
\[ \Delta G_f(T > 0 K) = \Delta H_f(0 K) + C_V(T) - \sum_{i} a_i G_i(T) \]

where \( \Delta H_f \) is the formation enthalpy at 0 K, \( C_V \) the Gibbs free energy descriptor that depends on the atomic volume \( V \), the reduced atomic mass \( m \), and the temperature \( T \). \( a_i \) is the stoichiometric weight of the \( i \)th element in the compound and \( G_i \) the corresponding Gibbs free energy obtained from tabulated experimental or calculated results.[49] In this work, the crystal structures and \( \Delta H_f \) of inorganic solid compounds were retrieved from the Material Project[30]. It was worth emphasizing that only the polymorph with the lowest \( \Delta H_f \) was considered in the calculations, where detailed descriptions of the workflow to retrieve and filter out data can be found in Section S2, Supporting Information. The algorithm used for computing the \( \Delta G_f \) for all solids was written based on the GibbsComputedStructureEnergy module in the pylmatgen package,[82] whereas the thermodynamic data of gaseous species (\( H_2O, NH_3 \)) were extracted from the NIST-JANAF tables of experimental thermochemical data. Benchmark of this physical descriptor with DFT calculations can be found in Section S4.1, Supporting Information.

**Machine Learning Approaches for Fast Free Energy Calculations: Structure Optimization and Formation Energy Prediction:** In order to further extend the searching domain of possible candidates, hypothetical cation-substituted hydrides and nitride-hydrides were constructed for MH-CL and fast optimized by a recently-released B0K0R.[98] This algorithm utilized a surrogate model to determine the optimal lattice parameters and atomic coordinates. MEGNet[59] was subsequently used to predict the formation energies (\( \Delta H_f \)) of the optimized crystals, in which this machine learning model was trained on a large amount of DFT-computed data from MP and had managed to achieve very low cross-validated mean absolute error (MAE) of 26 meV atom\(^{-1}\) in a wide range of materials. The benchmarking results (Figure S6, Supporting Information) have shown that, by coupling B0K0R and MEGNet, this workflow was capable of producing reasonably accurate \( \Delta H_f \) as compared to the expensive DFT-computed energies. The MAEs calculated on the \( M_1-M_2-H \) and \( M_1-M_2-N-H \) datasets were both falling below the reported average value, which made it a reliable approach for energy predictions while greatly boosting the screening efficiency. Benchmark of this machine learning workflow with DFT calculations can be found in Section S4.2, Supporting Information.

**Assessing the Thermodynamic (Dis)Advantages of Redox Systems:** With an easily accessible Gibbs free energy for each reactant/product in the CLAS cycles, the Gibbs reaction free energies (\( \Delta G_r \)) of one specific subreaction in any chemical looping process can be calculated by

\[ \Delta G_r(T) = \sum_{products} \sum_{reactants} \nu_i \Delta G_{f,i}(T) - \nu_i \Delta G_{f,i}(T) \]

where \( \nu_i \) is the stoichiometric coefficient of species \( i \). The optimal temperature (\( T_{opt} \)) for one sub-reaction was determined as it minimized the \( \Delta G_r(T) \) in a range of discrete numbers

\[ T_{opt} = \arg \min_T \Delta G_r(T), T = T_0, T_1, \ldots, T_{max} \]

Therefore at \( T_{opt} \), the chemical equilibrium shifted to have the strongest tendency to form the products. Promising redox systems will be given by the pairs that led to the most negative \( \Delta G_r \) in all individual steps, meaning that they allowed the spontaneous conversion within the entire cycle. The overall evaluation of each redox pair in entire CLAS cycle required a global descriptor that comprised the thermodynamic information from all correlated steps. The thermodynamic assessment was often referred as the "limiting reaction," which can be defined as the step with the highest reaction energy. Considering an arbitrary CLAS process which carried out the \( i \)th sub-reaction at \( T_{i, opt} \), the limiting reaction free energy can be denoted as

\[ \Delta G_{r, \text{lim}} = \max \left\{ \Delta G_{r,1, \text{opt}}, \Delta G_{r,2, \text{opt}}, \ldots, \Delta G_{r,n, \text{opt}} \right\} \]

As such, whether a redox pair would enable spontaneous looping can be determined.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work is supported by grants DP190103661 and DP220103229 from the Australian Research Council. The computational resources were provided by the National Computing Infrastructures (project dy3), Australia, under the merit allocation scheme from the Research Technology Service, UNSW.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are openly available in Harvard Dataverse at https://doi.org/10.7910/DVN/4PG3R8 and https://doi.org/10.7910/DVN/EOOPKN, reference number 0.

**Keywords**

bicaticonic redox pairs, chemical looping ammonia synthesis, cooperative effect, high-throughput materials screening, machine learning, reaction engineering
[61] C. J. Bartel, A. Trewartha, Q. Wang, A. Dunn, A. Jain, G. Ceder, *npj Comput. Mater.* 2020, 6, 97.
[62] W. Sun, A. Holder, B. Orvañanos, E. Arca, A. Zakutayev, S. Lany, G. Ceder, *Chem. Mater.* 2017, 29, 6936.
[63] A. K. Singh, J. H. Montoya, J. M. Gregoire, K. A. Persson, *Nat. Commun.* 2019, 10, 443.
[64] S. O’Donnell, C.-C. Chung, A. Carbone, R. Broughton, J. L. Jones, P. A. Maggard, *Chem. Mater.* 2020, 32, 3054.
[65] C. J. Bartel, *J. Mater. Sci.* 2022, 57, 10475.
[66] J. Odahara, W. Sun, A. Miura, N. C. Rosero-Navarro, M. Nagao, I. Tanaka, G. Ceder, K. Tadanaga, *ACS Mater. Lett.* 2019, 1, 64.
[67] P. K. Todd, M. J. Fallon, J. R. Neilson, A. Zakutayev, *ACS Mater. Lett.* 2021, 3, 1677.
[68] J. Guo, P. Chen, *Acc. Chem. Res.* 2021, 54, 2434.
[69] J. Wu, Z. Wang, S. Li, S. Niu, Y. Zhang, J. Hu, J. Zhao, P. Xu, *Chem. Commun.* 2020, 56, 6834.
[70] K. Chu, Q.-q. Li, Y.-h. Cheng, Y.-p. Liu, *ACS Appl. Mater. Interfaces* 2020, 12, 11789.
[71] Y. Li, L. Ma, Y. Fu, C. Zhang, Y. Shi, Y. Xu, J. Li, *J. Electroanal. Chem.* 2022, 905, 115981.
[72] I. A. Amar, R. Lan, C. T. Petit, S. Tao, *Int. J. Electrochem. Sci* 2015, 10, 3757.
[73] M. Andersen, C. Panosetti, K. Reuter, *Front. Chem.* 2019, 7, 202.
[74] A. Bruix, J. T.Margraf, M. Andersen, K. Reuter, *Nat. Catal.* 2019, 2, 639.
[75] B. W. Chen, L. Xu, M. Mavrikakis, *Chem. Rev.* 2020, 121, 1007.
[76] P.-L. Kang, Z.-P. Liu, *iScience* 2021, 24, 102013.
[77] M. Meuwly, *Chem. Rev.* 2021, 121, 10218.
[78] A. Lyngfelt, *Energy Fuels* 2020, 34, 9077.
[79] N. R. Singstock, C. J. Bartel, A. M. Holder, C. B. Musgrave, *Adv. Energy Mater.* 2020, 10, 2000685.
[80] J. Bustnes, D. Sichen, S. Seetharaman, *Metall. Mater. Trans. B* 1995, 26, 547.
[81] A. Togo, I. Tanaka, *Scr. Mater.* 2015, 108, 1.
[82] S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, G. Ceder, *Comput. Mater. Sci.* 2013, 68, 314.