

Self-foaming Fe-Sn Powder Beds for Durable Hydrogen Storage and Release

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Self-foaming Fe-Sn Powder Beds for Durable Hydrogen Storage and Release

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Abstract

Hydrogen storage and release via redox cycling of oxide-metal powders offers advantages in safety and scalability as compared to pressurized tanks, but long-term storage capacity loss due to sintering and densification of powder beds remains a major challenge. In this work, we demonstrate that a transient liquid-phase swelling effect, triggered by the addition of a low-melting element to a high-melting powder bed, can effectively preserve powder-bed porosity and reactive surface area during extended redox cycling. By incorporating up to 40 at. % Sn into Fe powder beds, we induce a self-foaming behavior that counteracts powder densification and enables stable hydrogen storage/release performance over 50 redox cycles at 650 °C. In situ X-ray diffraction and thermodynamic analysis reveal that both the added Sn and the resulting Fe-Sn intermetallic phase undergo reversible transformations throughout cycling, helping maintain high hydrogen storage/release capacity. Microstructural analysis shows that the continuous formation of “liquid-depletion porosity” at former Sn powder sites and the volumetric expansion of solid particles from imbalanced diffusion contribute to the retention of a porous architecture. This strategy achieves a hydrogen capacity of up to 261 mL/g, which is 22 times higher than that of pure Fe after 50 redox cycles. It provides a new materials design approach for durable metal/oxide systems in hydrogen storage, with other potential applications in solar thermochemical water splitting, carbon dioxide utilization, and chemical looping technologies.

Introduction

Safe, inexpensive, scalable hydrogen storage is a key enabler for a hydrogen-based economy¹, and current industrial solutions rely on compressed gas cylinders, cryogenic vessels (and caverns for much larger scale); other technologies being developed include metal hydrides², complex hydrides³, metal-organic frameworks (MOFs)⁴, liquid organic hydrogen carriers (LOHCs)⁵ and chemical carriers (e.g., ammonia⁶ and methane⁷). Metal oxides (MeO_x) such as Fe oxides ($\text{FeO}/\text{Fe}_3\text{O}_4$), WO_2 , and MoO_2 are an attractive alternative for hydrogen storage through reversible hydrogen (H_2) reduction and steam (H_2O) oxidation⁸. In this process, metal oxides are first reduced by hydrogen to form reduced metals and steam ($\text{MeO}_x + x\text{H}_2 = \text{M} + x\text{H}_2\text{O}$), which is then condensed and stored, effectively storing hydrogen as water⁹. When hydrogen is needed, water is turned into steam which is then reacted with the reduced metals exothermically to regenerate the oxides and release hydrogen ($\text{Me} + x\text{H}_2\text{O} = \text{MeO}_x + x\text{H}_2$), completing a reversible redox cycle for hydrogen storage and release. Among metal oxides, Fe oxides are promising for large-scale hydrogen storage and transport due to their abundance, low cost, low toxicity, and higher safety^{8, 10}. In particular, green hydrogen produced by water electrolysis using renewable power can be utilized for industrial decarbonization, such as in the production of green ammonia¹¹, sustainable aviation fuel¹², and steel¹³. It can also be converted back into electricity using gas turbines or fuel cells¹⁴ to help balance the grid or to arbitrage electricity cost (Figure 1 (a)). For example, rechargeable oxide batteries, using redox cycling of Fe oxides, have been developed for grid-level energy storage and release^{15, 16, 17, 18}.

A major challenge in the redox cycling of Fe oxides to store hydrogen is the rapid loss of reactive surface area, driven by fast sintering kinetics of oxides or metals at high temperatures, which significantly limits their practical viability.^{16, 19, 20} This challenge also applies to solar thermal water splitting^{21, 22, 23}, carbon dioxide utilization^{24, 25}, and chemical looping combustion^{26, 27, 28}, where metal oxides are utilized as oxygen carriers. Three strategies currently exist to achieve sintering inhibition. First, adding inert powders such as titania²⁹, zirconia³⁰, and MgAl_2O_4 ³¹ can prevent the adjacent Fe/Fe oxide powders from contacting and sintering. However, it decreases the specific hydrogen capacity and volumetric energy density of the powder blend. Second, alloying with reversible (H_2 -reducible and steam-oxidizable) refractory metals such as Mo^{32, 33}, and W^{10, 34}, which exhibit slow sintering kinetics, is another effective approach without significantly decreasing the specific hydrogen storage capacity. However, the formation of volatile $\text{MoO}_2(\text{OH})_2$ ³⁵ and $\text{WO}_2(\text{OH})_2$ ³⁶ phases can cause slow loss of alloying elements during the reaction. The last strategy is to form porous architectures with high surface area by freeze casting¹⁹ or 3D printing³⁷, which, however, is not suitable for scaling up due to their complicated processing and high cost.

Here, we introduce a novel approach - based on imbalanced diffusion - for maintaining a highly porous morphology during the redox cycling of iron oxide powder beds. We show that Sn powders, when blended to Fe powders, facilitates porosity development through a swelling effect during transient liquid sintering. By systematically varying the Sn concentration in Fe powder beds from 0 to 40 at.%, we reveal its influence on phase evolution, sintering behavior, and morphological transformation during cyclical hydrogen reduction and steam oxidation. This diffusion-mediated

strategy generates “liquid-depletion pores” at former Sn powder sites, drives the expansion of Fe-particles, and preserves high hydrogen storage capacity through stable and accessible porous structures. As a result, it does not reduce specific hydrogen capacity (unlike inert ceramics), avoids the formation of chemical vapor phases (unlike W and Mo), and eliminates the need for complex shaping methods (such as freeze casting or 3D printing). Thus, Sn and other similar low-melting elements added to Fe powders establishes a new pathway for durable reversible hydrogen storage and release.

Results and Discussion

Swelling Effect

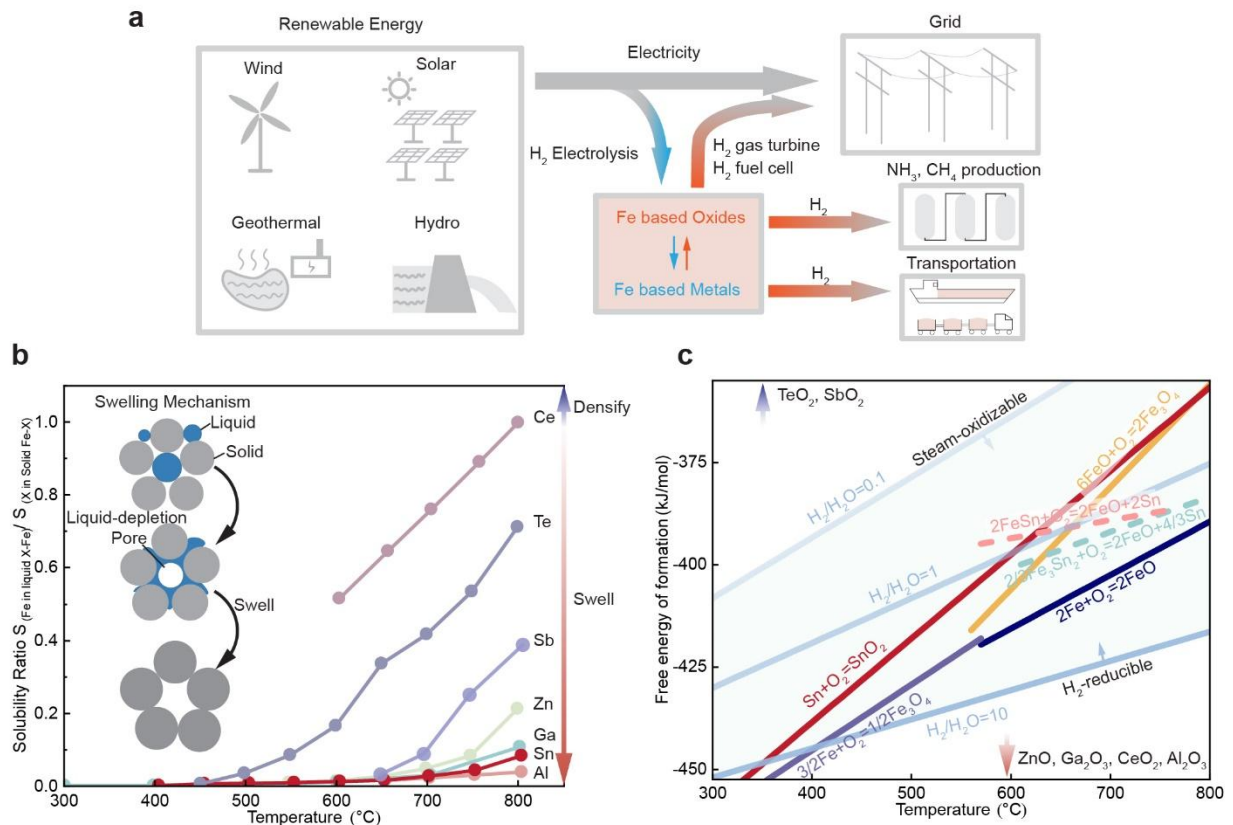


Figure 1. Application scenario and composition design

(a) Schematic illustration of application scenarios where Fe-X-based oxides serve as reversible hydrogen storage materials. (b) Solubility ratio ($S_{\text{Fe in liquid X-Fe}} / S_{\text{X in solid Fe-X}}$) as a function of temperature for seven low-melting metals (X). The insert is a schematic illustration of swelling from transient liquid sintering (TLS) via formation of “liquid-depletion pores” (c) Gibbs free energy of formation for Fe₃O₄, FeO, and SnO₂ in the temperature range of 300-800°C. Other oxides that could leverage the swelling effect from TLS (shown in (b)) are excluded due to their difficulty to undergo steam oxidation or hydrogen reduction during redox cycling.

On heating a blend of powders, when a liquid phase forms temporarily and disappears after sufficient diffusion in the remaining solid powders during sintering, the process is called transient liquid-phase sintering. This phenomenon can result in either densification (pore elimination) or swelling (pore formation or foaming), depending primarily on the solubility ratio S_R ³⁸:

$$S_R = \frac{S_{SL}}{S_{LS}} \quad (1)$$

where the S_{SL} is the solubility of the solid phase (high-melting element) in the liquid phase, and the S_{LS} is the solubility of the liquid phase (low-melting element) in the solid phase. When $S_R > 1$, the liquid tends to dissolve and reprecipitate the solid, facilitating powder rearrangement and densification, as observed in systems such as W-Fe³⁹ and Fe-Ti⁴⁰. In contrast, when $S_R < 1$, transient liquid-phase sintering tends to induce a swelling effect in the powder bed. In this case, the liquid phase diffuses into the solid particles, leaving behind pores at the former liquid sites. This behavior has been observed in systems such as Al-Zn⁴¹, Cu-Sn⁴², Fe-Al⁴³, where Zn-, Sn-, and Al-rich liquids exhibit low solubility ratios. Although swelling is usually considered undesirable in powder metallurgy as it hinders densification, we propose here, for the first time, that this phenomenon can be leveraged to engineer porous structures with long-lasting high surface area for redox cycling. Such porosity is advantageous not only for metal oxide-based hydrogen storage systems but also for applications in solar thermal water splitting^{21, 22, 23}, carbon dioxide utilization^{24, 25}, and chemical looping combustion^{26, 27, 28}.

To harness the transient liquid-phase swelling effect in Fe powder beds, the added metallic element X must either melt or form a eutectic liquid with Fe at relatively low temperatures, prior to significant densification of the Fe powders. Some alloying elements capable of forming a liquid phase between 300-800 °C and exhibiting a low solubility ratio $S_R = S_{\text{Fe in liquid X-Fe}}/S_{\text{X in solid Fe-X}}$ are listed in Figure 1 (b). For simplicity, $S_{\text{X in Fe-solid X}}$ refers to either the solubility of X in the Fe solid solution or the concentration of X in the X-richest intermetallic phase which is adjacent to the liquid phase lines in the phase diagrams. Elements such as Ce, Te, Sb, Zn, Ga, Sn, and Al exhibit low S_R ratios under the operating conditions of Fe-based redox cycling and are thus favorable for the swelling effect. Notably, the Fe-Al and Fe-Sn systems have solubility ratios $S_R < 0.1$, ensuring the occurrence of the swelling effect.

In addition to forming a transient liquid phase for the swelling effect, the added element X must exhibit reversible redox behavior under hydrogen and steam to enable high specific hydrogen capacity and volumetric energy density. As shown in the Ellingham diagram (Figure 1 (c)), the Gibbs free energy of formation for H₂O is plotted for three partial pressure ratios of H₂ to H₂O: $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.1, 1$, and 10. The lines corresponding to $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.1$ and 10 are used as thermodynamic boundaries for selecting metal/metal oxide pairs suitable for redox cycling. Oxides that lie below the $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.1$ line are thermodynamically favored to form in steam, indicating that the corresponding metals can be oxidized to generate H₂. Conversely, oxides above the $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 10$ line can easily be reduced by H₂, as steam is much more stable under those conditions. Fe₃O₄ and FeO fall within these two boundaries, enabling their reversible redox behavior and making them well-suited for hydrogen storage and production applications^{19, 44}.

However, several potential candidates X for the swelling effect are excluded due to their poor redox reversibility. Specifically, Te and Sb are difficult to oxidize in steam, while CeO_2 , ZnO , GaO , and Al_2O_3 are not reduced by hydrogen under typical operating conditions. Among the candidates considered, only the Sn/SnO_2 redox pair lies within the thermodynamic window defined by the $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.1$ and 10 boundaries (Figure 1 (c)), demonstrating reversible behavior during both hydrogen reduction and steam oxidation. Pure Sn/SnO_2 systems have previously been utilized for hydrogen production⁴⁵, solar thermal water splitting⁴⁶, carbon dioxide utilization⁴⁶. However, pure liquid Sn tends to coalesce due to surface tension, leading to agglomeration and loss of reactive surface area. Here, Sn is selected as an addition to Fe powder beds that produces the swelling effect and maintains high surface area in Fe powders, enabling long-term, efficient redox cycling.

Phase evolution

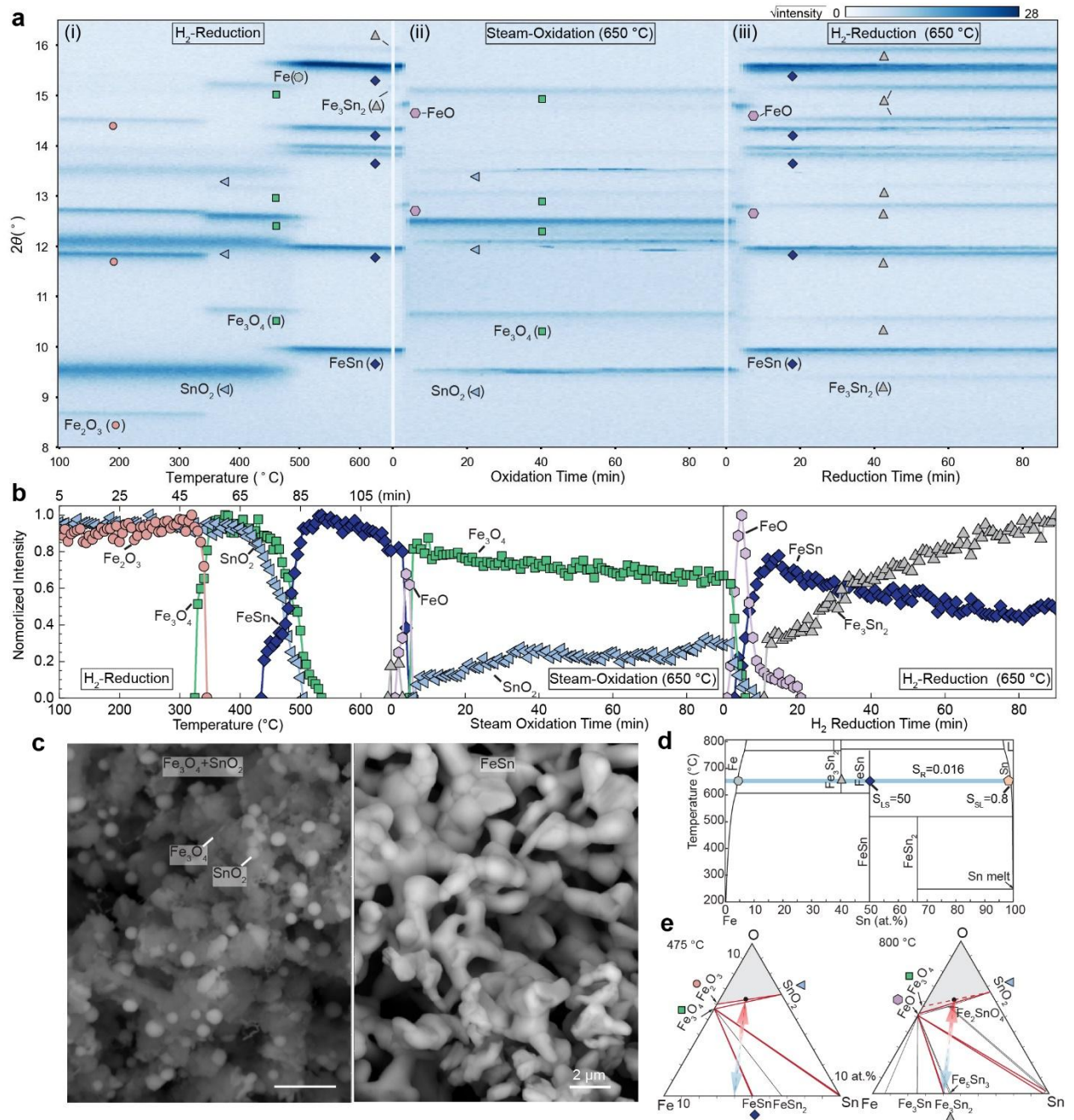


Figure 2. Phase evolution and surface morphology

(a) In situ X-ray diffraction patterns of a powder blend of Fe_2O_3 - SnO_2 (target composition: Fe-40Sn) during three sequential stages: (left) first H_2 reduction during initial heating (100-650 °C), (middle) steam oxidation at 650°C for 90 minutes, (right) hydrogen reduction at 650 °C for 90 minutes. (b) Normalized peak intensity of the phases identified in (a), corresponding to the three

stages shown in (a) as diffraction patterns. (c) Surface morphology of Fe-40Sn powders: (left) $\text{Fe}_3\text{O}_4\text{-SnO}_2$ after first steam oxidation and (right) FeSn intermetallic phase after subsequent H_2 reduction at 650 °C. (d) Fe-Sn binary phase diagram, showing $S_{\text{SL}} = 0.8 \text{ at}\%$ and $S_{\text{LS}} = 50 \text{ at}\%$ at 650 °C and (e) Fe-Sn-O ternary phase diagrams at 475 and 800 °C (650°C not available); the blue and red arrows illustrate the average composition trajectory and phases forming (red tie lines) during reduction and oxidation of a Fe-40Sn powder bed.

The phase evolution of a $\text{Fe}_2\text{O}_3\text{-59 wt}\%$ SnO_2 powder blend, designed to yield Fe-40 at.% Sn upon reduction, is first investigated using in situ X-ray diffraction during sequential steam oxidation and hydrogen reduction. As shown in Figure 2 (a-b), the phase transitions were monitored across three redox half cycles: (i) initial H_2 reduction from 100 to 650 °C, (ii) first steam oxidation at 650 °C for 90 minutes, and (iii) second H_2 reduction at 650 °C for 90 minutes. During the initial H_2 reduction on heating (100-650 °C), Fe_2O_3 undergoes a first reduction step to Fe_3O_4 , beginning at 330 °C and ending at 345 °C. The reduction of SnO_2 begins at 420 °C and completes at 505 °C, forming liquid Sn, which is not detectable by XRD due to its lack of crystallinity. No intermediate Sn-containing oxide phases (e.g., SnO , Sn_2O_3 , Sn_3O_4) were detected. Concurrently, Fe_3O_4 is reduced to metallic Fe, which reacts with liquid Sn to form the FeSn intermetallic phase, starting at 440 °C and completing by 535 °C. This indicates that the swelling effect induced by the formation of liquid Sn begins at ~ 440 °C. The total reduction of the $\text{Fe}_3\text{O}_4\text{-SnO}_2$ powder blend is complete at 535 °C, suggesting that this is the minimum operating temperature required for complete H_2 reduction. Previously, oxidation of pure Fe and pure Sn powders in steam were studied at 550 °C^{46, 47}. The kinetics of Sn oxidation at this temperature are slow, with only $\sim 34\%$ of Sn oxidized after 90 minutes⁴⁶. In contrast, the Sn oxidation rate improves significantly at 650 °C⁴⁶. Therefore, we select this temperature for the isothermal redox experiments. The reduction sequence follows the arrowhead guideline shown in the ternary Fe-Sn-O phase diagram at 475 °C⁴⁸ (Figure 2 (e)), with a three-step reduction: Fe_2O_3 first converts to Fe_3O_4 , followed by the reduction of SnO_2 to Sn, and finally Fe_3O_4 reduces to Fe, some of which reacts with Sn to form the Fe-Sn intermetallic. The Fe {011} diffraction peak from the Fe-Sn solid solution overlaps with the FeSn intermetallic peak near 15.6° , making peaks fitting challenging in this region. The FeSn_2 phase is not observed because SnO_2 is predominantly reduced at temperatures close to its peritectic temperature of 513 °C.

As shown in Figure 2 (a-b), after hydrogen reduction on heating, the Fe-40Sn powders were subjected to isothermal steam oxidation at 650 °C. The FeSn phase begins to decompose at 2 minutes, forming solid FeO and liquid Sn. By 6 minutes, the FeO phase is fully converted to Fe_3O_4 , and the formation of SnO_2 begins at 7 minutes. The evolution of these phases generally follows the arrowhead guideline in the Fe-Sn-O ternary phase diagram at 800 °C (Figure 2 (e)), with the exception of Fe_5Sn_3 and Fe_2SnO_4 , which are not thermodynamically stable at 650 °C. The formation of the original binary oxides (Fe_3O_4 and SnO_2) rather than ternary oxides, after steam oxidation, suggests that the swelling effect associated with reduced liquid Sn can occur repeatedly in the subsequent reduction step. This consistent regeneration of liquid Sn supports the durability of the swelling effect across multiple redox cycles, enabling stable, repeated cycles of hydrogen storage/release. Following initial decomposition and oxidation, Fe_3O_4 reaches its maximum normalized XRD intensity within 7 minutes, indicating fast oxidation kinetics of Fe and FeO at

this temperature. In contrast, the normalized intensity of SnO_2 continues to increase steadily from 7 to 90 minutes, suggesting a slower oxidation rate for liquid Sn compared to Fe. The subsequent slight decrease in Fe_3O_4 intensity could result from increased X-ray absorption by the growing SnO_2 phase, which contains more oxygen atoms and attenuates the transmitted X-rays more strongly than the liquid Sn phase.

Finally, Figure 2 (a-b) shows the isothermal reduction at 650 °C of the steam-oxidized Fe_3O_4 - SnO_2 powder blends by switching the gas atmosphere to H_2 at 1 minute. Fe_3O_4 begins to partially reduce to FeO at 2 minutes and is fully reduced by 6 minutes. Simultaneously, SnO_2 begins to reduce to liquid Sn at 2 minutes and is fully reduced by 9 minutes, indicating a slower reduction kinetics for SnO_2 compared to Fe_3O_4 . The FeO phase reaches its maximum intensity at 5 minutes and is completely reduced to metallic Fe by 21 minutes. The nascent solid Fe immediately reacts with liquid Sn to form FeSn and Fe_3Sn_2 intermetallic phases. This reduction sequence aligns again with the arrowhead guideline indicated in the Fe-Sn-O ternary phase diagram at 800 °C (Figure 2e). At later times, the normalized intensity of FeSn decreases while that of Fe_3Sn_2 increases, suggesting a reaction pathway in which liquid Sn initially forms FeSn upon contact with Fe, followed by further diffusion of Sn into Fe to produce Fe_3Sn_2 .

The surface morphology of the steam-oxidized and H_2 -reduced Fe-40Sn powder blend is shown in Figure 2 (c). Submicron-sized SnO_2 particles are observed on the oxidized powders, exhibiting near-spherical morphology. During steam oxidation, Fe_3O_4 forms rapidly, whereas the liquid Sn oxidizes more slowly to SnO_2 , as shown in Figure 3 (a-b). As a result, Fe_3O_4 and liquid Sn coexist during the gradual steam oxidation of Sn. The shape and small size of the submicron-sized SnO_2 particles suggest that the precursor liquid Sn has a high contact angle on the Fe_3O_4 surface. Liquid Sn is known to exhibit poor wetting on oxidized Fe surfaces, with a contact angle of $\sim 90^\circ$, whereas good wetting is observed on cleaner Fe surfaces, with the contact angle decreasing to $\sim 25^\circ$ after sufficient time at 400 °C⁴⁹. When a liquid droplet (such as Sn) forms between two closely spaced solid particles (such as Fe_3O_4), the liquid with high contact angle tends to push the solid particles apart by capillary forces, particularly in systems with a high-volume fraction of such liquid phase⁵⁰. Thus, in addition to the swelling effect of Sn during the reduction stage, the poor wetting of liquid Sn on the oxide surface also contributes to the foaming, and thus stabilization of the porous microstructure. After reduction, as shown in Figure 2 (c), a porous FeSn intermetallic phase is observed on the surface, further confirming the preservation of structural porosity.

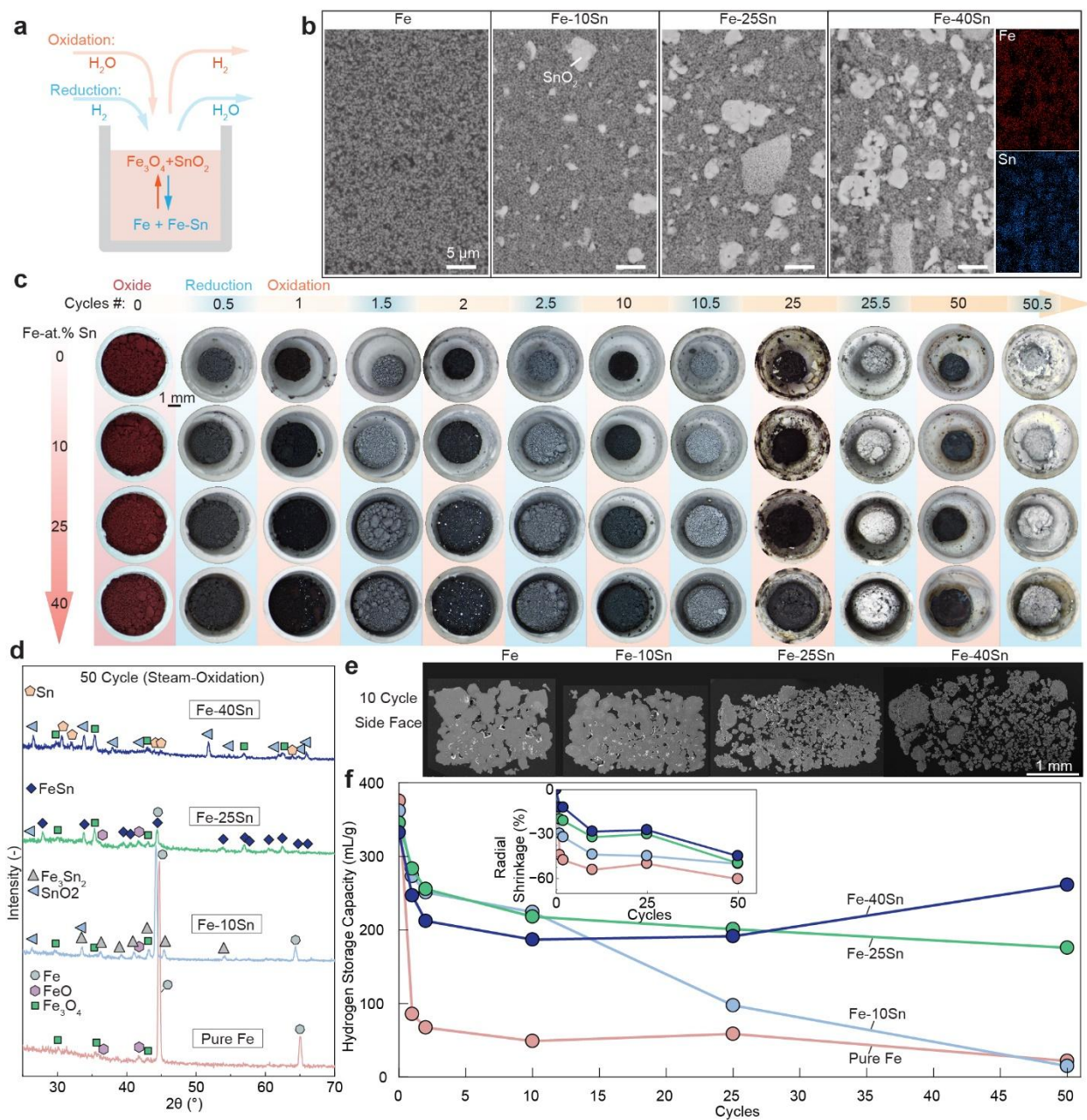


Figure 3. Redox of Fe-Sn powder blends

(a) Schematic illustration of Fe-Sn powder beds in alumina crucibles enabling hydrogen storage and release through steam oxidation and hydrogen reduction. (b) SEM-BSE images of reduced $\text{Fe}_3\text{O}_4 + \text{SnO}_2$ powder blends, with target compositions of Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn after reduction. (c) Optical top-view images of the powder beds (Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn) showing the evolution of shrinkage during redox cycling at 650 °C, from the initial oxide state (0 cycle) to the final reduced state (50.5 cycles). (d) XRD patterns of cross-sections of the steam-oxidized powder beds (Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn) after 50 redox cycles. (e) SEM-BSE images of the cross-sections (side views) of the reduced powder beds (Fe, Fe-10Sn, Fe-25Sn,

and Fe-40Sn) after 10.5 cycles redox cycling. (f) Hydrogen storage capacity (determined from mass change) of Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn powder beds, as a function of redox cycles (taking H_2 density at standard conditions, 0 °C and 1 atm) Inset: corresponding radial shrinkage of powder beds as a function of redox cycles for each composition.

Redox Cycling of Fe-Sn powder beds

Powder beds composed of Fe_2O_3 and SnO_2 were mixed and loaded into alumina crucibles, then subjected to H_2 reduction at 650 °C for 90 minutes to store chemical energy, followed by steam oxidation at 650 °C for 90 minutes to release H_2 , as illustrated in Figure 3 (a). The swelling effect of Sn in these Fe-based powder bed was investigated by varying Sn content from 0 to 40 at.% (Figure 3 (b)). Initially, all four oxide powder beds have diameters defined by the inner diameter of the crucibles in which they are contained (Figure 3 (c)). After the initial H_2 reduction (0.5 cycle), the oxide blends are transformed into Fe and the Fe_3Sn_2 and FeSn intermetallic phases. Oxygen removal during reduction causes particle shrinkage, and when combined with sintering, this leads to densification of the powders and a loss of reactive surface area. For the pure Fe powder bed, a significant radial shrinkage of -43% occurs, indicating severe densification and reduction in surface areas. In contrast, the addition of SnO_2 effectively mitigates this shrinkage: Fe-10Sn, Fe-25Sn, and Fe-40Sn (at.%) powder beds exhibited decreased shrinkages of -31, -21, and -14%, respectively. Thus, increasing Sn content enhances the swelling effect, which counteracts densification and helps preserve reactive surfaces. The trend aligns with previous powder sintering observations in the Al-Zn⁴¹ (500 °C) and Cu-Sn⁴² (250 °C) systems, where higher Zn or Sn content promotes more pronounced swelling due to increased liquid-depletion porosity and volumetric expansion of solid particles, arising from imbalanced diffusion between liquid and solid phases. For the Fe-40Sn powder bed, the relatively small shrinkage is attributed to the volume contraction caused by oxide-to-metal reduction being nearly balanced by the expansion from the swelling effect. Following H_2 reduction, the powder beds were subjected to steam oxidation (1 cycle). The steam-oxidized pure Fe powder bed shows a linear shrinkage of -44% (all values are given with respect to the original diameter of the powder bed), similar to that after the initial reduction. In contrast, the Fe-10Sn, Fe-25Sn, and Fe-40Sn (at.%) powder beds showed decreased shrinkages of -30, -20, and -12%, respectively.

Cross-sectional SEM images of the reduced powder beds after 10.5 redox cycles are shown in Figure 3 (e). The Fe-10Sn, Fe-25Sn, and Fe-40Sn (at.%) powder beds display similar, or slightly greater, heights compared to the pure Fe powder bed. This is unlike the significantly different shrinkage observed in the radial direction. This anisotropic shrinkage is likely attributed to the downward flow and rearrangement of particles induced by the transient liquid phase under the influence of gravity. However, when considering the radial shrinkage, these results confirm that the addition of Sn effectively suppresses densification and shrinkage during redox cycling.

Extended redox cycling up to 50 cycles was conducted, and the corresponding radial shrinkage is presented in Figure 3 (f). All four compositions exhibit gradual increases in absolute shrinkage over repeated cycles, primarily due to cumulative sintering effects. However, powder beds containing higher Sn content show decreased shrinkage compared to those with lower or no Sn.

After 50 cycles, the Fe-40Sn powder bed exhibits the smallest absolute radial shrinkage at -45.0 %, in contrast to -60.5% for pure Fe, -50.1% for Fe-10Sn, and -49.8% for Fe-25Sn; this demonstrates that the incorporation of Sn effectively mitigates sintering-induced densification during long-term cycling.

XRD patterns after 50 redox cycles are shown in Figure 3 (d). For the oxidized pure Fe powder bed, the diffraction peaks are dominated by metallic Fe (87.7 vol.%), with minor contributions from FeO (7.8 vol.%) and Fe₃O₄ (4.5 vol.%). The predominance of unoxidized metallic Fe indicates limited participation in redox reactions and corresponds to the observed low hydrogen storage capacity. In the oxidized Fe-10Sn powder bed, metallic Fe remains the dominant phase (82.2 vol.%), accompanied by small fractions of Fe₃O₄ (5.2 vol.%), SnO₂ (2.9 vol.%), and Fe₃Sn₂ intermetallic (9.7 vol.%), suggesting that only a limited portion of the material is redox capable and contributing to hydrogen generation. The phase composition of the oxidized Fe-25Sn powder bed shifts significantly, with a higher fraction of oxide phases: Fe₃O₄ (47.2 vol.%) and FeO (21.5 vol.%). The remaining metallic phases include FeSn (19.5 vol.%) and Fe (11.8 vol.%), indicating greater participation in redox reactions compared to lower Sn content powder beds. For the oxidized Fe-40Sn powder bed, oxide formation is even more pronounced, with Fe₃O₄ accounting for 74.9 vol.% and SnO₂ for 8.5 vol.%. A residual metallic Sn phase (16.6 vol.%) remains consistent with its slower steam oxidation kinetics, as previously observed in Figure 2 (a-b). After 50.5 cycles (in the reduced state), nearly all oxide phases are fully reduced in all four compositions (Figure S4). Only a few Fe₃O₄ particles are observed near the powder-bed surface for the Fe and Fe-10Sn samples (Figure S3).

The hydrogen storage capacity of the powder beds was evaluated based on mass change measurements over cycles 1-10 and XRD phase quantification at cycles 25 and 50, as shown in Figure 3 (f). As the Sn content increases, the initial hydrogen capacity per gram of powder decreases due to the higher molar mass of Sn compared to Fe. During redox cycling, the hydrogen capacity of the pure Fe powder bed declines rapidly, stabilizing at a low value after just two cycles. With the addition of 10 at.% Sn, the powder bed maintains a hydrogen capacity above 224 mL g⁻¹ during the first 10 cycles. However, by cycles 25 and 50, the capacity drops to 15 mL g⁻¹, comparable to that of pure Fe, suggesting that the porosity generated by the swelling effect of Sn is gradually lost due to long-term sintering. In contrast, the Fe-25Sn powder bed exhibits improved long-term stability, maintaining a capacity of 176 mL g⁻¹ after 50 cycles. This suggests that the competing effects of swelling-induced porosity and sintering reach a quasi-equilibrium. The best performance is observed for the Fe-40Sn powder bed, which achieves a hydrogen capacity of 261 mL g⁻¹, approximately 22 times higher than that of pure Fe. These results demonstrate that leveraging the swelling effect of transient liquid Sn during redox cycling is an effective strategy for enhancing the hydrogen storage performance of Fe-based powder beds.

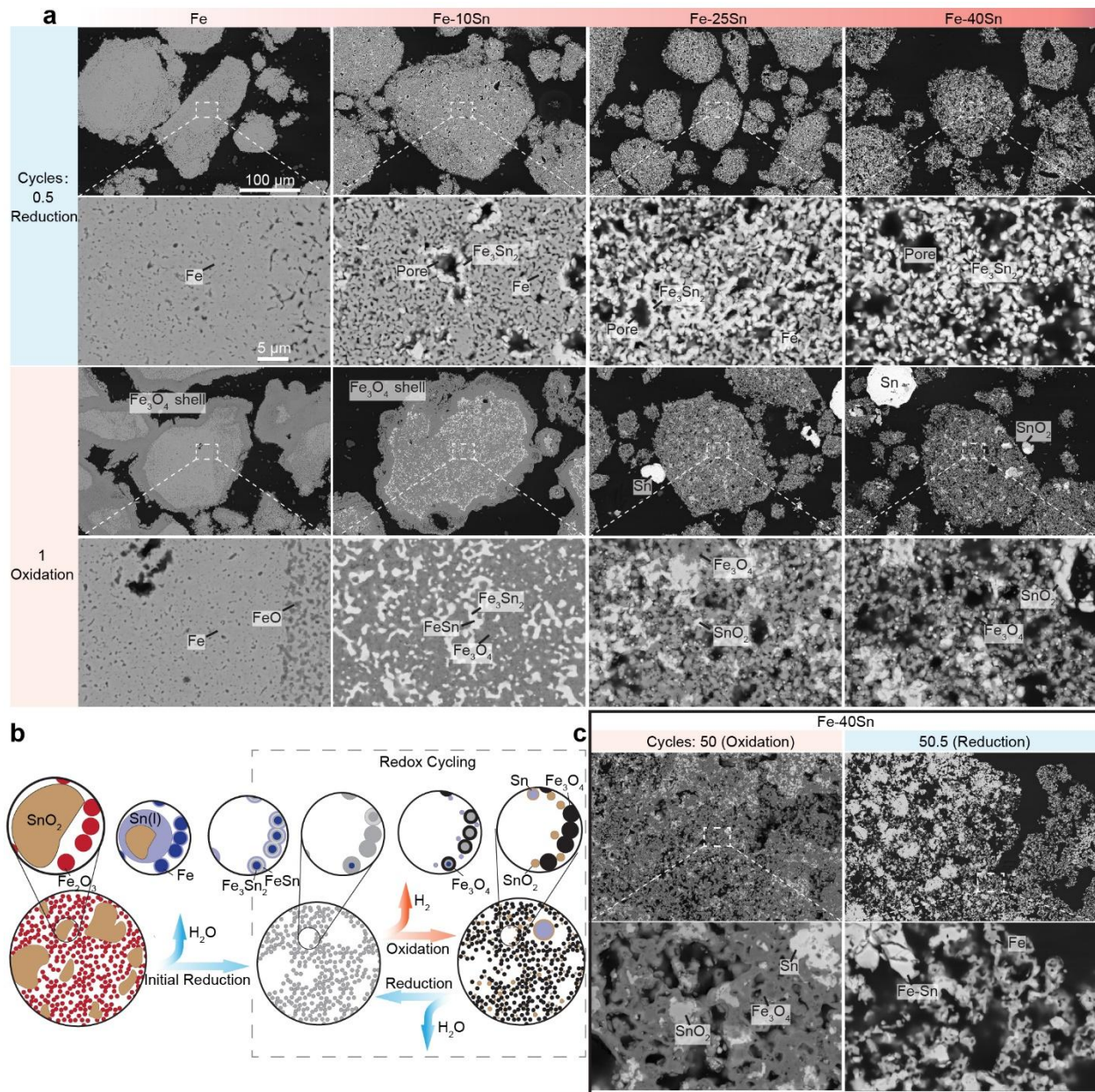


Figure 4. Microstructural evolution

(a) SEM-BSE cross-section images of Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn powder beds after the first H_2 reduction from the oxide state (0.5 cycle) and after subsequent steam oxidation (1 cycle). (b) Schematic illustration of hydrogen reduction followed by steam oxidation process for the loosely packed Fe-40Sn powder blend, highlighting the mechanism for pore formation driven by transient liquid swelling. (c) SEM-BSE cross-section images of Fe-40Sn powder beds after 50 (oxidized) and 50.5 (reduced) redox cycles.

Microstructural evolution of Fe-Sn powder beds

Cross-sectional microstructures of Fe, Fe-10Sn, Fe-25Sn, and Fe-40Sn (at.%) powder beds after the first H_2 reduction (0.5 cycle) and subsequent steam oxidation (1 cycle) are shown in Figure 4 (a). Following H_2 reduction, all powder beds comprise 10-250 μm agglomerates (much larger than the original oxide powders: $<3\text{-}\mu m$ for Fe_2O_3 and $0.5\text{-}12\text{ }\mu m$ for SnO_2), separated by a network of $\sim 20\text{-}120\text{-}\mu m$ -wide channels. The internal microstructures of these agglomerates vary significantly depending on Sn content. Agglomerates in the pure Fe powder bed exhibits the most densified microstructure, attributed to rapid sintering kinetics of the fine Fe/ Fe_2O_3 powder during the redox cycle, that promote substantial densification. In contrast, the Fe-10Sn agglomerates show a more porous structure characterized by two distinct pore types. The first is liquid-depletion pores located at former Sn sites, typically surrounded by a bright Fe_3Sn_2 intermetallic phase formed via reactions between Fe and adjacent liquid Sn. The second consists of pores distributed within the Fe matrix, which is comprised of reduced and partially-sintered Fe particle whose densification was slowed by the liquid-depletion porosity. In the Fe-25Sn powder bed, the number density of liquid-depletion pores increases, and the Fe matrix within agglomerates becomes even more porous. This enhanced porosity arises not only from the liquid-depletion porosity and slowed densification but also from the volumetric expansion associated with the formation of Fe-Sn intermetallic phases, which absorb liquid Sn during reduction. Finally, the Fe-40Sn powder bed exhibits the most porous microstructure, driven by a combination of extensive liquid-depletion porosity formation, decreased sintering kinetics, and significant particle growth due to intermetallic formation.

After the first steam oxidation cycle for the Sn-free powder bed (Figure 4 (a)), Fe agglomerates develop a Fe_3O_4 shell on their surface, while their core largely remains in a metallic state. Similar Fe_3O_4 shell have been observed in Ref [16, 51] for the case of steam oxidation of Fe powder bed at $800\text{ }^\circ C$. During oxidation, the unreacted metallic core is not accessible to steam and therefore does not contribute to hydrogen generation within the reaction time. The rapid loss of reactive surface area severely limits the utilization of metallic Fe in subsequent redox cycles. As a result, redox reactions in pure Fe powder beds are confined primarily to the oxide shell regions, as illustrated in Figures S1-S3, with only a small portion of the material participating in the redox process. Consequently, the hydrogen capacity of pure Fe powder declines sharply within the first two cycles and then stabilizes at a low level, as shown in Figure 3(f).

For the Fe-10Sn powder bed after the first steam oxidation (Figure 4 (a)), a Fe_3O_4 shell has formed on the surface of the agglomerates, while their core is enriched with Sn-rich phases. This morphology results from the slower oxidation kinetics of Sn compared to Fe. As Fe oxidizes more rapidly, liquid Sn is expelled and migrates towards the core of the agglomerates, where it reacts with metallic Fe to form intermetallic phases. Notably, Fe_3O_4 is observed within the agglomerates instead of residual metallic Fe, indicating that a greater Fe fraction oxidizes and participates in hydrogen generation. This explains the relatively high hydrogen capacity observed in Fe-10Sn powder beds during the initial redox cycles. Liquid-depletion porosity and pores retained due to slowed densification maintain open microchannels within agglomerates that allow steam to penetrate and react with internal metallic phases, and the formed hydrogen to exit the agglomerates. However, some Sn-rich intermetallic regions remain unoxidized as they become

encapsulated by the rapidly-forming Fe_3O_4 shell and lose access to steam. The microstructure remains largely unchanged through 10 cycles (Figures S1-S2), but it undergoes significant degradation after extended cycling: by 50 cycles (Figure S3), the agglomerates have coalesced, and steam oxidation occurs primarily at the outer surface of the whole powder bed. This leads to a substantial drop in hydrogen capacity, approaching that of pure Fe powder beds (Figure 3(f)).

The steam-oxidized Fe-25Sn powder bed, after a first redox cycle, shows agglomerates with a porous microstructure, albeit without the formation of a dense Fe_3O_4 shell as observed in the Fe-10Sn composition (Figure 4 (a)). Both Fe_3O_4 and SnO_2 phases are present within the agglomerates, enabled by open microchannels that promotes efficient steam access and oxidation, as well as hydrogen egress. In addition, near-spherical metallic Sn particles are observed outside the agglomerates (Figure 4 (a)). These Sn droplets are formed via liquid-phase migration, driven by the high contact angle of liquid Sn on the Fe_3O_4 surface, and remain mostly unoxidized due to their limited surfaces for oxidation. After 10 redox cycles, the powder bed maintains a porous microstructure (Figure S2), but becomes relatively denser after 50 cycles (Figure S3). The oxidized powder beds at this stage consist of a Fe_3O_4 -rich outer shell encompassing a Sn-rich intermetallic core, which is shielded from steam and therefore difficult to oxidize. This observation is consistent with the presence of the FeSn phase, as identified by XRD after steam oxidation, as shown in Figure 3 (d).

Finally, the Fe-40Sn powder bed exhibits the most porous microstructure after the first steam oxidation (Figure 4 (a)), driven by the pronounced swelling effect associated with its high Sn content. Within the agglomerates, Fe_3O_4 particles remain isolated, providing an abundance of reactive surfaces for subsequent redox reactions. In addition to uniformly distributed submicron-sized SnO_2 particles, larger aggregates of SnO_2 (~2-25 μm) are also observed. These are attributed to the relatively slow steam oxidation kinetics of Sn, where the transient liquid Sn phase can flow and coalesce prior to full oxidation, resulting in large SnO_2 particles. Furthermore, large (~80 μm), near-spherical metallic Sn particles are also found outside the Fe_3O_4 -rich agglomerates (Figure 4 (a)). Over repeated redox cycling (Figure S1-S3), the Fe-40Sn powder bed consistently maintains the most porous microstructure among all compositions, even after 50 and 50.5 cycles (Figure 4 (c)), highlighting its superior microstructural stability in maintaining abundant reactive surfaces. The evolution of this microstructure is schematically illustrated in Figure 4 (b). Porosity arises from a combination of (i) liquid-depletion voids forming at former Sn particle sites, (ii) volumetric expansion of solid phases, and (iii) suppressed sintering due to decreased interparticle connectivity. During each steam oxidation step, Fe and Sn separate from the intermetallic phases (FeSn and Fe_3Sn_2) and convert into Fe_3O_4 and SnO_2/Sn , respectively, allowing the swelling effect to persist after reduction and to remain effective in subsequent redox cycles.

In summary, this work presents the first utilization of the transient-liquid swelling effect to inhibit sintering during redox cycling of metal oxides. The findings offer a new pathway to enhance the redox cyclability and efficiency of Fe-based systems for hydrogen production and storage. Introducing reversible Sn/ SnO_2 into the Fe powder bed effectively preserves highly reactive surface areas over repeated redox cycles. This compositional design strategy can be broadly applied to engineer porous microstructures in other materials subjected to high-temperature redox

cycling, e.g., for solar thermal water splitting, carbon dioxide utilization, and chemical looping combustion technologies.

Experimental:

Powder blends and Redox Cycling

Fe₂O₃-SnO₂ powder blends were prepared by mixing Fe₂O₃ (Noah Technologies, 99.9%, <3 μm) and SnO₂ (US Nano Research, 0.5-12 μm, 99.7%) using zirconia balls in a ball mill for 24 h with a ball-to-powder weight ratio of 5:1. To achieve specific compositions, varying amounts of SnO₂ powder were added, resulting in three compositions after reduction: Fe-10 at.% Sn (Fe-19 wt.% Sn), Fe-25 at.% Sn (Fe-41 wt.% Sn), and Fe-40 at.% Sn (Fe-59 wt.% Sn). Approximately 40 mg of the ball-milled, loosely packed powder blend was weighed and placed into alumina crucibles for redox cycling. These experiments were conducted at 650 °C with a heating rate of 10 °C/min in an alumina tube furnace (inner diameter: 20 mm, length: 500 mm). Pure H₂ gas (UHP, 200 sccm) and H₂O vapor (steam) were alternately introduced into the furnace. Argon gas (UHP, 120 sccm) was used to carry the H₂O vapor by passing through a heated deionized water bubbler maintained at 93 °C, creating a water vapor pressure of 770 mbar. Each redox cycle comprised a 90-minute reduction step in H₂ gas, followed by a 90-minute oxidation step in H₂O vapor. After completing the assigned redox cycles, the powder beds were cooled to room temperature at a rate of ~5 °C/min. Reduced powder beds were cooled under 100 sccm H₂, while oxidized powder beds were cooled under 20 sccm of Ar-4% H₂.

Characterization:

In-situ X-ray diffraction was performed with a STADI MP (Ag source) on a Fe₂O₃-SnO₂ powder blend (target composition: Fe-40 Sn) lodged in a quartz capillary (1.0 mm ID, 1.2 mm OD). This powder-loaded capillary was placed into a longer, wider, externally-heated quartz capillary (1.5 mm ID, 1.8 mm OD, 165 mm length) with quartz wool and ceramic rods positioning and securing the powder-loaded capillary in the center of the hot zone of a resistance furnace. Diffraction data were collected over a 2θ coverage of 18.5° during a 90 s exposure, with 5 °C steps during heating from 100 to 650 °C, with a heating rate of 10 °C/min under a pure hydrogen (UHP) flow 20 sccm/min. The 650 °C temperature was maintained for 90 min and the atmosphere switched to steam (H₂O vapor) after 1 min, with argon (UHP) used to carry H₂O vapor, creating ~1 bubble per second while venting downstream. After the 90 min oxidation, the atmosphere was switched to pure H₂ (20 sccm) and the temperature was maintained at 650 °C for another 90 min. The ex-situ X-ray diffraction was performed after cooling to ambient temperature, on cross-sections of sintered powder beds, using a Smartlab 3 kW Gen2 diffractometer.

Metallographic characterization was done on surface or polished cross-sections of powder beds which were cold mounted in epoxy resin, ground with SiC grinding papers, polished with diamond suspensions (3 and 1 μm) and colloidal silica (0.05 μm). Optical micrographs were taken using a stereo microscope and scanning electron microscopy (SEM) was performed on a Quanta 650 instrument, after coating the samples with 4-8 nm Os.

Contributions

D.Z. proposed the concept. D.Z., D.C.D, and J.Q. designed the experiments. D.Z. performed the in situ XRD experiment. D.Z. and J.Q. performed redox cycling and characterization experiments. D.Z., J.Q., and D.C.D. analyzed data and discussed the findings. D.Z. wrote the first manuscript. D.Z., and D.C.D. contributed to the manuscript writing.

Data availability

The main text or Supplementary Information contains all the available data. The data generated or analyzed during the current study are accessible from the corresponding author upon reasonable request.

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Conflict of Interest

A provisional patent application covering this work has been filed by Northwestern University (U.S. Provisional Patent Application No. 63/830,599), with D.Z. and D.C.D. as inventors and applicants. DCD discloses a financial interest in IROX Inc. (USA), which is applying iron-based powders to various redox scenarios.

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