

Effects of Mn doping on the reactivity, elastic, and magnetic properties of α -Fe₂O₃ based on DFT calculation

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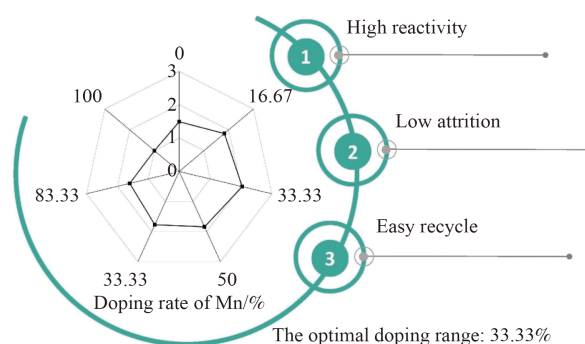
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Abstract: Oxygen carriers play a fundamental role in chemical looping combustion (CLC). Iron-based carriers have been extensively investigated owing to their abundance and environmentally friendly. However, the reactivity and separability of iron-based carriers require further enhancement. This study investigates the effect of the concentration of Mn doping on reactivity, elastic properties and magnetic properties based on density functional theory (DFT) calculations. Theoretical results demonstrate that Mn doping effectively enhances reactivity by reducing the oxygen vacancy formation energy (E_{vac}) from 2.33 to 0.87 eV. However, Mn doping introduces lattice distortions that deteriorate elastic properties, thereby reducing wear resistance, as evidenced by a 54.54% decrease in the hardness-to-Young's modulus ratio (H_v/E_v) for α -Fe₂O₃ and an 83.33% reduction for Fe₃O₄. Furthermore, Mn doping also modifies magnetic properties. The maximum of saturation magnetization (M_s) of Fe₃O₄ reaches 121.02 emu/g at 33.33% Mn doping concentration. Finally, systematic evaluation identifies 33.33% as the optimal Mn doping concentration, achieving a balance in enhanced reactivity, superior magnetic performance, and retained elastic stability.

Key words: oxygen carrier; Mn-doped α -Fe₂O₃; reactivity; elastic properties; magnetic properties

Performance comparison of Mn-doped α -Fe₂O₃ oxygen carriers



Chemical looping combustion (CLC) is one of the most promising technologies for CO₂ emission reduction owing to its low energy consumption. The system generally consists of an air reactor and a fuel reactor (utilizing natural gas, coal, biomass, etc.)^[1–3] (Figure 1). Oxygen carriers circulate between these two reactors, releasing oxygen to react with fuel in the fuel reactor and then being regenerated through air reoxidation in the air reactor, thereby preventing direct contact between fuel and air. Investigations into the solid fuel CLC have predominantly targeted oxygen carrier

development, reactor design, and process optimization^[4–6], such as improving the reactivity of oxygen carriers^[7], the elastic properties of oxygen carriers^[8], and the separation efficiency of oxygen carriers from the mixture of solids (fuel-derived ash and reduced oxygen carriers)^[9].

Fe-based oxygen carriers (such as α -Fe₂O₃) have been extensively investigated due to their high thermal stability, low cost and abundant raw material sources on earth, and environmental friendliness^[10–12]. However, the reactivity of Fe-based carriers requires further improvement^[13–15].

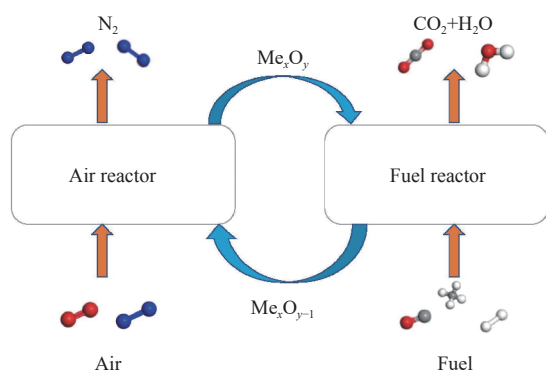
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Note: Blue, red, gray and white spheres represent N, O, C, and H atoms, respectively.

Fig. 1 Schematic diagram of a CLC system

Doping $\alpha\text{-Fe}_2\text{O}_3$ with transition metals (e.g., Mn) can enhance the reactivity and different doping concentrations have significantly influence on the reaction activity. Mn-doped $\alpha\text{-Fe}_2\text{O}_3$ modulated the Fe-O bonds and reduced the oxygen vacancy formation energies, thereby increasing the reactivity, and significantly improving the adsorption capacity of NH_3 and O_2 ^[15–16]. Nevertheless, Mn-doped $\alpha\text{-Fe}_2\text{O}_3$ exhibits reduced cycling stability^[17]. Thus, achieving a balance between the competing effects of high reactivity and cycling stability is crucial; however, relevant studies on this aspect remain scarce in the literature.

The oxygen carrier inevitably undergoes attrition during solid fuel CLC processes, resulting in both reduced combustion efficiency and shortened operational lifetime. The attrition rate is directly correlated with the elastic properties of the carrier^[3]. While bimetallic doping enhances oxygen carrier reactivity, the concomitant lattice distortions induce structural instability during redox cycling, consequently compromising operational stability. However, systematic investigations of these competing effects between reactivity and structural instability remain limited in current literature.

To separate the reduced iron-based oxygen carrier from the ash, the magnetic properties of Mn-doped Fe-based oxygen carriers should be exploited for carrier recovery, thereby increasing the utilization rate of the oxygen carrier and decreasing system costs^[18–20] (Figure 2). Notably, the magnetic properties of oxygen carriers is also influenced by the doping concentrations^[18].

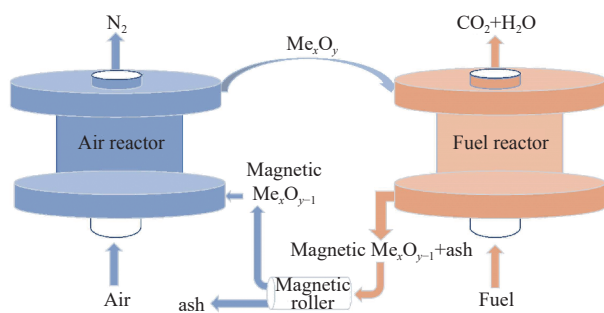


Fig. 2 Schematic diagram of a solid fuel CLC system with the recovery of oxygen carriers

The separability requires further enhancement. Furthermore, a comprehensive assessment of both reactivity and magnetic recyclability in oxygen carriers is rarely reported in literature.

In this study, Mn-doped $\alpha\text{-Fe}_2\text{O}_3$ bimetallic oxygen carriers were systematically investigated by DFT calculations, with special emphasis on three critical aspects: (1) the correlation between doping concentration and reactivity evolution of oxygen carriers, (2) the transformation of elastic properties during redox cycles before and after Mn doping, and (3) the modulation of magnetic properties induced by dopant incorporation. Finally, the investigation culminated in a multi-criteria optimization that identified the superior doping concentration through comprehensive evaluation of the tripartite relationship between reactivity, elastic properties, and magnetic recyclability.

1 Computational method and models

1.1 Computational method of $\alpha\text{-Fe}_2\text{O}_3$ model

In this study, all DFT calculations were performed using the CASTEP module^[21]. The electronic exchange-correlation interactions were treated with the generalized gradient approximation (GGA)^[22] using the Perdew-Burke-Ernzerhof (PBE) functional^[23]. Rigorous convergence testing^[24] of the $\alpha\text{-Fe}_2\text{O}_3$ system established optimal computational parameters of 500 eV plane-wave cutoff energy and a $2 \times 2 \times 1$ Monkhorst-Pack k-point grid^[25–26]. The DFT+U approach with $U = 4.5$ eV was applied to Fe 3d orbitals to better describe the strongly correlated electronic structure characteristic of transition metal systems^[27], and the U value of Mn was also set to 4.5 eV. The values of the convergence standard for SCF, energy, maximum stress, maximum displacement and maximum force were 2.0×10^{-6} , 2.0×10^{-5} eV/atom, 1.0×10^8 Pa, 2.0×10^{-3} Å and 0.05 eV/Å, respectively^[28].

To accurately determine the magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$, the primitive unit cell was employed with antiferromagnetic spin ordering (+, −, −, +) for the iron atoms to reach the ground state^[29]. The conventional unit cell (Figure 3), which is triple the size of the primitive cell, contains 12 Fe and 18 O atoms.

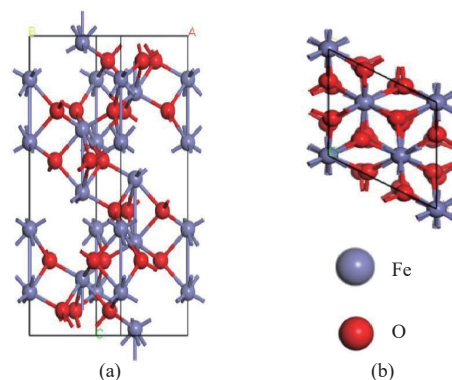


Fig. 3 (a) $\alpha\text{-Fe}_2\text{O}_3$ side view and (b) $\alpha\text{-Fe}_2\text{O}_3$ top view

After optimization, the lattice constants ($a = b = 5.035$ Å, $c = 13.720$ Å) were observed, which aligned well with experimental data ($a = b = 5.035$ Å, $c = 13.747$ Å)^[30]. To investigate doping effects, Fe was substituted with Mn at counts of 0, 2, 4, 6, 8, 10 and 12, corresponding to a Mn/(Mn+Fe) ratio of 0–100%. Figure S1 shows the variation in the unit cell parameters of α -Fe₂O₃ with Mn doping concentration during optimization. Mn doping maintains the three unit cell angles while causing a slight expansion (<10%) in all lattice parameters (a , b and c), compared to the pristine cell.

1.2 Computational method of α -Fe₂O₃(001) model

The (001) plane is the most prevalent and thermodynamically stable facet of α -Fe₂O₃ in natural conditions^[31]. Therefore, the crystal was cleaved along this plane to generate the reactive surface, with a 15 Å vacuum layer incorporated to eliminate periodic boundary interactions^[32]. The constructed model includes nine atomic layers, which consist of five fixed bottom layers and four relaxed top layers. Structural optimization formed the minimum-energy geometric configuration, exhibiting a calculated band gap of 1.912 eV. This value shows excellent agreement with the experimentally reported value (1.9–2.2 eV)^[24], validating the appropriateness of the selected parameters. The oxygen vacancy formation energy was computed using a $2 \times 2 \times 1$ supercell model of α -Fe₂O₃(001) (Figure 4). The top surface layer of ($2 \times 2 \times 1$) Fe₂O₃(001) model contained 4 Fe atoms. Substitutions targeted only the top-layer Fe atoms, which serve as the active sites for reactions^[8,13]. The surface doping concentrations can be controlled from 0 to 100%, by systematically varying the number of substituted Mn atoms from 0 to 4.

1.3 Computational method of Fe₃O₄ model

α -Fe₂O₃ is reduced to Fe₃O₄ during the reaction process^[11]. Therefore, Fe₃O₄ unit cell was used to calculate the magnetic properties before and after Mn doping. Fe₃O₄ has an inverse spinel face-centered cubic structure with ferrimagnetic ordering, where the spins of octahedral Fe and tetrahedral Fe are aligned antiparallel ($\uparrow$ and $\downarrow$, respectively). There are 24 Fe atoms and 32 O atoms in the conventional unit cell (Figure 5). The Hubbard U values were set to 3.8 eV for Fe^[33] and 4.5 eV for Mn^[34], with a plane-wave cutoff energy of 400 eV and a $5 \times 5 \times 5$ Monkhorst-Pack k-point grid^[35]. After optimization, the lattice constants were determined to be $a = b = c = 8.320$ Å, showing good agreement with experimental values ($a = b = c = 8.396$ Å^[36]). To investigate doping effects, Fe was substituted with Mn at counts of 0, 4, 8, 12, 16, 20 and 24, corresponding to a Mn/(Mn+Fe) ratio of 0–100%.

The integrated spin density (32.05 μ_B) and absolute spin density (96.03 μ_B) are both non-zero and Mulliken population analysis reveals atomic magnetic moments with both positive and negative values, confirming the ferrimagnetic nature of the Fe₃O₄ unit cell.

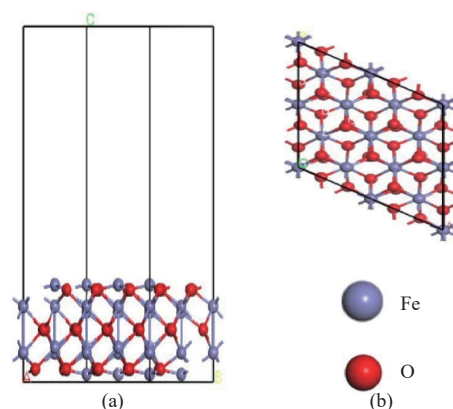


Fig. 4 (a) α -Fe₂O₃(001) $2 \times 2 \times 1$ side view and (b) α -Fe₂O₃(001) $2 \times 2 \times 1$ top view

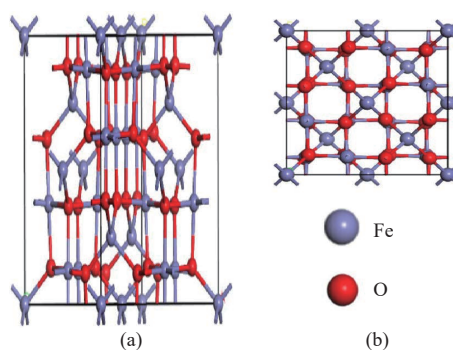


Fig. 5 (a) Fe₃O₄ side view and (b) Fe₃O₄ top view

The magnetic moment of octahedral Fe is 3.85 μ_B , being in line with the experimental value (4.05 μ_B). For tetrahedral Fe, the calculated magnetic moment is -3.93 μ_B , which is smaller than the theoretical prediction (5.00 μ_B ^[37]), but matches well with the literature data (4.05 μ_B ^[33]). These results, supported by reference^[33], validate the electronic properties of Fe₃O₄ and the appropriateness of current computational parameters. Figure S2 shows the evolution of Fe₃O₄ unit cell parameters with Mn doping levels during optimization. Mn doping maintains all three unit cell angles while inducing lattice expansions: parameters a and b show slight increases (<10%), whereas the c -axis undergoes more significant elongation (15%), in comparison with those of the undoped structure.

2 Results and discussion

2.1 Impact of Mn doping on the reactivity property of α -Fe₂O₃

Oxygen vacancies play crucial role in determining the surface properties and the catalytic reactivity in metal oxides. In this study, the oxygen vacancy formation energy (E_{vac}) is used as the indicators of reactivity of α -Fe₂O₃. The E_{vac} was defined as the energy required to remove a surface oxygen atom, calculated by equation 1^[38]:

$$E_{vac} = E_{defect} + 0.5E_{O_2} - E_{perfect} \quad (1)$$

where E_{defect} , E_{perfect} and E_{O_2} represent the total energies of the oxygen-deficient surface, pristine surface, and oxygen molecule, respectively.

The E_{vac} in the pure $(2 \times 2 \times 1)$ $\alpha\text{-Fe}_2\text{O}_3(001)$ surface model is calculated to be 2.33 eV, in good agreement with reported values (2.01^[15], 2.37 eV^[16]). Doping of single-atom transition metal (e.g., Mn, Co, Ni, Cu, Zn) on $\alpha\text{-Fe}_2\text{O}_3(001)$ consistently reduces E_{vac} , showing higher reactivity than that of undoped surfaces. Among these, Mn exhibits lower E_{vac} than Co, Ni, or Zn while remaining marginally higher (by 0.1 eV) than Cu^[15]. As revealed by the density of states (DOS) in Figure 6 (undoped system), the DOS value at the Fermi level (E_F) is zero, which is consistent with the literature^[39]. The hybridization between Fe 3d and O 2p orbitals in the -7.5 to 2.5 eV range forms stable bonding states, resulting in two distinct characteristic peaks.

With the increase of the concentration of Mn doping at the surface, E_{vac} decreases progressively, with the rate of decline becoming more evident at higher doping levels (Figure 7). This trend aligns directly with the evolution of doping-induced electronic structure, as shown in Figure 8 (a)–(d). At 25% Mn doping (Figure 8(a)), the incorporated Mn 3d states produce distinct localized peaks at -5 eV (-2.65 states/eV) and 5 eV (5.55 states/eV), respectively. The elongated Mn–O bond length (1.97 Å for Mn–O versus 1.81 Å for Fe–O) weakens transition metal-oxygen bonding strength, consequently lowering E_{vac} . With increasing doping concentration to 75%–100% (Figure 8(c), (d)), the DOS corresponding to Mn 3d orbitals exhibits substantial enhancement, rising from 10.80 to 20.00 states/eV at 5 eV and from -4.98 to -12.10 states/eV at -5 eV, which significantly strengthens the hybridization between Mn 3d and O 2p.

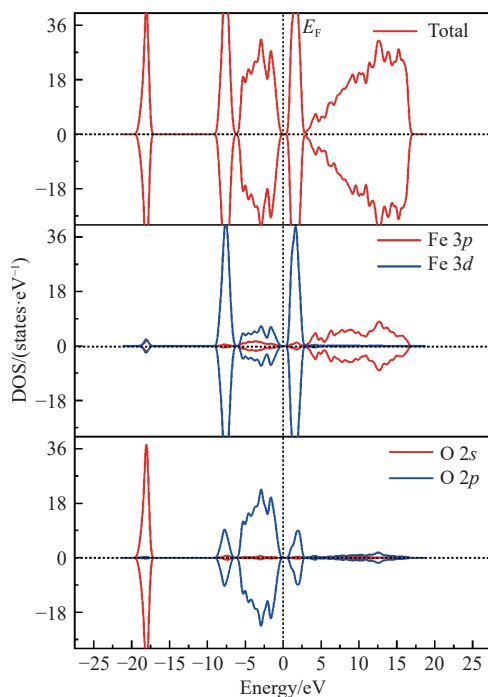


Fig. 6 The DOS plots of the $(2 \times 2 \times 1)$ $\text{Fe}_2\text{O}_3(001)$ model

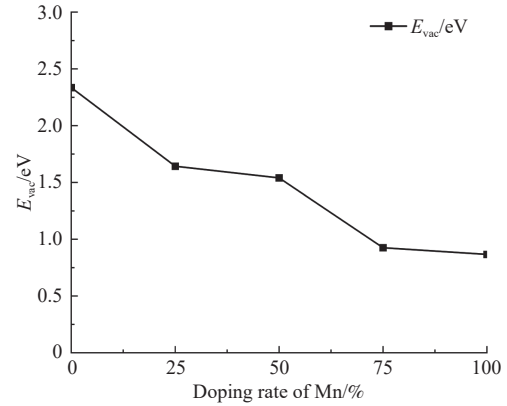


Fig. 7 The E_{vac} of the $(2 \times 2 \times 1)$ $\text{Fe}_2\text{O}_3(001)$ surface model

This hybridization markedly destabilizes surface oxygen and results in lower E_{vac} value. This indicates that higher Mn doping concentration is beneficial for enhancing the reactivity of $\alpha\text{-Fe}_2\text{O}_3$.

2.2 Impact of Mn doping on the elastic properties of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4

In CLC, $\alpha\text{-Fe}_2\text{O}_3$ is transferred from the air reactor to the fuel reactor. At that position, it is reduced by fuel to form Fe_3O_4 , which is then cycled back to the air reactor for regeneration into $\alpha\text{-Fe}_2\text{O}_3$. In this section, the elastic properties of both $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 were calculated and discussed.

Elastic properties are crucial indicators for evaluating the mechanical stability and practical application potential of Mn-doped $\alpha\text{-Fe}_2\text{O}_3$ materials. Calculation of elastic constants enables prediction of the deformation resistance and structural stability of the materials under practical CLC operating conditions. The durability of the materials during high-temperature redox cycles is directly determined by these parameters, which governs the ability to withstand repeated volume changes without structural failure, while simultaneously reflecting the strengthening or weakening effects of Mn doping on the $\alpha\text{-Fe}_2\text{O}_3$ lattice structure. The quality of elastic properties fundamentally influences the reactor compatibility, cycling lifetime, and determination of optimal process parameters for the material^[40–43].

2.2.1 Elastic properties of $\alpha\text{-Fe}_2\text{O}_3$

The elastic constant tensor is a 6×6 symmetric matrix^[40]. The $\alpha\text{-Fe}_2\text{O}_3$ is trigonal crystal system. The representation of the elastic stiffness matrix C_{ij} ^[41] is shown as follows:

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & \frac{C_{11} - C_{12}}{2} \end{bmatrix}$$

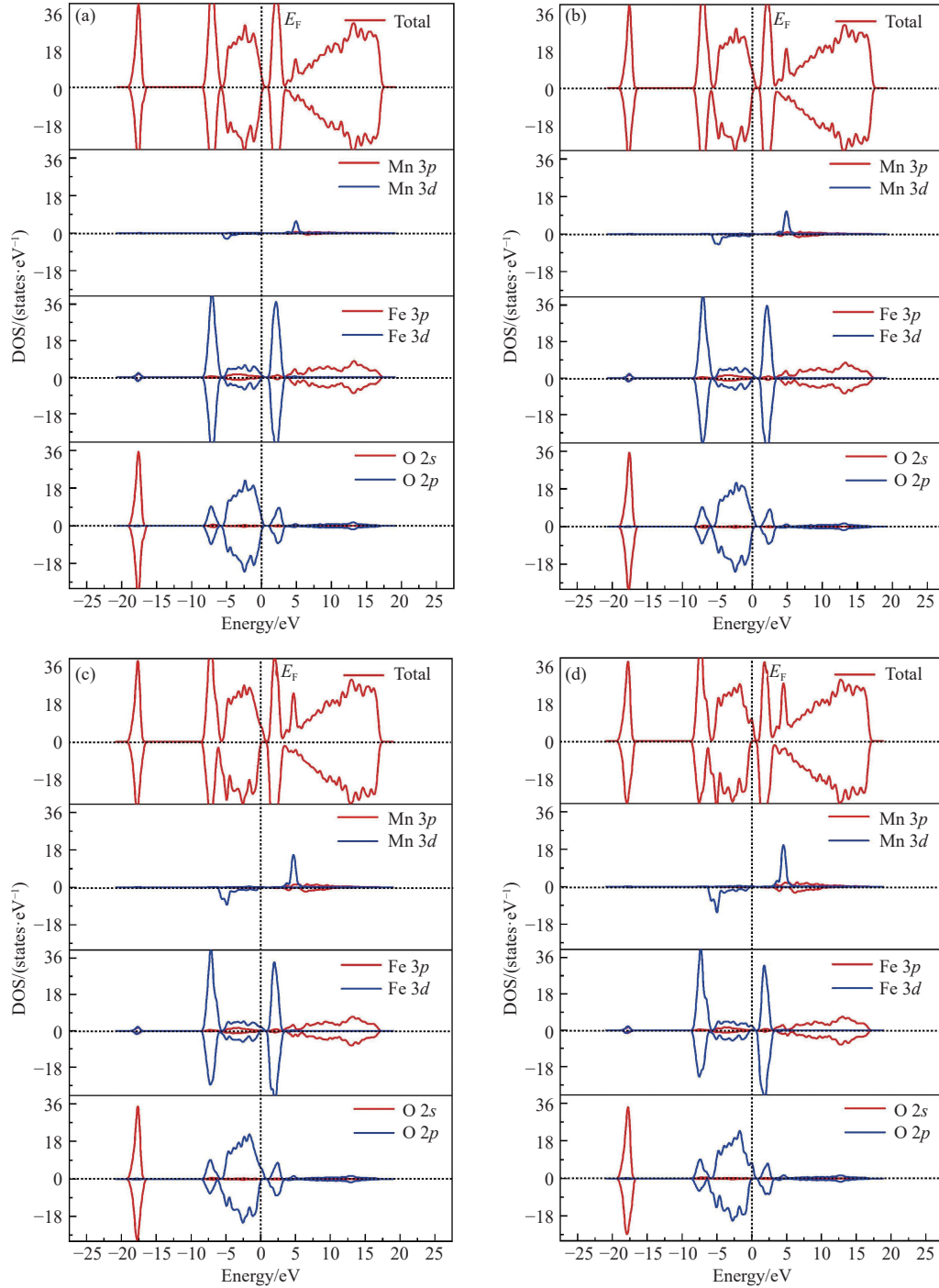


Fig. 8 The DOS plots under different surface doping rates ((a) 25%, (b) 50%, (c) 75%, (d) 100%)

The independent constants are C_{11} , C_{12} , C_{13} , C_{14} , C_{33} and C_{44} . These independent constants are adopted to calculate elastic properties such as the bulk modulus (B , the resistance of a material to uniform compression under isotropic pressure), the shear modulus (G , its resistance to shear deformation), and Young's modulus (E , its linear elastic stiffness under uniaxial tension or compression)^[42–43]. According to the Born-Huang stability criteria^[44], the trigonal crystals lattice remains mechanically stable when the following conditions are satisfied: $C_{11} > |C_{12}|$, $C_{13}C_{33} > C_{13}^2$, $C_{44} > 0$ and $(C_{11} - C_{12})C_{44} > 2C_{14}^2$.

According to the Voigt's definition^[42], the bulk mo-

dulus B_v is calculated by:

$$B_v = \left(\frac{1}{9}\right) [2(C_{11} + C_{12}) + 4C_{13} + C_{33}] \quad (2)$$

The shear modulus G_v is calculated by:

$$G_v = \left(\frac{1}{15}\right) (2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44}) \quad (3)$$

The Young's modulus E_v is calculated by:

$$E_v = \frac{9B_v G_v}{3B_v + G_v} \quad (4)$$

The Poisson's ratio (ν) is a dimensionless parameter that

reflects the ratio of transverse strain to axial strain under uniaxial loading^[45]. It can be calculated from E_v and G_v by the following equation:

$$\nu = \frac{E_v}{2G_v} - 1 \quad (5)$$

Hardness (H_v) quantifies the resistance of a material to permanent deformation under localized stress, reflecting its ability to maintain geometric integrity during mechanical indentation or penetration. The hardness can be calculated via the following equation^[46]:

$$H_v = 0.92k^{1.137}G_v^{0.708} \quad (6)$$

where the dimensionless parameter $k = G_v/B_v$ represents the shear-to-compressibility ratio.

Although hardness is a fundamental parameter for wear resistance evaluation, the elastic modulus play vital role in determining tribological behavior. The hardness-to-Young's modulus ratio (H_v/E_v), which quantifies elastic deformation capacity before yielding occurs and serves as a more reliable wear resistance indicator than isolated hardness measurements^[47]. In metallic and cermet systems, materials with high hardness and low elastic modulus exhibit superior wear resistance, consequently resulting in a decreased wear rate, along with the increase of H_v/E_v ratio^[48].

The elastic properties of Mn-doped α -Fe₂O₃ at varying doping rates (0–100%) were systematically investigated and the results were summarized in Table 1. The calculated values for α -Fe₂O₃ ($B_v = 225.177$ GPa, $E_v = 238.444$ GPa, $H_v = 7.894$ GPa) agree well with the experimental data published in literature ($B_v = 230 \pm 5$ GPa, $E_v = 250$ – 350 GPa and $H_v = 8.2$ GPa)^[40,49]. Furthermore, all other elastic constants can be obtained from these values through established mechanical relationships, demonstrating the reasonableness of the parameter selection. The Born-Huang stability criteria is not obeyed only at the full doping concentration (100%), which loses the mechanical stability in the crystal structure due to complete substitution of Fe by Mn.

The elastic properties of Mn-doped α -Fe₂O₃ exhibit a concentration-dependent transition from mechanical stability to instability. Regardless of the doping concentration, both G_v and E_v values in Mn-doped samples are lower than those in undoped α -Fe₂O₃, while H_v decreases from 7.894 to 1.835 GPa at full doping. This

weakening effect is attributed to the elongation of Mn³⁺–O bonds compared to Fe³⁺–O bonds, as well as the disruption of the homogeneous bonding network in α -Fe₂O₃ induced by Mn.

When the Mn doping concentration is no higher than 83.33%, E_v progressively decreases from 239.447 to 156.063 GPa, while G_v declines from 90.474 to 58.792 GPa, along with the decrease of B_v from 225.842 to 150.568 GPa. Correspondingly, hardness exhibits non-monotonic variation, while the H_v/E_v ratio decreases by 15.15%, indicating a decline in the wear resistance of the material.

Meanwhile, complete Mn substitution (100% doping) induces distinct mechanical anomalies: E_v sharply drops to 125.476 GPa (47.5% reduction versus pure phase) and G_v collapses to 44.242 GPa, while B_v inversely increases to 255.243 GPa. The hardness plunges to 1.835 GPa (76.75% reduction) with the lowest H_v/E_v ratio, representing a 54.54% decrease compared to the undoped material. This anomalous coexistence of enhanced compressibility (elevated B_v) with degraded stiffness (reduced E_v , G_v) and diminished H_v/E_v , along with increased ν (0.418), indicates fundamental changes in deformation mechanisms.

2.2.2 Elastic properties of Fe₃O₄

Fe₃O₄ crystallizes in the cubic system, and its elastic stiffness matrix C_{ij} can be described as follows:

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$

For Fe₃O₄, all elastic moduli can be calculated from the three independent stiffness constants (C_{11} , C_{12} and C_{44}) through standard relations. According to the Born-Huang stability criteria^[44], the cubic crystals lattice remains mechanically stable when the following conditions are satisfied: $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{11} - C_{12} > 0$.

The elastic properties of Mn-doped Fe₃O₄ at varying doping rates (0–100%) were investigated in detailed and the results were summarized in Table 2.

Table 1 Elastic properties of α -Fe₂O₃ at different doping rate

Doping rate/%	Bulk modulus B_v /GPa	Shear modulus G_v /GPa	Young's modulus E_v /GPa	Poisson's ratio ν	Hardness H_v /GPa	H_v/E_v
0	225.842	90.474	239.447	0.323	7.894	0.033
16.67	226.105	88.450	234.741	0.326	7.561	0.032
33.33	204.423	75.749	202.423	0.336	6.370	0.031
50	212.258	67.055	181.999	0.357	5.298	0.029
66.67	231.748	76.448	206.624	0.351	5.618	0.027
83.33	150.568	58.792	156.063	0.327	4.422	0.028
100	255.243	44.242	125.476	0.418	1.835	0.015

Table 2 Elastic properties of Fe₃O₄ at different doping rate

Doping rate/%	Bulk modulus B_V /GPa	Shear modulus G_V /GPa	Young's modulus E_V /GPa	Poisson's ratio ν	Hardness H_V /GPa	H_V/E_V
0	195.800	81.922	215.686	0.316	7.778	0.036
16.67	208.014	52.283	144.725	0.384	3.149	0.022
33.33	231.625	44.294	124.920	0.410	2.054	0.016
50	236.740	39.670	112.715	0.421	1.635	0.015
66.67	242.276	30.516	87.859	0.439	0.981	0.011
83.33	249.489	22.357	65.121	0.456	0.535	0.008
100	260.830	17.579	51.578	0.467	0.326	0.006

Calculated elastic properties of Fe₃O₄ ($B_V = 195.800$ GPa, $E_V = 215.686$ GPa) match well with experimental data ($B_V = 183$ GPa^[50], $E_V = 175$ GPa^[41], 230.33 GPa^[51]), while $\nu = 0.316$ approaches to reported values (0.33 ^[40]). This consistency with established ranges confirms the validity of the chosen computational parameters.

The calculated B_V exhibits a monotonic increase with Mn concentration, indicating that doping Mn enhances resistance to volume deformation. In contrast, the material rigidity is gradually softened with the decrease of G_V and E_V . As the doping concentration progressively increases to 50%, H_V gradually decreases by 78.98%, while the H_V/E_V ratio declines by 58.33%, collectively demonstrating a continuous deterioration in wear resistance. The rise of ν from 0.316 to 0.467 reflects an increased ductility trend.

Notably, the structures at higher doping levels (66.67%–100%) violate the Born-Huang mechanical stability criteria despite their positive elastic moduli ($B_V > 0$, $G_V > 0$ and $E_V > 0$), with the H_V/E_V ratio ultimately decreasing by 83.33%. This implies metastability or potential phase transitions under external stress, as the severe reduction in G_V and E_V undermines shear resistance.

2.2.3 Elastic properties contrast and wear implications in α -Fe₂O₃/Fe₃O₄ redox systems

At identical doping levels, α -Fe₂O₃ exhibits higher G_V , E_V and H_V than Fe₃O₄ (Tables 1 and 2), indicating its superior resistance to elastic deformation and plastic yielding. Although a marginally greater H_V/E_V is observed on undoped Fe₃O₄ (0.036) than α -Fe₂O₃ (0.033), Mn doping reverses this trend. All doped α -Fe₂O₃ systems show higher H_V/E_V ratios than equivalently doped Fe₃O₄ counterparts. As a consequence, the material wear is accelerated due to reduced wear resistance during reduction.

2.3 Impact of Mn doping on the magnetic properties of Fe₃O₄

The magnitude of the atomic magnetic moment can be described as the integral difference between the spin-up and spin-down DOS of states below the E_F ^[52]:

$$m = \left[\int_{E_0}^{E_F} \text{DOS}(\text{spin-up}) dE - \int_{E_0}^{E_F} \text{DOS}(\text{spin-down}) dE \right] \quad (7)$$

where m represents the magnetic moment; DOS(spin-up) and DOS(spin-down) denote the spin-up and spin-down DOS, respectively. The integration limits are defined by the E_F and the DOS at the valence band edge. The magnetic moment of an atom can be qualitatively analyzed through its DOS.

The saturation magnetization (M_s) of Fe₃O₄ ferrite was determined through the following equation^[53]:

$$M_s = \frac{N \times \beta \times M_{\text{tot}}}{M_w} \quad (8)$$

where N represents the Avogadro constant, β is a conversion factor with a magnitude of 9.27×10^{-21} erg/G, M_{tot} corresponds to the total magnetic moment for each formula unit, and M_w refers to the molar mass per formula unit, expressed in grams per mole. The calculated M_s of Fe₃O₄ was determined to be 96.59 emu/g, being in line with previously reported experimental values (90.00 emu/g^[54]).

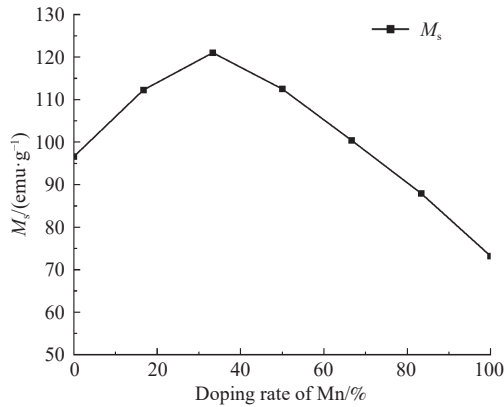
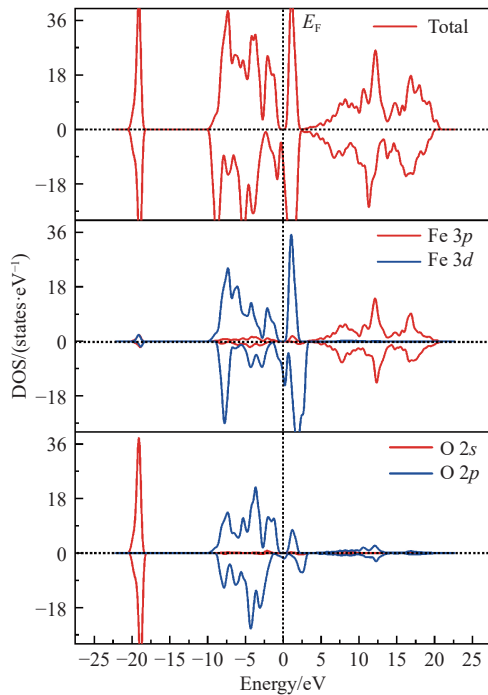
Previous studies have shown that Mn dopants initially occupy tetrahedral sites in spinel ferrites^[55–56]. In accordance with these findings, the present work adopts this tetrahedral-site-preferential doping strategy. The atomic magnetic moments and total magnetic moments at different doping concentrations are presented in Table 3 and Figure 9. With the increase of doping concentration, the M_s first increases and then decreases, and it gets to a maximum value at a doping level of 33.33% (121.02 emu/g). Within the doping range of 16.67%–66.67%, the M_s values are consistently higher than those of the undoped sample. The magnetic moments of both octahedral and tetrahedral Fe ions have a slight fluctuation within a reasonable range (3.90–4.10 μ_B ^[33]). The magnetic moment of octahedral Mn decreases from 4.34 to 4.09 μ_B , while that of tetrahedral Mn remains around 4.70 μ_B . This indicates that Mn primarily exists as Mn³⁺ (typical range: 3.56–3.92 μ_B ^[57]) in octahedral sites, whereas the majority of Mn is Mn²⁺ (typical range: 4.58–4.79 μ_B ^[58]) in tetrahedral sites.

In the DOS plot of Fe₃O₄ (Figure 10), the β -spin channel (negative values) exhibits a clear value at the E_F , while it is absent in the α -spin channel (positive values), confirming the half-metallic character.

In low-concentration Mn-doped Fe₃O₄ (16.67%–33.33%, Figure 11(a), (b)), Mn²⁺ preferentially substitutes tetrahedral Fe³⁺ sites. This substitution weakens the antiferromagnetic coupling between tetrahedral and octahedral Fe ions, giving rise to an increase in total magnetic moment.

Table 3 Magnetic moments of atoms at different doping rates

Doping ratio/%	Total magnetic moment $m/\mu\text{B}$	Octahedral Fe/ μB	Tetrahedral Fe/ μB	Octahedral Mn/ μB	Tetrahedral Mn/ μB
0	32.05	3.85	-3.93	—	—
16.67	35.99	3.96	-3.92	—	-4.71
33.33	40.00	4.10	—	—	-4.71
50	35.93	4.05	-3.81	4.34	-4.70
66.67	32.00	4.04	-3.84	4.23	-4.77
83.33	27.97	4.04	-3.83	4.17	-4.79
100	24.00	—	—	4.09	-4.79

Fig. 9 The M_s moment of each doping rate modelFig. 10 The DOS plots of the Fe_3O_4 model

The introduction of Mn modifies the electronic structure near E_F , as evidenced by the decline in the absolute value of the β -spin DOS from 13.9 to 1.09 states/eV (where the negative sign denotes spin orientation). These changes originate from the disruption of charge ordering at octahedral $\text{Fe}^{2+}/\text{Fe}^{3+}$ sites, and the hybridization between Mn 3d, Fe 3d and O 2p orbitals, which introduces additional

electronic states near E_F .

In Fe_3O_4 with higher Mn doping concentration (50%–100%, Figure 11(c)–(f)), Mn^{3+} substitutes octahedral Fe sites, leading to a 7.05%–39.52% reduction in M_s compared to its maximum value. This decrease is due to the antiferromagnetic alignment of Mn^{2+} and Mn^{3+} moments with surrounding Fe^{3+} spins, and the dilution of ferrimagnetic Fe^{2+} - Fe^{3+} exchange networks. DFT calculations reveal significant electronic reconstruction, where the β -spin DOS at E_F is increased from 7.33 to 17.60 states/eV. This enhancement is driven by two aspects: the formation of Mn3d-derived impurity bands near E_F , and the strong p - d hybridization between Mn 3d and O 2p orbitals that broadens the conduction band.

2.4 Optimal doping concentration selection

Figure 12 shows the multivariate performance assessment of Mn-doped Fe-based oxygen carriers through normalized radar chart analysis. Three key parameters were evaluated across the doping concentration range (0–100%):

(1) E_{vac} , (lower values preferred):

$$\text{Normalized } E_{\text{vac}} = \frac{E_{\text{vac,max}} - E_{\text{vac}}}{E_{\text{vac,max}} - E_{\text{vac,min}}} \quad (9)$$

The E_{vac} data was first interpolated to align with the doping concentrations of other parameters and subsequently normalized to a 0–1 scale, with 1 representing optimal performance (minimum formation energy).

(2) H_V/E_V , (higher values preferred):

$$\text{Normalized } H_V/E_V = \frac{(H_V/E_V) - (H_V/E_V)_{\min}}{(H_V/E_V)_{\max} - (H_V/E_V)_{\min}} \quad (10)$$

(3) M_s , (higher values preferred):

$$\text{Normalized } M_s = \frac{M_s - M_{s,\min}}{M_{s,\max} - M_{s,\min}} \quad (11)$$

After normalization, all parameters were scaled to the range of [0,1], where 1 represents the theoretically optimal value for each performance metric. The H_V/E_V is the average value from both $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 phases, reflecting the wear resistance evolution during reaction processes. Figure 12 displays comprehensive performance scores derived from summing three normalized parameters.

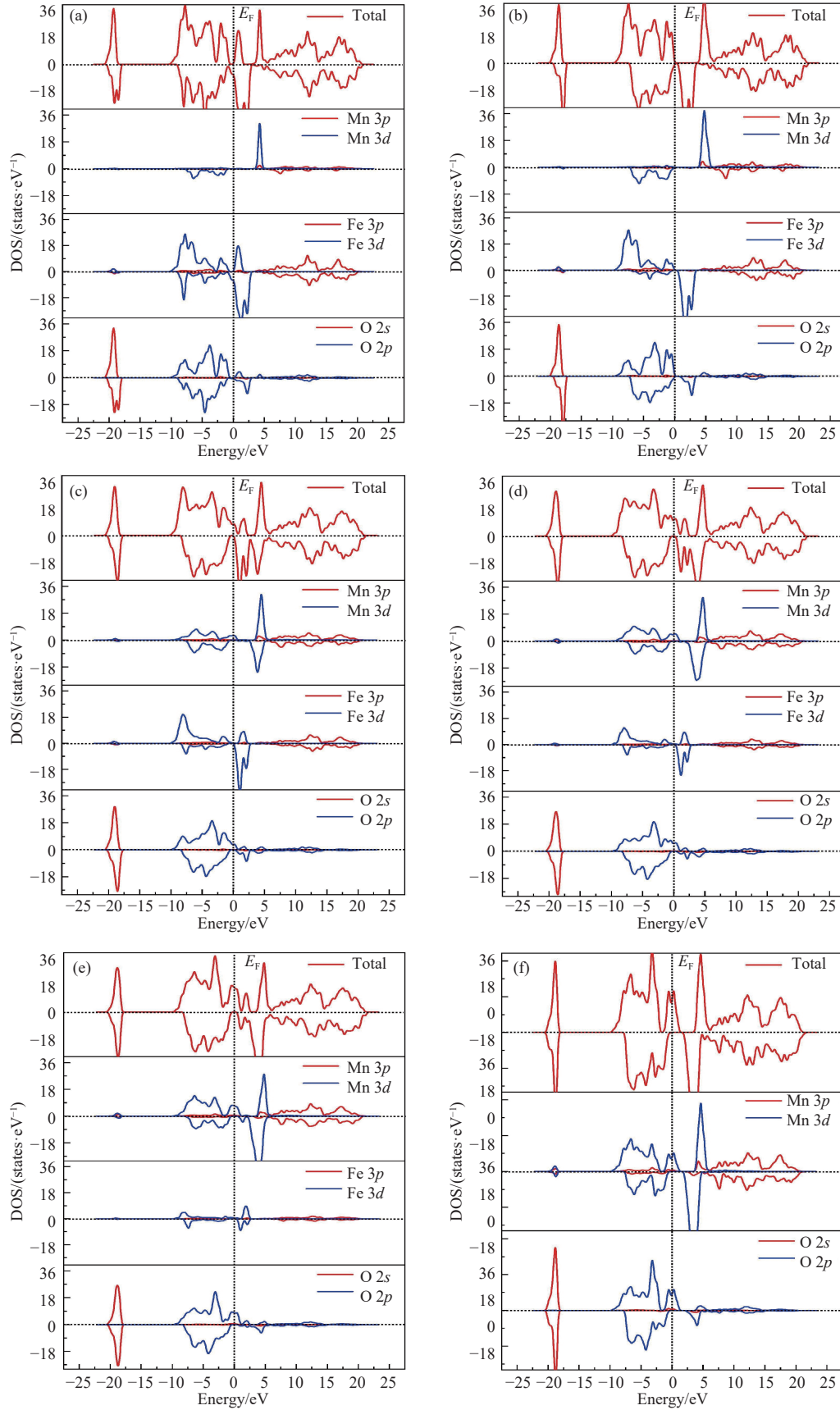


Fig. 11 The DOS plots under different doping rates ((a) 16.67%, (b) 33.33%, (c) 50%, (d) 66.67%, (e) 83.33%, (f) 100%)

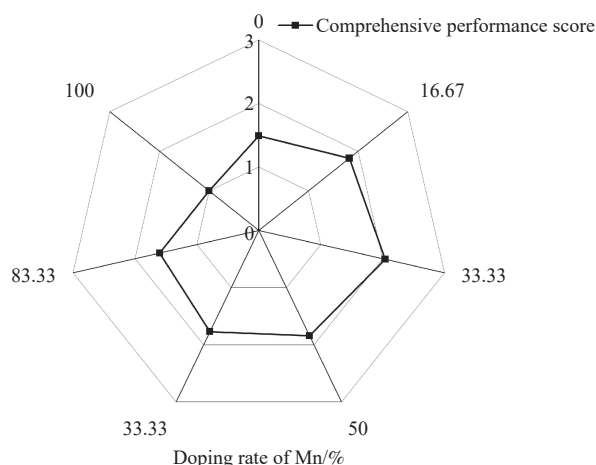


Fig. 12 Comprehensive performance comparison chart

This work employs the baselines evaluation with equal weighting across the following three metrics (oxygen vacancy formation energy, wear resistance, and magnetism) for cross-property comparability. However, their prioritization remains tunable to accommodate specific fuel chemistries and process configurations. The maximum score with optimal material performance is obtained at 33.33% Mn doping concentration. At this doping level, the H_v/E_v ratio exhibits a 6% reduction, in comparison with the undoped reference. Empirical evidence from similar material systems suggest that this modest decrease remains within acceptable operational thresholds for practical applications^[47–48].

According to previous studies, a Mn/(Mn + Fe) molar ratio of 0.5 (corresponding to a doping rate of 50% in this paper) makes the Mn-Fe material present an inert and magnetic carrier, enabling recycling and exhibiting the optimal comprehensive performance^[20]. Therefore, a doping rate of 33.33% was selected as the optimal one, as it induces the best reactivity of the Mn-Fe material as an oxygen carrier.

3 Conclusions

A comprehensive evaluation of $\alpha\text{-Fe}_2\text{O}_3$ with varying Mn doping concentrations was conducted to systematically assess their suitability as oxygen carriers. Special emphasize focus on reactivity (quantified by E_{vac}), wear resistance (quantified by the H_v/E_v ratio), and post-reduction recoverability (via M_s).

For Mn-doped $\alpha\text{-Fe}_2\text{O}_3(001)$, increasing the doping ratio leads to the decrease of oxygen vacancy formation energy (2.33–0.87 eV) in the models, indicating enhanced reactivity. The doping of Mn elevated Mn-3d orbital DOS values from 5.55 to 20.00 states/eV at 5 eV and from –2.65 to –12.10 states/eV at –5 eV. This enhancement is accompanied by strengthened hybridization with O 2p orbitals. In $\alpha\text{-Fe}_2\text{O}_3$ systems with varying Mn-doping concentrations, the elastic properties decline (G_v : 90.474–44.242 GPa, E_v : 239.447–125.476 GPa, H_v :

7.894–1.835 GPa) due to elongation of $\text{Mn}^{3+}\text{-O}$ bonds and disruption of the native bonding network, thereby failing to meet Born-Huang stability criteria at 100% doping. Similar phenomenon is observed in Mn-doped Fe_3O_4 systems; elastic properties decrease (G_v : 81.922–17.579 GPa, E_v : 215.686–51.578 GPa, H_v : 7.778–0.326 GPa), and the material becomes unstable at 66.67%–100% doping levels. The material is softened, as evidenced by a paradoxical combination of increased B_v but significantly reduced G_v and E_v . These reductions in elastic performance correlate with diminished wear resistance, where the H_v/E_v ratios decrease by 54.54% and 83.33% in for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 systems, respectively. In Mn-doped Fe_3O_4 , the M_s initially increases and then decreases with doping concentration, and it gets to a maximum value of 121.02 emu/g at a doping ratio of 33.33%. The Mn^{3+} occupies octahedral sites while Mn^{2+} resides in tetrahedral sites after doping. The increase in Mn ions enhances the hybridization between Mn 3d, Fe 3d and O 2p orbitals.

Overall, the 33.33% Mn-doped composition confirmed the well-balanced performance, combining enhanced reactivity, superior magnetic properties, and favorable elastic stability. These findings offer quantitative guidance for optimizing their reactivity and cyclability in solid fuel CLC.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Mn 掺杂对 α -Fe₂O₃ 反应活性、弹性及磁性能影响的 DFT 计算研究

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摘 要: 载氧体在化学链燃烧(CLC)过程中起着关键作用。铁基载氧体因其储量丰富且对环境友好而备受关注, 但其反应活性和分离性能仍需进一步提升。本研究基于密度泛函理论(DFT)计算, 研究了 Mn 掺杂浓度对 α -Fe₂O₃ 反应活性、弹性性能和磁性能的影响规律。结果表明, Mn 掺杂通过将氧空位形成能(E_{vac})从 2.33 eV 降低至 0.87 eV, 显著提升了材料反应活性; 但会引发晶格畸变导致弹性性能劣化, 使耐磨性下降, 具体表现为 α -Fe₂O₃ 的硬度-杨氏模量比(H_V/E_V)降低 54.54%, Fe₃O₄ 降低 83.33%; 同时 Mn 掺杂会改变材料磁性能, 当掺杂浓度为 33.33% 时, Fe₃O₄ 的饱和磁化强度(M_s)达到最大值 121.02 emu/g。通过综合评估, 最终确定 33.33% 为最佳 Mn 掺杂浓度, 可在提升反应活性的同时兼顾磁性能优化与弹

性稳定性。

关键词: 载氧体; Mn 掺杂 α -Fe₂O₃; 反应活性; 弹性性质; 磁性性质

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