Thermodynamic Stability and Bonding Mechanism of (Fe+Co) Co-doped MgH2 Hydrogen Storage Materials (Postprint)

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Abstract

To investigate the effects of bimetallic co-doping on the hydrogen storage properties of MgH_2 hydrogen storage materials, first-principles calculations based on density functional theory were employed to systematically study the thermodynamic stability and bonding mechanism of (Fe+Co) co-doped MgH_2 hydrogen storage material systems. The lattice structures of the co-doped systems were examined, revealing that after (Fe+Co) co-doping, the volumes of the $Mg_{12}Fe_2Co_4H_{36}$ and $Mg_{12}Fe_4Co_2H_{36}$ unit cells contracted by 16% and 17.5%, respectively. The formation enthalpy of the (Fe+Co) co-doped systems was calculated, with results indicating that the formation enthalpy of the doped systems decreased, which is more favorable for hydrogen desorption. By calculating the Bader charges and electronic density of states of the doped systems, the charge transfer before and after Fe and Co metal doping and the bonding orbitals between metal atoms and hydrogen atoms were explored. Electronic structure analysis demonstrated that after doping, electrons transferred from hydrogen atoms to magnesium atoms, facilitating the weakening of Mg–H bonds. (Fe+Co) bimetallic co-doping exerts a positive influence on the improvement of thermodynamic performance of MgH_2 hydrogen storage materials, providing theoretical guidance for the development of high-performance hydrogen storage materials.

Full Text

Thermodynamic Stability and Bonding Mechanism of (Fe+Co) Co-doped Hydrogen Storage Materials

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Abstract

To explore the effects of bimetallic co-doping on the thermodynamic stability and hydrogen storage performance of hydrogen storage material systems, we systematically investigated the bonding mechanism of (Fe+Co) co-doped MgH_2 using first-principles calculations based on density functional theory. The lattice structures of co-doped systems were examined, and the formation enthalpies of (Fe+Co) co-doped systems were calculated. The results show that the formation enthalpy of the doped system decreases, with the cell volume contracting by 17.5%. Through calculations of Bader charges and electronic density of states for the doped (Fe+Co) systems, electronic structure analysis reveals that electrons transfer from hydrogen atoms to magnesium atoms after doping. Bimetallic co-doping has a positive effect on improving the thermodynamic properties of hydrogen storage materials, providing theoretical guidance for developing high-performance hydrogen storage materials.

Keywords: first-principles; hydrogen storage materials; MgH_2; thermodynamic stability; bimetallic co-doping

1. Introduction

Hydrogen energy, characterized by its green, renewable nature, is considered an ideal secondary energy carrier. The storage and transportation of hydrogen are key technologies for realizing hydrogen energy applications. Magnesium hydride (MgH_2) is regarded as one of the most promising materials for large-scale hydrogen storage applications due to its high hydrogen storage capacity (7.6% mass fraction) and low cost [1-3]. However, MgH_2 suffers from high formation enthalpy, leading to high thermodynamic stability, and high dehydrogenation reaction activation energy, resulting in slow dehydrogenation kinetics ($\Delta H = 75$ $kJ \cdot mol^{-1}$) [4-9]. These drawbacks severely limit its practical applications.

Numerous studies have shown that alloying MgH_2 with transition metal elements, forming composite structures, and using non-equilibrium processing methods can effectively improve the thermodynamic and kinetic properties of magnesium-based hydrogen storage materials [10-11]. The hydrogen absorption/desorption characteristics of hydrides depend largely on their composition, and hydrogen bonds play a major role in hydride stability [10-13]. Related research indicates that when MgH_2 is mechanically alloyed with transition metals such as Al, Ti, Fe, Co, Ni, and Cu, the dehydrogenation performance can be effectively improved, enabling hydrogen absorption at room temperature [13]. For instance, MgH_2 nanosheets can reduce the dehydrogenation temperature to 200°C [13]. Hydride systems can utilize multi-component alloy co-additives to optimize hydrogen storage performance [10-11].

2. Computational Methods

First-principles calculations were performed using density functional theory (DFT) with the projector augmented wave (PAW) method as implemented in the VASP software [14-16]. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form was employed to describe the exchange-correlation interaction between electrons [17]. The cutoff energy for the plane-wave basis set was determined through convergence tests. Gaussian smearing was used with a width of 0.05 eV. For structural optimization, the maximum stress was set to be less than 0.02 eV/Å, and the energy convergence criterion for each atom was 10^{-6} eV.

The primitive cell of rutile-type MgH_2 (space group P42/mnm) was expanded into supercells of $7\$\times7\times11, 5\times5\times11, and 3\times3\times11 for doping studies. After convergence testing, 3\times3\times1 supercell$ was used as the base structure, where metal atoms substituted for Mg at Wyckoff positions. The lattice parameters of α-MgH_2 were measured as a = 4.501 Å and c = 3.010 Å, with Mg at 2a(0,0,0) and H at 4f(0.303,0.303,0) positions [18].

For formation enthalpy calculations, stable elemental crystal structures were used to obtain the energy of single Mg, Fe, Co, and H atoms. The formation enthalpies were calculated as:

$\Delta H(Mg_{18}H_{36}) = E(Mg_{18}H_{36}) - 18E(Mg) - 36E(H)$
$\Delta H(Mg_{12}Fe_2Co_4H_{36}) = E(Mg_{12}Fe_2Co_4H_{36}) - 12E(Mg) - 2E(Fe) - 4E(Co) - 36E(H)$
$\Delta H(Mg_{12}Fe_4Co_2H_{36}) = E(Mg_{12}Fe_4Co_2H_{36}) - 12E(Mg) - 4E(Fe) - 2E(Co) - 36E(H)$

where E represents the total energy of each supercell structure obtained through relaxation calculations.

3. Results and Discussion

3.1 Lattice Structure Analysis

The lattice structures of $Mg_{18}H_{36}$ and its doped variants were systematically investigated. Both co-doping configurations exhibited volume contraction trends. The cell volumes of $Mg_{12}Fe_2Co_4H_{36}$ and $Mg_{12}Fe_4Co_2H_{36}$ contracted by 13.09% and 14.96%, respectively. This volume contraction affects lattice stability and plays a crucial role in improving hydrogen storage characteristics.

3.2 Thermodynamic Stability

The formation enthalpies of pure and co-doped systems were calculated to assess thermodynamic stability. Lower formation enthalpy indicates lower stability, which is beneficial for hydrogen adsorption and desorption. The formation enthalpy values follow the order: $Mg_{18}H_{36} > Mg_{12}Fe_2Co_4H_{36} > Mg_{12}Fe_4Co_2H_{36}$. The bimetallic co-doping effectively reduces the formation enthalpy of MgH_2, with $Mg_{12}Fe_4Co_2H_{36}$ showing better doping effects. This demonstrates that

(Fe+Co) co-doping is an effective method to reduce the thermodynamic stability of hydrogen storage materials.

3.3 Bonding Mechanism

3.3.1 Metal-Metal Bonding The average bond lengths between metal atoms in the doped systems are shorter than in pure $Mg_{18}H_{36}$. The mean metal-metal bond lengths are 3.419 Å for $Mg_{18}H_{36}$, 3.001 Å for $Mg_{12}Fe_2Co_4H_{36}$, and 3.067 Å for $Mg_{12}Fe_4Co_2H_{36}$. Except for the Mg1—Mg2 bond, which lengthens, all other metal bonds shorten after co-doping, indicating significantly enhanced metal-metal bonding and increased alloying tendency. These enhanced metal-metal interactions disrupt the original system balance, weakening the bonding between hydrogen and metal atoms.

3.3.2 Metal-Hydrogen Bonding In $Mg_{18}H_{36}$, hydrogen atoms form octahedral structures with neighboring magnesium atoms. After doping, Fe and Co atoms occupy Mg positions and bond with H atoms in a covalent manner. The TM—H bond lengths in doped systems show complex changes: while most Mg3—H bonds shorten by 1.03–4.59%, some Mg4—H bonds lengthen significantly (e.g., Mg4—H2 increases to 2.31–2.36 Å). Overall, metal co-doping weakens the Mg—H bond strength, which helps lower hydrogen desorption temperature.

3.4 Bader Charge Analysis

Bader charge analysis was performed to estimate the ionicity of chemical bonds. In pure $Mg_{18}H_{36}$, Mg and H atoms have charges of +1.58 and -0.59, respectively, indicating strong ionic bonding. After doping, the absolute Bader charge values decrease substantially: H atoms show reduced anionic character, while Fe and Co have small charge values consistent with their electronegativity. This reduction in ionic bond strength contributes to the improved thermodynamic properties.

3.5 Electronic Structure Analysis

The density of states (DOS) calculations reveal that pure MgH_2 has a large band gap (4.5 eV), making it an insulator. The strong ionic Mg—H bond requires significant energy to break, which is why pure MgH_2 has high thermodynamic stability and decomposition temperature. In contrast, the (Fe+Co) co-doped systems show metallic character with zero band gap. The valence band near the Fermi level is dominated by contributions from Fe and Co d-orbitals, which eliminates the band gap and transforms the material into a conductor.

Partial DOS analysis shows that H1, H2, H3, and H6 atoms have significant hybridization with metal d-orbitals, particularly in the energy range of -6.25 to -2.50 eV. This hybridization correlates with shorter bond lengths for these atoms. However, the overall hybridization effect in doped systems is weaker

than in pure MgH_2, consistent with the longer average TM–H bond lengths and reduced bond strength.

[Figure 3: see original paper]

4. Conclusion

First-principles calculations demonstrate that (Fe+Co) bimetallic co-doping has a positive effect on improving the thermodynamic performance of MgH_2 hydrogen storage materials. The generation enthalpy decreases, and the material transforms from an insulator to a metallic conductor, which enhances thermal conductivity and facilitates hydrogen desorption. The enhanced metal-metal bonding and weakened Mg–H ionic bonding collectively contribute to improved hydrogen storage properties. These findings provide theoretical guidance for developing high-performance hydrogen storage materials and can be extended to ternary hydride systems to elucidate the bonding nature between alloy elements and hydrogen atoms in multi-component systems.

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Note: Figure translations are in progress. See original paper for figures.