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## Studying the Electrocatalytic Hydrogen Evolution Reaction Performance of $Ll_0$ -NiM Intermetallic Compounds by DFT Calculation

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**ABSTRACT:** The intermetallic compounds with modulated electronic structure can provide more catalytically active sites and enhance electrocatalytic performance. In this study, the first-principles calculation method has been employed to investigate the potential of  $Ll_0$ -NiM (M = Mn, Fe, Co, Cu, Zn, Mo) intermetallic compounds for electrocatalytic hydrogen evolution reaction (HER). Firstly, the  $Ll_0$ -NiM present a homogenized charge transfer environment, where the Bader charge difference on the catalyst surface is below 0.13 e, significantly mitigating the locally strong adsorption of adsorbates in Ni. Additionally, the  $Ll_0$ -NiM also fine-tunes the antibonding orbital interactions with adsorbates, facilitating both water dissociation and proton reduction. Furthermore, the  $Ll_0$ -NiCu exhibits better HER electrocatalytic activity, with a water dissociation energy barrier of 0.49 eV and a Gibbs free energy of hydrogen adsorption of  $-0.524$  eV. A scaling relationship analysis reveals a good linear correlation between HER activity and adsorption descriptors across the investigated  $Ll_0$ -NiM intermetallic compounds, providing a theoretical foundation for the development of low-cost catalysts.

**KEYWORDS:** Intermetallic compound;  $Ll_0$ -phase; Ni-based alloys; HER; first-principles calculations

### 1 Introduction

Recently, the establishment of a sustainable, zero-emission energy system has attracted more and more attention [1]. Compared with steam methane reforming and coal gasification, the production of green hydrogen by water electrolysis plays a crucial role in hydrogen energy application and in reducing environmental pollution [2]. The hydrogen evolution reaction (HER) is one of the key reactions in water electrolysis, and it is the common pursuit of researchers to develop HER electrocatalysts with high activity, enhanced chemical stability, and excellent selectivity [3].

Nickel-based alloy catalysts are widely utilized in low-cost alkaline electrolyzers. Compared with pure Ni catalysts, the NiM (M = Mn, Fe, Co, Cu, etc.) alloys can improve the electrocatalytic HER performance by controlling the exposure of active atoms, adjusting the reaction potentials, and enhancing thermal stability at high temperatures [4–6]. Alloying also improves the d-band centre and changes the hydrogen adsorption Gibbs free energy of Ni; the NiCu electrocatalyst is reported to exhibit an approximately optimal  $\Delta G_H$  when compared with Ti, V, Mn, Fe, and Co. The overpotential is only 23 mV at a current

density of  $10 \text{ mA/cm}^2$  [6]. In addition, alloying Ni with similar thermal workability elements (such as Fe, Co, Cu, and so on) can induce the formation of the intermetallic  $L1_0$ -phase to improve catalytic activity [7–10]. The formation of an orderly  $L1_0$ -phase can change the electronic structure, provide more active sites, promote  $\text{H}_2\text{O}$  dissociation, and facilitate H adsorption, which significantly enhances the efficiency of the HER and the oxygen reduction reaction [7–10]. However, the research on ordered intermetallic compounds in electrocatalysis mainly focuses on Pt-based noble metal alloys. Typically, the Fe became more stable in the core-shell structure of  $L1_0$ -FePt/Pt with a 5 Å Pt shell, which enhances the electrocatalysis performance under fuel cell operating conditions by Pt shell compression [11]. The ordered NiPt alloy can be prepared at a lower temperature by tuning the strength of the metal bond, which can be used in fuel cells [12]. Optimizing the composition, size, and ordering degree of Pt-based intermetallic compounds to promote electrocatalysis performance has been widely studied [13–16]. The excellent electrocatalytic performance of ordered Pt-based alloys encourages us to develop ordered non-precious metal catalysts, especially Ni-based intermetallic compounds. Therefore, it is of great significance to analyze the effect of Ni-based intermetallic compounds on HER, revealing the catalytic mechanism will provide a reference for the development of a new high-performance Ni-based electrocatalyst.

In this research, the electrocatalytic HER properties of typical  $L1_0$ -NiM ( $M = \text{Mn, Fe, Co, Cu, Zn, Mo}$ ) intermetallic compounds were studied by First-principles calculations based on Density Functional Theory (DFT). Through key measurement methods such as geometric configuration reorganization, electronic structure changes, and the free energy of the reaction rate-determining step, a comprehensive analysis and discussion of ordered  $L1_0$ -NiM intermetallic compounds is conducted. By understanding the contribution degree of the outer orbitals and the electron migration ability of the active surface, the regularity of HER activity is expounded, expecting to provide effective guidance for the design and development of ordered intermetallic compounds in combination with scaling relationships.

## 2 Calculation Method

The DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) version 5.4.4 [17]. The projective additive wave (PAW) method based on the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation energy function was applied [18]. The super-cell models used in this paper were a  $2 \times 2 \times 2$  expansion of Ni with *fcc* structure and ordered  $L1_0$ -NiM ( $M = \text{Mn, Fe, Co, Cu, Zn, Mo}$ ) alloys with a *fcc* structure. The surface models were the (100) and (111) faces of *fcc*-Ni and  $L1_0$ -NiM. The cutoff energy and *K*-point were selected as 700 eV and  $4 \times 4 \times 1$  by convergence testing. The spin polarization was turned on during calculations to ensure structural stability [19]. To precisely calculate the density of states (DOS), the *K*-point grid was expanded to  $8 \times 8 \times 1$  [20]. Meanwhile, to avoid the mutual interference of the periodic arrangement and eliminate the weak force of interlayer atoms, the thickness of the vacuum layer was selected as 15 Å, and the atom layer is set as 4. To ensure the accuracy of the calculations, the geometry optimization was stopped when the force reached  $0.02 \text{ eV/\AA}$ , the energy reached  $10^{-6} \text{ eV}$ , and the maximum displacement tolerance was  $0.02 \text{ \AA}$ . Free energy corrections for all intermediate species were performed using VASPKIT [21]. The implicit solvation model VASPsol was employed to determine the computational PZCs, where a bulk dielectric constant  $\epsilon_k = 78.4$ , dielectric cavity width  $\sigma = 0.6$ , cutoff charge density  $\rho_{\text{cut}} = 0.0025 \text{ \AA}^{-3}$ , and a surface tension parameter of  $0.525 \text{ meV/\AA}^2$  were used [22]. The LDA + U electronic correlation was used to adopt strong localization in transition metals, the LDAU was set as TRUE, and the initial Hubbard  $U = 4 \text{ eV}$  and  $J = 1 \text{ eV}$  were applied for Ni 3d, Mn 3d, Fe 3d, Co 3d, Cu 3d, Zn 3d, and Mo 4d orbitals. Figures were visualized and analyzed using VESTA [23]. The climbing image nudged elastic band (CI-NEB) method was used to obtain the transition

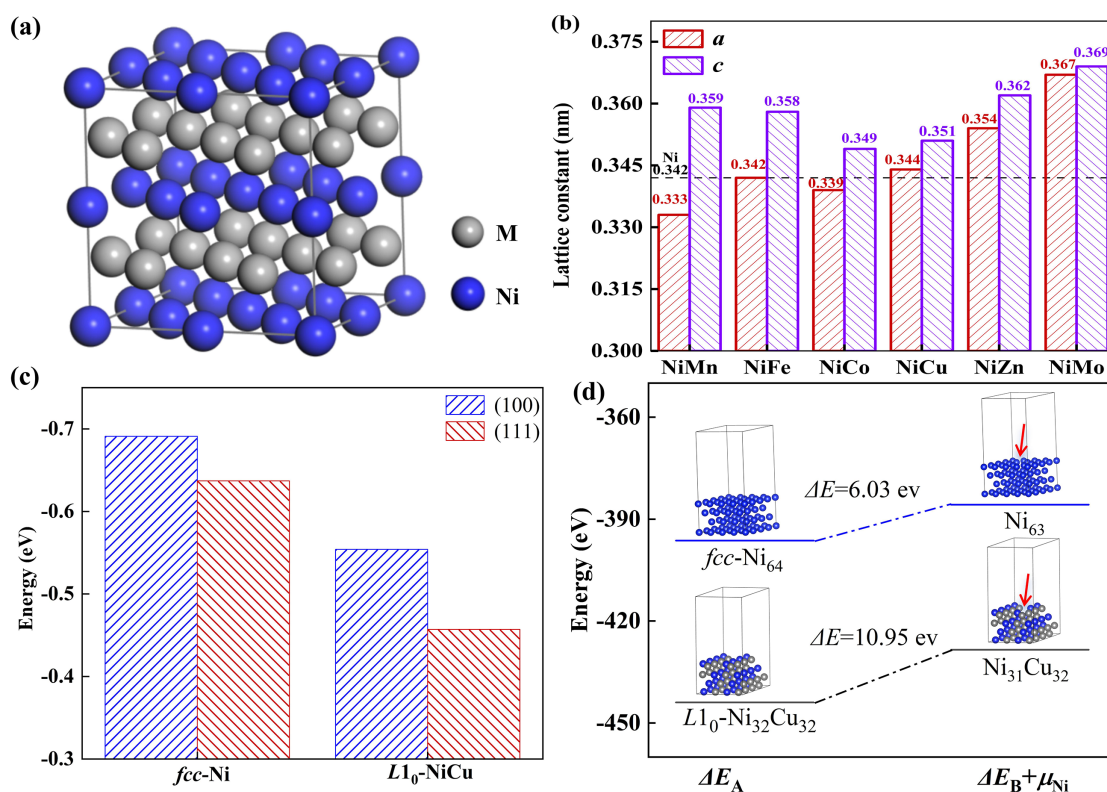
states, where the spring constant  $K$  was set as  $-5$ , and the transition states were verified through vibrational frequency analysis [24].

The electronic and catalytic parameters obtained in this paper were calculated as follows. The energy required for surface dissociation  $\Delta E_d = -\Delta E_A + \Delta E_B + u_x$ , where  $\Delta E_A$  is the total energy of the normal surface,  $\Delta E_B$  is the total energy of the vacant surface, and  $u_x$  is the chemical potential of the  $x$  atom ( $u_{Ni} = -4.51$  eV) [25]. The Gibbs free energy for H adsorption ( $\Delta G_{H^*}$ ) in HER followed the definition described by Nørskov,  $\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$ , where  $\Delta E_{ZPE} = 0.04$  eV was the value of hydrogen adsorption on different metallic surfaces,  $\Delta S_H$  was the entropy difference of H between the adsorption state and the gas phase,  $T$  was the room-temperature 298.15 K, and  $T\Delta S_H$  was determined to be  $-0.20$  eV [26,27]. The effectiveness of the hydrogen catalytic improved with increasing exchange current density ( $i_0$ ), and the  $i_0$  at pH = 0 is calculated as  $i_0 = -ek_0/[1 + \exp(-\Delta G_{H^*}/k_B T)]$ , where the rate constant  $k_0$  is set to 1, and the  $k_B$  is the Boltzmann constant [28]. The  $d$ -band center was determined as  $\epsilon_d = \int_{-\infty}^{\infty} p(\epsilon) \epsilon d\epsilon / \int_{-\infty}^{\infty} p(\epsilon) d\epsilon$ , where  $p$  was the density of states and  $\epsilon$  was the energy width of the  $d$ -orbital [29].

### 3 Results and Discussion

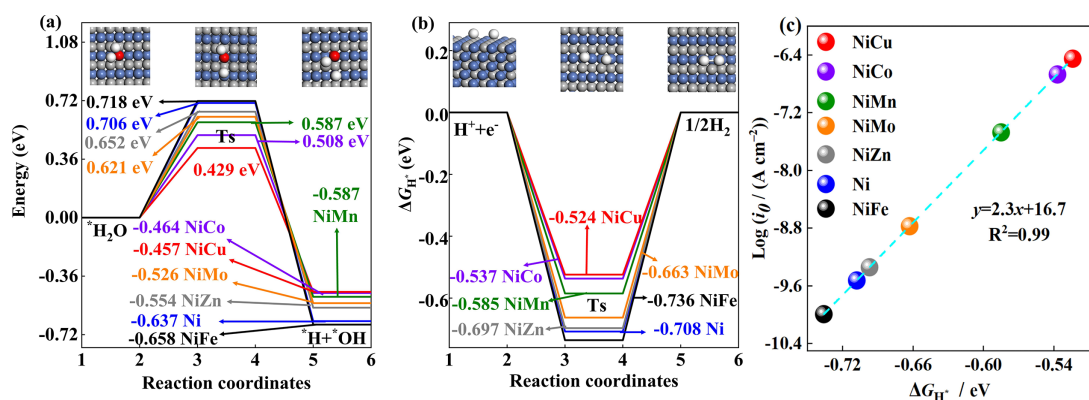
Fig. 1a illustrates the supercell models of  $L1_0$ -NiM ( $M = \text{Mn, Fe, Co, Cu, Zn, Mo}$ ) intermetallic compounds, where Ni and M atoms are periodically arranged along the  $\langle 001 \rangle$  direction. The (111) crystal plane with a lower index of Ni-based alloys is easy to expose on the surface of nanoparticles, which is used to analyze the electrocatalytic HER performance [6,30]. After geometric optimization, the lattice parameters  $a$  and  $c$  of  $L1_0$ -NiM are shown in Fig. 1b. The  $a$  of  $L1_0$ -NiM is unequal to  $c$ , which is different from the  $fcc$  structure [31]. The  $a$  and  $c$  of  $L1_0$ -NiM are related to the atomic radius and Ni-M bond length. All the  $a$  and  $c$  values are around 0.35 nm, falling within the range of 0.33~0.37 nm, which is consistent with the previous calculation results for NiM alloys [6,32]. As the Mn, Fe, and Co atoms show similar atomic radius to Ni, the  $a$ -axis is compressed, and the  $c$ -axis is stretched when forming the  $L1_0$ -phase. In contrast, both the  $a$ -axis and  $c$ -axis are stretched in  $L1_0$ -NiCu,  $L1_0$ -NiZn, and  $L1_0$ -NiMo.

In the process of electrocatalytic alkaline HER, the adsorption of  $H_2O$  on the catalyst surface initiates the reaction, with the dissociation of  $H_2O + e^- \rightarrow OH^- + ^*H$  (Volmer step) being a rate-determining step [4,5,10]. Then, the generation of  $H_2$  follows two typical routes, the Heyrovsky step  $H_2O + e^- + ^*H \rightarrow OH^- + H_2$ , and the Tafel step  $^*H + ^*H \rightarrow H_2$ . Fig. 1c shows the  $H_2O$  dissociation energy of  $fcc$ -Ni and  $L1_0$ -NiCu on both (111) and (100) faces. Clearly, the  $H_2O$  dissociation energy of  $L1_0$ -NiCu is lower than that of  $fcc$ -Ni in both faces, and the  $H_2O$  dissociation energy from (111) faces is lower than that from (100) faces in both alloys. It means the (111) face is a more important electrochemically active center when compared with the (100) face. Fig. 1d shows the energy evolutions of  $fcc$ -Ni and  $L1_0$ -NiCo (111) face to dissociate a Ni atom. Clearly, the total energy  $\Delta E_A$  of  $L1_0$ -NiCo is lower than that of  $fcc$ -Ni, and the energy required for surface dissociation  $\Delta E_d$  of  $L1_0$ -NiCo is higher than that of  $fcc$ -Ni. Both results illustrate that the (111) face of  $L1_0$ -NiCo is more stable and harder to dissociate, revealing a stronger stability in the electrocatalytic HER process.



**Figure 1:** (a) Supercell models and (b) lattice parameters of  $L_{10}$ -NiM intermetallic compounds. (c) The  $H_2O$  dissociation barrier of  $fcc$ -Ni and  $L_{10}$ -NiCu on both (111) and (100) faces. (d) The energy evolutions of  $fcc$ -Ni and  $L_{10}$ -NiCu (111) face to dissociate a Ni atom.

Fig. 2a illustrates the transition state barrier of  $L_{10}$ -NiM intermetallic compounds in the  $H_2O$  dissociation process. The transition state energy barrier of  $H_2O$  dissociation of  $L_{10}$ -NiFe is about 0.718 eV, slightly higher than that of  $fcc$ -Ni (0.706 eV). After the addition of Mn, Co, Cu, Zn, and Mo elements, the  $H_2O$  dissociation transition state barriers of  $L_{10}$ -NiM compounds are decreased. These elements enhance the  $H_2O$  dissociation in the HER process [9,30]. The  $H_2O$  dissociation transition state barrier of  $L_{10}$ -NiCu is the lowest, which indicates that adding the Cu element can promote the  $H_2O$  dissociation process more effectively. The releasing energy of  $L_{10}$ -NiCu for dissociation of  $H_2O$  to  $*H^+$  and  $*OH^-$  is the lowest, which also indicates that the  $L_{10}$ -NiCu is the most suitable intermetallic compound for electrocatalytic  $H_2O$  dissociation. Another important step in the electrocatalytic alkaline HER process is the reduction of  $*H^+$  (Tafel step), which is usually the rate-determining step of electrocatalytic HER in an acidic environment [30–32]. Fig. 2b shows the H-adsorption Gibbs free energy ( $\Delta G_{H^*}$ ) of the  $L_{10}$ -NiM intermetallic compounds. The  $\Delta G_{H^*}$  of  $L_{10}$ -NiFe is about  $-0.736$  eV, lower than that of  $fcc$ -Ni ( $-0.708$  eV). Upon adding Mn, Co, Cu, Zn, and Mo elements, the  $\Delta G_{H^*}$  of  $L_{10}$ -NiM is increased. Similar results can also be found in  $fcc$ -NiM alloys, alloying Mo increases the  $\Delta G_{H^*}$  from  $-0.22$  to  $-0.13$  eV [33], and alloying Cu increases the  $\Delta G_{H^*}$  from  $-0.39$  to  $-0.29$  eV [34] or from  $-0.27$  to  $-0.16$  eV [35]. The  $\Delta G_{H^*}$  of  $L_{10}$ -NiCu is the highest at  $-0.524$  eV, closer to 0 eV, which means the  $L_{10}$ -NiCu is the most suitable intermetallic compound for electrocatalytic H reduction [36,37].



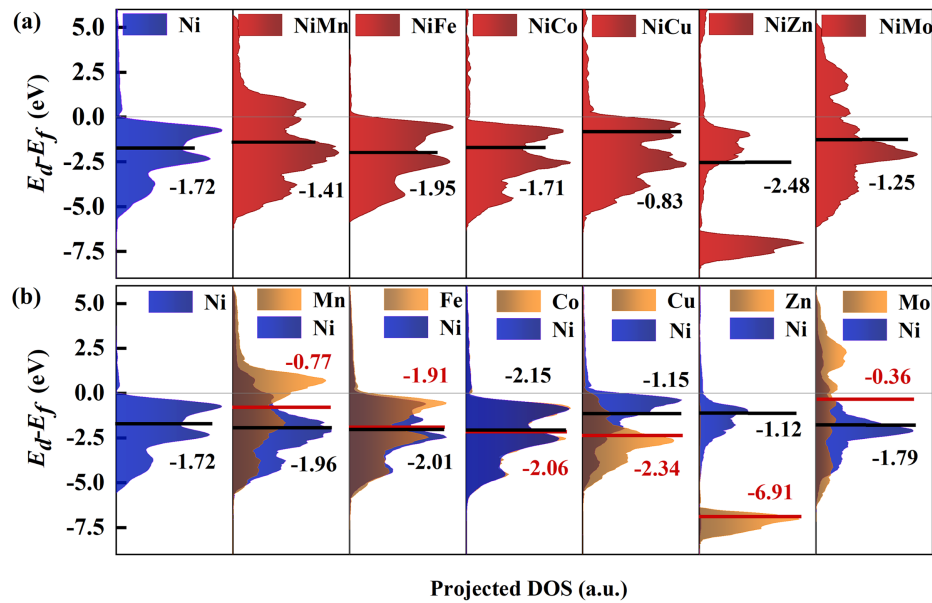
**Figure 2:** (a) H<sub>2</sub>O dissociation energy barrier, (b) H-adsorption Gibbs free energy, and (c) scale relationship between  $\Delta G_{H^*}$  and exchange current density of *L*<sub>10</sub>-NiM intermetallic compounds.

The scale relationship between  $\Delta G_{H^*}$  and exchange current density is established in Fig. 2c, which can visually compare the electrocatalytic HER performance of *L*<sub>10</sub>-NiM intermetallic compounds. The goodness of linear fitting  $R^2$  is as high as 0.99, consistent with the “volcanic plot” on the side of  $\Delta G_{H^*} < 0$ . The *L*<sub>10</sub>-NiCu presents the highest exchange current density and better electrocatalytic H reduction ability [38]. Indeed, electrocatalytic HER is a complex process that is influenced by various factors such as the electrolysis potential, acid or alkaline environment, and concentration. The H<sub>2</sub>O dissociation barrier and single-site  $\Delta G_{H^*}$  are effective parameters for evaluating the electrocatalytic HER activity [4,5,10,31]. Combining the electrocatalytic H<sub>2</sub>O dissociation and H adsorption abilities of *L*<sub>10</sub>-NiM intermetallic compounds, it can be concluded that *L*<sub>10</sub>-NiCu presents better electrocatalytic alkaline HER performance, followed by *L*<sub>10</sub>-NiCo, *L*<sub>10</sub>-NiMn, *L*<sub>10</sub>-NiMo, and *L*<sub>10</sub>-NiZn. The linear scale relationship between  $\Delta G_{H^*}$  and exchange current density further confirms that the *L*<sub>10</sub>-NiM intermetallic compounds present promising applications toward alkaline electrolyzers, which provides a reference for developing similar catalytic systems.

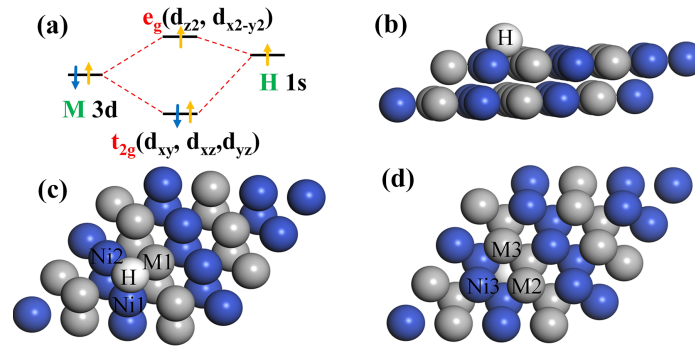
Fig. 3 shows the state densities and the *d*-band centers of the *L*<sub>10</sub>-NiM intermetallic compounds after hydrogen evolution. According to the Sabatier principle, the adsorption of intermediates should not be too strong or too weak, which will lead to the enhancement or weakening of the bonding of the outer electrons. Neither of them is conducive to the formation of electron interaction and directional transport between the adsorbate and the catalysts [39]. The state density of *fcc*-Ni is mainly located below the Fermi level, demonstrating a strong H adsorption ability and confining the electrocatalytic HER performance. The *d*-band center of *fcc*-Ni is calculated to be -1.72 eV, which is comparable with other reports [6–8,10]. Alloying with Mn, Cu, and Mo raises the *d*-band center to the near Fermi level, which will reduce the strong adsorption effect of Ni on proton H<sup>+</sup> and provide favorable conditions for the detachment of H-H\* from the surface of the catalyst. In addition, except for *L*<sub>10</sub>-NiZn and *L*<sub>10</sub>-NiFe, electrons gradually shift in the direction of the empty orbitals of Ni atoms, to achieve a charge-energy equilibrium, when the outer *d*-orbital electrons of the other alloying elements couple with the Ni atoms’ empty orbitals. At this stage, the antibond orbitals will increase, decreasing the surface capacity to adsorb \*H [40]. It also indicates that the introduction of Zn increases the adsorption strength of H, so that the center of the *d*-band of the alloy will move down from -2.48 to -4.53 eV, which is not conducive to the formation of H<sub>2</sub>.

The *d* orbital states of the various atoms were examined following the adsorption of H (Fig. 3b). The peaks of the 3*d* orbitals of Ni and Zn atoms do not intersect when both of them are alloyed, suggesting that there is no interaction between the two atoms, and the alloying effect in *L*<sub>10</sub>-NiZn is insufficient. Additionally, the 3*d* orbital of the Zn atom is too poor, indicating that the *L*<sub>10</sub>-NiZn catalyst has an insufficient surface

adsorption capacity, which may have a substantial effect on surface charge transport [6]. After alloying with Mo and Mn atoms, the peak of the Ni-3d orbital moves in the positive direction across the Fermi level, and some electrons are filled in the antibonding orbital, resulting in stronger adsorption of the catalyst. The analogous electronic configurations of Co, Fe, and Ni atoms lead to equivalent peaks in the Ni-3d, Co-3d, and Fe-3d orbitals, rendering the electronic structures of  $L1_0$ -NiCo and  $L1_0$ -NiFe quite similar compared to that of Ni, thus resulting in a negligible impact on adsorption regulation. The adsorption of catalyst performance reaches the maximum in  $L1_0$ -NiCu, because the Ni-3d orbital becomes flatter and positively shifted, while the Cu-3d orbital is appropriately negatively evacuated ( $-2.34$  eV), the electrons then flow to the bonding orbital. The Mo and Mn atoms positively shift in the center of the  $d$ -band of the alloy catalyst, and the adsorption increases, which is not conducive to improving catalytic activity. Only the  $d$ -band center of the Cu atom ( $-2.12$  eV) is appropriately negatively displaced, indicating that the  $t_{2g}$ -filled electrons are enhanced and the antibond orbital is dragged down (Fig. 4a) [28]. Further analysis of the bonding characteristics can be conducted by observing the band structure of  $L1_0$ -NiCu [41]. The electrocatalytic performance of  $L1_0$ -NiCu alloy was enhanced, and the adsorption strength of the alloy surface to  $^*H$  was tuned while the alloy structure stabilized itself. Although it is hard to establish a quantitative relationship between the  $d$ -band center and adsorption behavior, it can be deduced that the  $L1_0$ -NiCu alloy presents a better  $d$ -band for electrocatalytic HER.

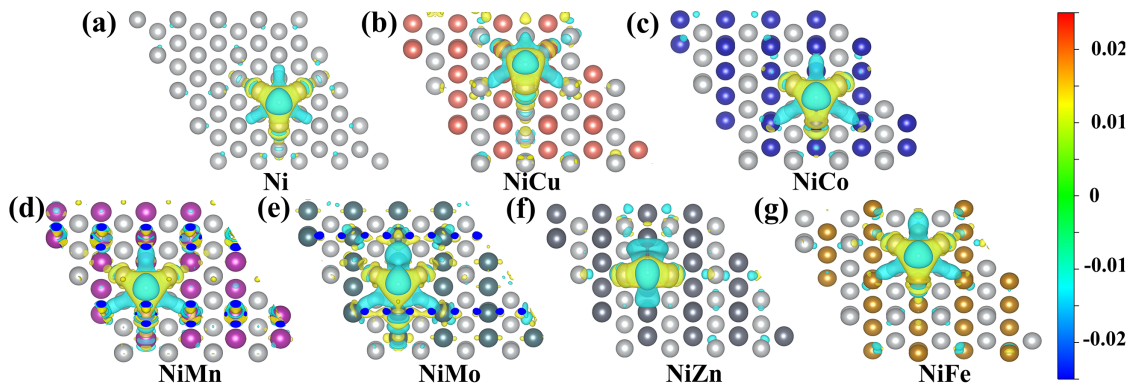


**Figure 3:** (a) States densities and (b) the  $d$ -band centers of  $L1_0$ -NiM intermetallic compounds.



**Figure 4:** (a) Schematic diagram of orbital coupling. Models of Bader charge atoms (b) H atom, (c) H, Ni1, Ni2 and M1 atoms, (d) Ni3, M2 and M3 atoms.

During H dissociation, proton H can interact electronically with multiple adjacent atoms simultaneously, illustrating that the adsorption binding energy of H is influenced by interactions with several atoms [42]. Fig. 5a–g demonstrates the differential charge densities when  $^*H$  is formed on the surface of the ordered  $L1_0$ -NiM catalyst, respectively, and the H atoms are also adsorbed in the hollow position (located at the center of every three atoms on the surface, and there are no atoms at this position one layer below the site). The charge distribution shows the characteristics of homogeneity and symmetry. Combined with the analysis in Table 1 (the atomic number is shown in Fig. 4), this law can also be proved by the Bader charge before the adsorption of H. When Mo, Mn, and Fe elements are added, the yellow area of the differential charge region is increased, and the accumulated Bader charge number of  $^*H$  is increased, from 0.17 e to 0.2~0.24 e of Ni. It means the adsorption of H is more stable, with enhanced charge transfer and interaction between H atoms and the catalyst surface, while the strong adsorption of Ni for H remained intact. When Co atoms are added, the yellow area of the differential charge region is all gathered around the Ni atoms, the charge migration degree of Co atoms is low, and the charge amount on H does not decrease. After the addition of Cu element, the yellow region of the differential charge region is attracted by the Cu element, which alleviates the strong adsorption of Ni atoms, and the Bader charge on  $^*H$  is the smallest of 0.161 e, which promotes the adsorption and charge transfer of H atoms. Although it is hard to establish a quantitative relationship between the Bader charge and energy barriers, it also indicates that the alloy surface could improve the HER activity at this stage.

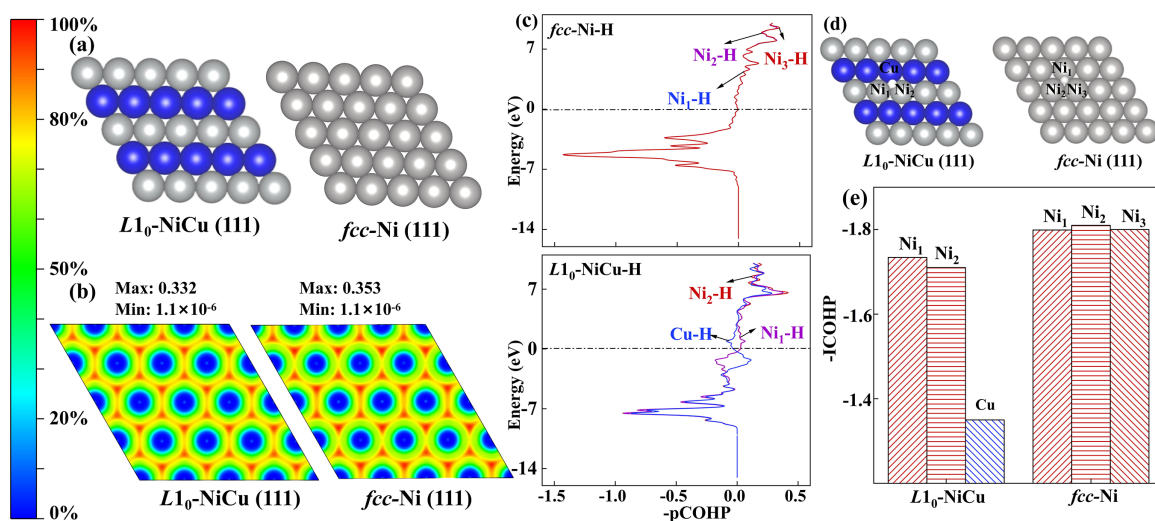


**Figure 5:** Differential charge density diagram of  $L1_0$ -NiM intermetallic compounds. (a)  $fcc$ -Ni, (b)  $L1_0$ -NiCu, (c)  $L1_0$ -NiCo, (d)  $L1_0$ -NiMn, (e)  $L1_0$ -NiMo, (f)  $L1_0$ -NiZn, and (g)  $L1_0$ -NiFe.

**Table 1:** Change of Bader charge (e) on the ordered alloy surface before and after adsorption of H (The lower corner of 0 represents the original model before hydrogen evolution).

|      | H     | Ni <sub>0</sub> 1 | Ni <sub>1</sub> | Ni <sub>0</sub> 2 | Ni <sub>2</sub> | Ni <sub>0</sub> 3 | Ni <sub>3</sub> | M <sub>0</sub> 1 | M <sub>1</sub> | M <sub>0</sub> 2 | M <sub>2</sub> | M <sub>0</sub> 3 | M <sub>3</sub> |
|------|-------|-------------------|-----------------|-------------------|-----------------|-------------------|-----------------|------------------|----------------|------------------|----------------|------------------|----------------|
| Ni   | 0.170 | 0.026             | 0.028           | 0.037             | -0.024          | -0.049            | -0.022          | —                | —              | —                | —              | —                | —              |
| NiCo | 0.181 | 0.112             | 0.059           | 0.112             | 0.048           | 0.061             | 0.050           | -0.07            | -0.091         | -0.07            | -0.083         | -0.104           | -0.093         |
| NiCu | 0.161 | 0.055             | 0.015           | 0.055             | 0.044           | 0.012             | 0.027           | -0.014           | -0.087         | -0.014           | -0.087         | -0.055           | -0.066         |
| NiMn | 0.208 | 0.266             | 0.195           | 0.266             | 0.190           | 0.265             | 0.266           | -0.220           | -0.277         | -0.220           | -0.277         | -0.294           | -0.288         |
| NiMo | 0.230 | 0.391             | 0.341           | 0.391             | 0.309           | 0.405             | 0.398           | -0.334           | -0.356         | -0.334           | -0.408         | -0.456           | -0.448         |
| NiZn | 0.197 | 0.221             | 0.163           | 0.221             | 0.158           | 0.173             | 0.174           | -0.18            | -0.268         | -0.18            | -0.214         | -0.22            | -0.212         |
| NiFe | 0.240 | 0.216             | 0.173           | 0.216             | 0.120           | 0.183             | 0.187           | -0.183           | -0.235         | -0.183           | -0.233         | -0.214           | -0.207         |

The electron location function (ELF) is used to quantitatively illustrate the peripheral electrons of *fcc*-Ni and *L*<sub>10</sub>-NiCu. The atom models and two-dimensional ELF from (111) faces of *fcc*-Ni and *L*<sub>10</sub>-NiCu are shown in Fig. 6a,b, respectively. Both the ELF values are lower than 0.5, which indicates that the peripheral electrons of the nucleus have a free distribution and typical metal bonding in *fcc*-Ni and *L*<sub>10</sub>-NiCu. The maximum ELF value of *L*<sub>10</sub>-NiCu (0.332) is lower than that of *fcc*-Ni (0.353), which means the freedom degree and delocalization of Ni peripheral electrons are enhanced by the formation of *L*<sub>10</sub>-NiCu. This is why the *L*<sub>10</sub>-NiCu can exhibit better electrocatalytic performance.



**Figure 6:** ELF calculation of *fcc*-Ni and *L*<sub>10</sub>-NiCu intermetallic compounds. (a) Models, (b) ELF. COHP calculation of *fcc*-Ni and *L*<sub>10</sub>-NiCu intermetallic compounds. (c) COHP diagrams, (d) models, and (e) bonding strength.

The crystal orbital Hamilton population (COHP) is used to quantitatively evaluate the bond strengths of \*H on the surface of the catalyst. The COHP diagrams and atom models from (111) faces of *fcc*-Ni and *L*<sub>10</sub>-NiCu are shown in Fig. 6c,d, respectively. The COHP diagrams of three Ni atoms in *fcc*-Ni show no significant changes, and the bonding strength is about -1.80 eV (Fig. 6e). On the contrary, the COHP diagrams of Ni and Cu atoms in *L*<sub>10</sub>-NiCu are quite different, the bonding strength of Cu-H (-1.35) is lower than that of Ni-H (-1.72). It means the Cu-H bond is easier to break, which facilitates the electrocatalytic HER process. In addition, the average bonding strength of *L*<sub>10</sub>-NiCu is lower than that of *fcc*-Ni, the strong adsorption effect of Ni is thus weakened by the formation of *L*<sub>10</sub>-NiCu. Both quantitative results indicate that the *L*<sub>10</sub>-NiCu presents better electrocatalytic HER performance, consistent with the analysis of reaction barriers, hydrogen adsorption free energies, *d*-band, and Bader charge.

## 4 Conclusion

This research evaluates the fundamental hydrogen evolution capacity of  $L1_0$ -NiM intermetallic compounds at a theoretical level. In  $L1_0$ -NiM ( $M = \text{Mn, Fe, Co, Cu, Zn, Mo}$ ) intermetallic compounds, the introduction of alloy elements can effectively modify the position of the electron orbitals, and the ordered  $L1_0$ -structure can better homogenize the electrons on the surface. The homogeneous electron distribution can effectively improve the hydrogen evolution activity, and the good charge distribution will not make the adsorbate strongly adsorbed on the surface of the catalyst. Therefore, there is no polarization of the non-homogeneous charge, which in turn causes strong adsorption of H. The addition of Cu, Co, Mo, and Mn elements in  $L1_0$ -NiM can weaken the binding of adsorbates by lowering the  $d$ -band center and inducing the reduction of the antibonding orbital. In this way, the  $\text{H}_2\text{O}$  dissociation barrier can be reduced, and the H adsorption Gibbs free energy can be increased to close to 0 eV, thereby improving the activity and stability of electrocatalytic HER. It was found that the  $L1_0$ -NiCu could achieve the highest HER activity, with free energy and hydrolysis energy barriers of  $-0.524$  and  $0.49$  eV, respectively. It was proven that a suitable  $d$ -band center and homogenized Bader charge could effectively optimize the HER process and accelerate the HER kinetics. This study provides an effective scientific foundation for the application of intermetallic compounds in HER and related catalytic reactions.

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