Front. Phys., 2011, 6(2): 214–219
DOI 10.1007/s11467-011-0172-5

RESEARCH ARTICLE

Substitution effects on the hydrogen storage behavior of AB_2 alloys by first principles

Fen LI[1,2,3], **Ji-jun ZHAO**[1,2,†], **Li-xian SUN**[3,*]

[1] *Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China*

[2] *College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China*

[3] *Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Dalian 116023, China*

E-mail: †*zhaojj@dlut.edu.cn,* **lxsun@dicp.ac.cn*

Received January 23, 2011; accepted March 22, 2011

The hydrogen storage behavior of the $TiCr_2$ and $ZrCr_2$ alloys substituted with the third components (Zr, V, Fe, Ni) have been studied using first-principles calculations. The change of the hydrogen absorption energies caused by metal doping is arising from the charge transfer among the doped alloys interior. Zr and V atoms devoted abundant electrons, leading to a great enhancement of the H absorption energy, while Fe and Ni atoms always accepted electrons, yielding a remarkable decrease of the H absorption energy. The hydrogen diffusion energy barrier is closely correlated with the geometry effect rather than the electronic structure.

Keywords alloy, hydrogen storage, doping, first-principles

PACS numbers 88.30.R-, 88.30.rd, 66.30.-h

1 Introduction

The search for ideal hydrogen storage materials has put forward huge demand for the industrialization of hydrogen energy. Many new materials, like carbon or boron based nanostructures, metal organic frameworks (MOFs) and covalent organic frameworks (COFs), have been proposed as potential candidates for hydrogen storage in virtue of their excellent characteristics, such as high gravimetric and volumetric density, low cost, safety, and moderate working conditions [1–7]. However, few of them have been utilized in practice due to some fundamental and technological bottlenecks. On the other hand, traditional hydrogen storage alloys still play a central role in the present market because of the mature technique and the flexible and controllable chemical compositions although their storage capacities have not yet reached the standard for on-broad applications [8, 9]. For example, the $LaNi_5$ based alloys as hydrogen storage medium have been commercialized. Hence, there is still much room for the development of alloys in their hydrogen storage applications.

There have been numerous fundamental studies on the hydrogen storage behavior of different types of binary alloys. Among them are the AB_5 type ($LaNi_5$) alloys, which, as the early generation of hydrogen storage materials, have been intensively studied for their superior hydrogen absorption-desorption properties, which is one of the key factors for realistic hydrogen storage applications. A lot of experimental and theoretical efforts have been devoted to understanding the thermodynamic/kinetic properties and electronic structures of the $LaNi_5H_x$ hydrides [10–12]. However, it is hard to further improve the hydrogen storage capacity for the AB_5 alloys. Compared to the AB_5 alloys, the alloys of AB (TiFe) and A_2B (Mg_2Ni) types exhibit relatively higher hydrogen storage capacity (about 1.89% for TiFe alloy and 3.59% for Mg_2Ni) with lower cost [9], whereas they also suffer from fatal technical bottlenecks such as difficulty in activation (for AB alloys [13]), sluggish hydriding/dehydriding kinetics and low electrochemical discharge capacity at room temperature (for A_2B alloys [14]). Among the available hydrogen storage materials, AB_2 type alloys show better integrated characteristics of high gravimetric percentage, long cycle life, and low cost.

Overall speaking, the hydrogen storage behavior of all these binary alloys still can not satisfy all of the commercial requirements. One feasible way to improve the hydrogen storage properties of those intermetallic compounds is alloying with other elements. It has been shown that the components and stoichiometry of these alloying

©Higher Education Press and Springer-Verlag Berlin Heidelberg 2011

elements remarkably affect the hydrogen storage properties of the host materials [15–18].

For the $LaNi_5$-related intermetallic compounds, their thermodynamic and the electrochemical properties rely strongly on the substituted element and its content [19–23]. By mechanically alloying with the catalytic element like Pd or Ni, the thermodynamic properties, activation process and the hydriding/dehydriding kinetic of TiFe systems have been substantially modified [24–26], similar to the behavior observed in the Mg_2Ni-based compounds [27–30]. For the AB_2-based systems, substitution of both A-type and B-type elements leads to the great improvements in the activation process, hydrogen storage capacity, thermodynamic properties and charging/discharging kinetics [31–36]. For instance, Mani *et al.* reported that partial substitution of B-type transition elements (M =V, Cr, and Al) in $ZrMnFe_{0.5}Ni_{0.5}$ and $ZrMnFe_{0.5}Co_{0.5}$ systems has significant effects on the lattice parameter, hydrogen storage properties including plateau pressure, plateau slope, and thermodynamic, etc. [17]. Kandavel *et al.* found that the increase of Zr content (A-type) leads to the decrease in the equilibrium hydrogen sorption pressure plateau and fast absorption kinetics, which are associated with the increase of hydrogen storage capacity for $Ti_{1.1}CrMn$ and $(Ti_{0.9}Zr_{0.1})_{1.1}CrMn$ [35]. Unfortunately, they are barely able to provide a thorough illumination for the mechanism of how components and stoichiometry of the alloying elements affect the hydrogen storage properties of the host binary metals.

Parallel to the experimental efforts, the theoretical investigations, especially the first-principles calculations, provide a possible way to the intrinsic mechanism. Zhang *et al.* investigated the role of Al in the $LaNi_5$-type hydrogen storage alloys by first-principles calculations [37]. At semi-empirical level, Li *et al.* studied the hybrid characteristics of the $Mg_{2-x}A_xNi_{1-y}B_y$ alloy systems and illustrated the relationship between the macroscopic characteristics and atomic structures [38]. In addition, some mathematical models have been applied to selected hydrogen storage properties (formation enthalpy and hysteresis) of AB_2-type alloys [39–41]. However, our current theoretical understanding on the multi-component alloys is still very limited. In particular, none of the previous first-principles calculations have been conducted on the AB_2-type alloys with third components to the best of our knowledge.

Recently, our group has systematically investigated the hydrogen storage behavior of the binary $TiCr_2$ alloy [42]. As an extension of this work, we perform here first-principles calculations to clarify the influences of components and stoichiometry on the hydrogen storage behavior of multi-component AB_2-based compounds. The hydrogen absorption sites, absorption energy, crystal structure, interaction between the hydrogen and the metal hosts, and the barrier energies in the A/B substituted AB_2 alloys have been computed and discussed.

2 Computational methods

All calculations were performed with the CASTEP program, which is based on the density functional theory (DFT) and planewave pseudopotential technique [43, 44]. Generalized gradient approximation (GGA) of the PW91 functional [45, 46] were adopted for describing the exchange–correlation interaction, and the ultrasoft pseudopotentials [47] was used for modeling the ion–electron interaction. A cutoff energy of 400 eV was used for the planewave basis. Most calculations were done on the unit cell of $TiCr_2$ of Laves phase (C14 type), which contains 4 formula units, 12 atoms. The Brillouin zone was sampled by a 6×6×4 $\boldsymbol{k}$ grid. Test calculations showed that further increasing the cutoff energy or $\boldsymbol{k}$ grid leads to little changes on the computed total energy and stress tensor. Our previous work in the same computational scheme have demonstrated that this method is appropriate for describing the $TiCr_2$ systems [42].

All the structures were fully relaxed during geometry optimizations. The convergence criteria were set as: the energy changes on each atom being less than 1×10^{-5} eV, the maximum force less than 0.05 eV, and the maximum stress less than 0.1 GPa. The calculated lattice constants of the $TiCr_2$ and $ZrCr_2$ crystals (of C14 type) were $a = b = 4.908$ Å, $c = 7.874$ Å and $a = b = 5.097$ Å, $c = 8.159$ Å, respectively, well consistent with the experimental values: $a = b = 4.918$ Å, $c = 7.962$ Å for $TiCr_2$ [48] and $a = b = 5.106$ Å, $c = 8.292$ Å for $ZrCr_2$ [49], respectively.

The absorption energy of an H atom in substituted AB_2 compounds can be obtained via the following formula:

$$E_{\mathrm{abs}} = \frac{1}{x}\left[E(\mathrm{TiCr_2H}_x) - E(\mathrm{TiCr_2})\right] - \frac{1}{2}E(\mathrm{H_2})$$

where $E(A)$ means the total energy of system A. The absorption energy measures the energy difference of an H atom inside the $TiCr_2H_x$ hydrides and in the gaseous H_2 molecule. Positive E_{abs} value represents endothermic reaction, and negative E_{abs} denotes exothermic reaction.

3 Results and discussion

We chose the $TiCr_2$ and $ZrCr_2$ compounds with C14 type Laves-phase structures as the representatives for AB_2 alloys. Within one unit cell, there are four Ti and eight Cr atoms. Starting from the binary $TiCr_2$ crystals, we substituted the Ti atoms (A-type) by Zr atoms in the stoichiometries of $Ti_{0.75}Zr_{0.25}Cr_2$ and $Ti_{0.5}Zr_{0.5}Cr_2$, and replaced Cr atom (B-type) by Fe or V atoms in the

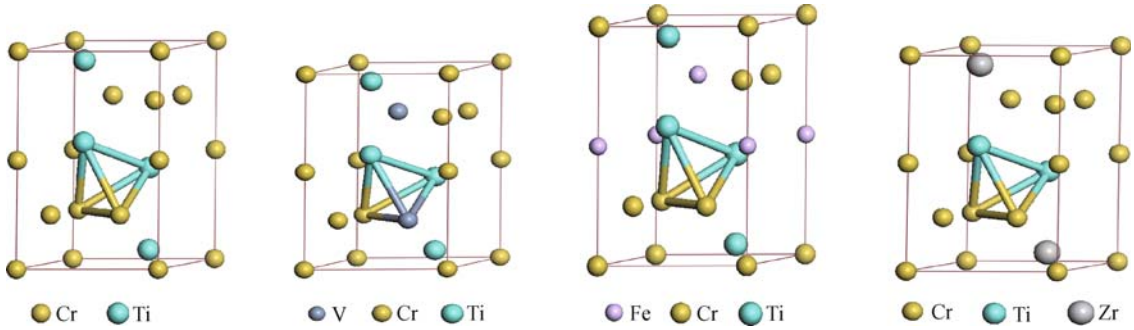

Fig. 1 Representative crystal structures of pure $TiCr_2$, V-substituted Ti–Cr–V ($TiCr_{1.5}V_{0.5}$), Fe-substituted Ti–Cr–Fe ($TiCr_{1.5}Fe_{0.5}$), and Zr-substituted Ti–Zr–Cr ($Ti_{0.5}Zr_{0.5}Cr_2$) compounds.

Table 1 Hydrogen absorption energies (eV/H) for the energetically favorable sites within $TiCr_2$- and $ZrCr_2$-based alloys.

$TiCr_2$-based alloys			$ZrCr_2$-based alloys		
Alloy	Favorable site	E_{ads} /(eV/H)	Alloy	Favorable site	E_{ads} /(eV/H)
$TiCr_2$	2Ti–2Cr	−0.17			
$Ti_{0.75}Zr_{0.25}Cr_2$		−0.30			
$Ti_{0.5}Zr_{0.5}Cr_2$		−0.30			
$TiCr_2$	2Ti–2Cr	−0.17	$ZrCr_2$	2Zr–2Cr	−0.28
$TiCr_{1.75}Fe_{0.25}$		−0.12	$ZrCr_{1.75}Ni_{0.25}$		−0.25
$TiCr_{1.5}Fe_{0.5}$		−0.09	$ZrCr_{1.5}Ni_{0.5}$		−0.25
$TiCr_{1.25}Fe_{0.75}$		−0.06	$ZrCr_{1.25}Ni_{0.75}$		−0.24
$TiCr_{1.0}Fe_{1.0}$		−0.06	$ZrCr_{1.0}Ni_{1.0}$		−0.09
$TiCr_2$	2Ti–Cr–V	−0.17	$ZrCr_2$	2Zr–Cr–V	−0.28
$TiCr_{1.75}V_{0.25}$		−0.31	$ZrCr_{1.75}V_{0.25}$		−0.46
$TiCr_{1.5}V_{0.5}$		−0.51	$ZrCr_{1.5}V_{0.5}$		−0.53
$TiCr_{1.25}V_{0.75}$		−0.52	$ZrCr_{1.25}V_{0.75}$		−0.52
$TiCr_{1.0}V_{1.0}$		−0.62	$ZrCr_{1.0}V_{1.0}$		−0.58

stoichiometries of $TiCr_{1.75}Fe_{0.25} \sim TiCr_{1.0}Fe_{1.0}$ or $TiCr_{1.75}V_{0.25} \sim TiCr_{1.0}V_{1.0}$, respectively. Similarly, as for the $ZrCr_2$ crystals we substituted Cr with Ni or V atoms in the stoichiometries of $ZrCr_{1.75}Ni_{0.25} \sim ZrCr_{1.0}Ni_{1.0}$ or $ZrCr_{1.75}V_{0.25} \sim ZrCr_{1.0}V_{1.0}$, respectively. The stoichiometries for all studied systems are summarized in Table 1 and a few representative alloy structures are presented in Fig. 1.

It is possible that the crystal structure of the ternary alloy may undergo some phase change when the third alloying element is added. However, we did not take into account such structural change due to the following reasons: i) In this work we mainly focus on the substitution effects on the hydrogen storage behavior rather than the structural change; ii) there are many possible structures for different ternary compositions and it would be difficult to include all of them; iii) the local circumstance of the hydrogen absorption site did not dramatically change with different structural phases.

For each alloy system, we have explored all the possible hydrogen absorption sites and determined the energetically favorable sites for accommodating H atom. For all circumstances, the H atom tends to occupy the tetrahedral interstitial sites, whereas the detailed chemical environment varies with the stoichiometry of the alloy, as summarized in Table 1. For example, the preferred H absorption sites are 2Ti2Cr for the $Ti_{1-x}Zr_xCr_2$ and $TiCr_{2-x}Fe_x$, and 2TiCrV for the $TiCr_{2-x}V_x$ and $ZrCr_{2-x}V_x$ compounds.

Although the atomic radius of Zr is larger than Ti, the most favorable hydrogen absorption site in Zr-substituted $TiCr_2$ alloy is surrounded by Ti and Cr atoms rather than Zr atoms. Our previous calculations revealed that the H prefers 2A2B site in binary $TiCr_2$ alloy due to the large interstitial space [42]. The present results, however, imply that the larger interstitial space is not the sole factor determining the most preferred absorption site. Influences by the electronic structures and the detailed hydrogen-metal interactions must be taken into account.

The calculated hydrogen absorption energies in the energetically favorable sites of these systems are listed in Table 1 and plotted in Fig. 2. Clearly, substitution of A-type Ti atoms with Zr leads to significant increase in the magnitude of H absorption energies. With one Zr atom per unit cell ($Ti_{0.75}Zr_{0.25}Cr_2$), the H absorption energy rises to 0.3 eV, compared to 0.17 eV in the binary $TiCr_2$ compound. In the $Ti_{0.5}Zr_{0.5}Cr_2$ compound with two Zr atoms per unit cell, the absorption energy reduces to 0.25 eV. The H absorption energy slightly oscillates with the Zr composition and rises to 0.28 eV in $ZrCr_2$ (see Fig. 2). Overall speaking, the Ti alloying effect on

the hydrogen storage behavior $ZrCr_2$ is not straightforward according to our present calculations. Experimentally, Kandavel *et al.* proved that the substitution of the A-type Zr increased the hydrogen storage capacity from 1.9% to 2.2% for $Ti_{1.1}CrMn$ and $(Ti_{0.9}Zr_{0.1})_{1.1}CrMn$, respectively [35].

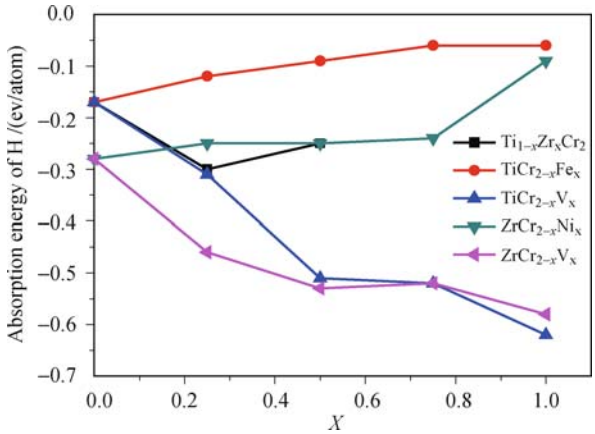

Fig. 2 Absorption energy of H (eV) versus the ratio of the third-component metal within $TiCr_2$ and $ZrCr_2$ based alloys.

For the B-type substitution, replacing Cr by Fe dramatically weakened the H absorption energy, i.e., from 0.17 eV for $TiCr_2$ to 0.12 eV for $TiCr_{1.75}Fe_{0.25}$ and 0.06 eV for $TiCr_{1.25}Fe_{0.75}$, as shown in Fig. 2. Similarly, the hydrogen absorption energy in the $ZrNi_xCr_{2-x}$-based alloy also gradually decreases as the Ni content increases (see Fig. 2). On the contrary, introducing V into both $TiCr_2$ and $ZrCr_2$ compounds greatly enhances the hydrogen absorption energy. Thus, the present theoretical results suggest that the Fe and Ni elements are helpful for hydrogen desorption while V is a terrific element for improving the affinity of H. Accordingly, Bobet *et al.* demonstrated that the Ni substitution caused an increase of the plateau pressure, while the V decreased the plateau pressure and increased the hydrogen storage capacity in previous experiments [32].

We now discuss the H–M interaction between hydrogen (H) and metal (M) atoms in terms of interatomic charge transfer by Mulliken analysis. Our theoretical results are shown in Table 2 for $TiCr_2$-based alloys and Table 3 for $ZrCr_2$-based alloys, respectively. The H atoms accept 0.33 electrons from Cr atom rather than Ti in the pure C14-type $TiCr_2$ alloy, consistent with our previous result of C15-type $TiCr_2$ alloy [42], implying a stronger interaction of H-B-type than H-A-type.

In the $TiCr_2$-based compounds with Ti, V and Fe substitution, the interstitial H atoms always accept about 0.35 electrons from the surrounding metal atoms. In the case of $Zr_xTi_{1-x}Cr_2$ compounds, the most favorable absorption site is surrounded by two Ti and two Cr atoms and the electrons donated from Zr atoms do not directly divert to the H atom. However, the electrons accepted by the Ti and Cr atoms enhance the H–Cr and H–Ti interaction and improve the hydrogen absorption energy. For the TiV_xCr_{2-x} systems, there are substantial amount of electrons (0.4–0.46 e) donated from V atoms, which partially accounts for the remarkable increase of H absorption energy. In addition, the extra electrons on H atom mainly come from V. Accordingly, the most favorable H absorption site is 2Ti2V rather than 2Ti2Cr. On the other hand, the existence of Fe atoms as electron acceptor in the $TiFe_xCr_{2-x}$ systems increases the on-site charge on Cr atoms and weakens the H–Cr and H–Ti interaction. Therefore, there is a clear correlation between the on-site charge of third alloying element and the variation of H absorption energy. Similar phenomena are also observed in the $ZrCr_2$-based systems, in which V is electron donor and Ni is acceptor. The former enhances the H–M interaction while the latter reduces the H absorption energy.

Table 2 On-site charge (e) for H absorbed $TiCr_2$-based alloys from Mulliken analysis.

System	Ti	Cr	Third element (Zr, Fe or V)	H
$TiCr_2$	−0.07	0.08		−0.33
$Ti_{0.75}Zr_{0.25}Cr_2$	−0.06	0.03	0.29	−0.32
$Ti_{0.5}Zr_{0.5}Cr_2$	−0.19	−0.01	0.41	−0.32
$TiCr_{1.75}Fe_{0.25}$	−0.09	0.15	−0.38	−0.33
$TiCr_{1.5}Fe_{0.5}$	−0.08	0.19	−0.25	−0.34
$TiCr_{1.25}Fe_{0.75}$	−0.09	0.26	−0.2	−0.33
$TiCr_{1.0}Fe_{1.0}$	−0.06	0.3	−0.15	−0.33
$TiCr_{1.75}V_{0.25}$	−0.11	0.06	0.41	−0.36
$TiCr_{1.5}V_{0.5}$	−0.17	0.02	0.45	−0.35
$TiCr_{1.25}V_{0.75}$	−0.21	−0.01	0.4	−0.36
$TiCr_{1.0}V_{1.0}$	−0.27	−0.10	0.46	−0.35

Table 3 On-site charge (e) for H absorbed $ZrCr_2$-based alloys from Mulliken analysis.

System	Zr	Cr	Third element (V/Ni)	H
$ZrCr_2$	0.3	−0.11		−0.32
$ZrCr_{1.75}V_{0.25}$	0.22	−0.13	0.39	−0.34
$ZrCr_{1.5}V_{0.5}$	0.13	−0.16	0.37	−0.33
$ZrCr_{1.25}V_{0.75}$	0.04	−0.18	0.36	−0.34
$ZrCr_{1.0}V_{1.0}$	−0.05	−0.26	0.4	−0.33
$ZrCr_{1.75}Ni_{0.25}$	0.30	−0.09	−0.27	−0.32
$ZrCr_{1.5}Ni_{0.5}$	0.32	−0.08	−0.24	−0.32
$ZrCr_{1.25}Ni_{0.75}$	0.30	−0.04	−0.22	−0.32
$ZrCr_{1.0}Ni_{1.0}$	0.33	−0.05	−0.20	−0.32

The direction of charge transfer can be interpreted in terms of the electronegativity (χ) [50]. Compared to these metal atoms (χ=1.33−1.91), H has a large electronegativity (χ=2.1); thus, it always accepts electrons from the metal atoms. Zr is a major electron donator since it has the least electronegativity (χ=1.33) among those metal atoms. V is also a significant electron donator since it has the less electronegativity (χ=1.63) than the original B-type Cr atom (χ=1.66). Owing to their rel-

atively larger electronegativity, the Fe (χ=1.83) and Ni (χ=1.91) elements inside the alloys usually accept electrons from the other metal atoms and then weaken the H–M interaction.

In addition, the substitution by the third component also affects the hydrogen diffusion behavior. With the rigid lattice model approximation, we computed the hydrogen diffusion barriers of the $TiCr_2$-based systems. In order to reveal the effects of the alloying elements, we focused on the absorption site surrounded by the third component rather than those energetical sites. The theoretical H diffusion barriers for different systems are listed in Table 4. In the $Ti_{0.5}Zr_{0.5}Cr_2$ compound, diffusion of H from one interstitial site surrounded by Zr atom to another requires to overcome an energy barrier of 0.21 eV, lower than the barrier of 0.39 eV in the binary $TiCr_2$ alloy. In other words, substitution of Zr by Ti can reduce the hydrogen diffusion barrier in the $TiCr_2$ alloy, in accordence with the previous experimental finding that the increase of Zr content leads to the decrease in the equilibrium hydrogen sorption pressure plateau and fast absorption kinetics [34]. As shown in Table 4, the addition of Fe also slightly lowers the diffusion barrier. In contrast, substitution of V improves the energy barrier although it is favorable for the hydrogen absorption. There seems no distinct relationship between the hydrogen diffusion barrier and the electronic structures of the alloys.

Table 4 Barrier energies of H atom in the pure $TiCr_2$, $Ti_{0.5}Zr_{0.5}Cr_2$, $TiCr_{1.5}V_{0.5}$ and $TiCr_{1.5}Fe_{0.5}$ compounds.

System	Barrier energy /eV
$TiCr_2$	0.39
$Ti_{0.5}Zr_{0.5}V$	0.21
$TiCr_{1.5}V_{0.5}$	0.55
$TiCr_{1.5}Fe_{0.5}$	0.34

4 Conclusions

We have studied the effects of the third-component metal (Zr, V, Fe, Ni) substitution on the hydrogen storage behavior of the binary $TiCr_2$ and $ZrCr_2$ alloys. The energetically preferred hydrogen absorption sites and the absorption energies have been obtained by means of first-principle calculations. Addition of Zr and V atoms greatly improves the H absorption energy, whereas Fe and Ni elements reduce the absorption energy. This can be interpreted by charge transfer between the H and the metal atoms determined from the Mulliken analysis. The hydrogen diffusion barrier is also affected by the third-component elements, that is, Zr greatly lowers the barrier and V significantly heightens it. The present first-principles results give some atomistic clue on the effect of alloying elements in the ternary hydrogen storage alloys of AB_2-type and might be helpful for further improving their hydrogen storage performance.

Acknowledgements The authors gratefully acknowledge the financial supports for this work from the Central Universities of China (No. DUT10ZD211), the National Natural Science Foundation of China (Grant Nos. 10774019, 20833009, 20873148, U0734005, 51071146, and 51071081), the National Basic Research Program of China (973 program) (Grant No. 2010CB631303), Dalian Scientific Fund (Grant No. 2009A11GX052), and the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology (Grant Nos. KFJJ08-5 and KFJJ10-1Z).

References

1. Y. F. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett., 2005, 94(15): 155504
2. M. Li, Y. F. Li, Z. Zhou, P. W. Shen, and Z. F. Chen, Nano Lett., 2009, 9(5): 1944
3. J. L. C. Rowsell and O. M. Yaghi, Angew. Chem. Int. Ed., 2005, 44(30): 4670
4. D. J. Collins and H. C. Zhou, J. Mater. Chem., 2007, 17(30): 3154
5. L. J. Murray, M. Dincă, and J. R. Long, Chem. Soc. Rev., 2009, 38(5): 1294
6. S. S. Han, H. Furukawa, O. M. Yaghi, and Goddard, J. Am. Chem. Soc., 2008, 130(35): 11580
7. H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131(25): 8875
8. L. Zaluski and A. Zaluska, J. Alloys Comp., 1997, 253(1–2): 70
9. L. Schlapbach and A. Züttel, Nature, 2001, 414(6861): 353
10. D. Ohlendorf and H. E. Flotow, J. Chem. Phys., 1980, 73(6): 2937
11. S. Srivastava and O. N. Srivastava, J. Alloys Comp., 1999, 290: 250
12. K. Tatsumi, I. Tanaka, H. Inui, K. Tanaka, M. Yamaguchi, and H. Adachi, Phys. Rew. B, 2001, 64(18): 184105
13. J. H. Sanders and B. J. Tatarchuk, J. Less Common Met., 1989, 147(2): 277
14. J. H. Woo and K. S. Lee, J. Electrochem. Soc., 1999, 146(3): 819
15. Y. H. Zhang, X. P. Dong, D. L. Zhao, S. H. Guo, Y. Qi, and X. L. Wang, Trans. Nonferrous Met. Soc., 2008, 18(4): 857
16. Y. H. Xu, C. P. Chen, X. L. Wang, Y. Q. Lei, and Q. D. Wang, J. Alloys Comp., 2002, 337: 214
17. N. Mani and S. Ramaprabhu, Int. J. Hydrogen Energy, 2005, 30(1): 53
18. C. Iwakura, H. Kasuga, I. Kim, H. Inoue, and M. Matsuoka, Electrochim. Acta, 1996, 41: 2694
19. Y. F. Liu, H. G. Pan, M. X. Gao, Y. F. Zhu, and Y. Q. Lei, J. Alloys Comp., 2004, 365: 246
20. S. Vivet, J. M. Joubert, B. Knosp, P. Ochin, and A. P. Guégan, J. Alloys Comp., 2008, 465: 517
21. Y. H. Zhanga, D. L. Zhao, B. W. Li, X. L. Zhao, Z. W. Wu, and X. L. Wang, Int. J. Hydrogen Energy, 2008, 33: 1868
22. S. L. Li, P. Wang, W. Chena, G. Luo, D. M. Chen, and K. Yang, J. Alloys Comp., 2009, 485: 867
23. Y. Li, D. Han, S. M. Han, X. L. Zhu, L. Hu, Z. Zhang, and Y. W. Liu, Int. J. Hydrogen Energy, 2009, 34(3): 1399

24. L. Zaluski, A. Zaluska, P. Tessier, J. O. Ström-Olsen, and R. J. Schulz, Mater. Sci., 1996, 31: 695
25. H. Miyamura, M. Takada, K. Hirose, and S. Kikuchi, J. Alloys Comp., 2003, 356–357: 755
26. T. Kondo, K. Shindo, and Y. Sakurai, J. Alloys Comp., 2005, 404–406: 511
27. L. Smardz, M. Jurczyk, K. Smardz, M. Nowak, M. Makowiecka, and I. Okonsk, Renew. Energy, 2008, 33(2): 201
28. D. H. Xie, P. Li, C. X. Zeng, J. W. Sun, and X. H. Qu, J. Alloys Comp., 2009, 478: 96
29. Y. H. Zhang, H. P. Ren, S. H. Guo, Z. G. Pang, Y. Qi, and X. L. Wang, J. Alloys Comp., 2009, 480: 750
30. Z. M. Wang, H. Y. Zhou, Z. F. Gu, G. Cheng, and A. B. Yu, J. Alloys Comp., 2004, 381(1–2): 234
31. X. Y. Song, Y. Chen, Z. Zhang, Y. Q. Lei, X. B. Zhang, and Q. D. Wang, Int. J. Hydrogen Energy, 2000, 25(7): 649
32. J. L. Bobet and B. Darriet, Int. J. Hydrogen Energy, 2000, 25(8): 767
33. W. E. Triaca, H. A. Peretti, H. L. Corso, A. Bonesi, and A. Visintin, J. Power Energy, 2003, 113: 151
34. T. Z. Huang, Z. Wu, B. J. Xia, and T. S. Huang, Mater. Chem. Phys., 2005, 93: 544
35. M. Kandavel, V. V. Bhat, A. Rougier, L. Aymarda, G. A. Nazri, and J. M. Tarascon, Int. J. Hydrogen Energy, 2008, 33(14): 3754
36. K. Young, T. Ouchi, J. Koch, and M. A. Fetcenko, J. Alloys Comp., 2009, 477: 749
37. R. J. Zhang, Y. M. Wang, D. M. Chen, R. Yang, and K. Yang, Acta Mater., 2006, 54(2): 465
38. Q. Li, Q. Lin, K. C. Chou, L. J. Jiang, and K. D. Xu, J. Alloys Comp., 2005, 397: 68
39. S. S. Fang, Z. Q. Zhou, J. L. Zhang, M. Y. Yao, F. Feng, D. O. Northwood, J. Alloys Comp., 1990, 293: 10
40. D. J. Davidson, S. S. Sai Raman, M. V. Lototskyc, and O. N. Srivastava, Int. J. Hydrogen Energy, 2003, 28(12): 1425
41. S. S. Fang, Z. Q. Zhou, J. L. Zhang, M. Y. Yao, F. Feng, and D. O. Northwood, Int. J. Hydrogen Energy, 2000, 25(2): 143
42. F. Li, J. J. Zhao, D. X. Tian, H. L. Zhang, X. Z. Ke, and B. Johansson, J. Appl. Phys., 2009, 105(4): 043707
43. M. C. Payne, M. P. Teter, D. C. Alan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys., 1992, 64(4): 1045
44. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, Z. Kristallogr., 2005, 220(5–6): 567
45. J. P. Perdew and Y. Wang, Phys. Rev. B, 1992, 45(23): 13244
46. M. R. Johnson, K. Parlinski, I. Natkaniec, and B. S. Hudson, Chem. Phys., 2003, 291(1): 53
47. D. Vanderbilt, Phys. Rev. B, 1990, 41(11): 7892
48. T. Z. Huang, Z. Wu, B. J. Xia, and N. X. Xu, Mater. Sci. Eng. A, 2005, 397: 284
49. J. L. Soubeyroux, M. Bououdina, D. Fruchart, and P. D. Range, J. Alloys Comp., 1995, 231(1–2): 760
50. L. Pauling, General Chemistry, 3rd Ed., San Francisco: W. H. Freeman Press, 1970