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Functional anion concept: effect of fluorine anion on hydrogen storage of sodium alanate†

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Doping NaAlH_4 with Ti-catalyst has produced a promising hydrogen storage system that can be reversibly operated at moderate temperature conditions. Of the various dopant precursors, TiCl_3 was well recognized due to its pronounced catalytic effect on the reversible dehydrogenation processes of sodium aluminium hydrides. Quite recently we experimentally found that TiF_3 was even better than TiCl_3 in terms of the critical hydrogen storage properties of the doped hydrides, in particular the dehydriding performance at $\text{Na}_3\text{AlH}_6/\text{NaH} + \text{Al}$ step at moderate temperature. We present here the DFT calculation results of the TiF_3 or TiCl_3 doped Na_3AlH_6 . Our computational studies have demonstrated that F^- and Cl^- anions differ substantially from each other with regard to the state and function in the doped sodium aluminium hydride. In great contrast to the case of chloride doping where Cl^- anion constitutes the “dead weight” NaCl , the fluoride doping results in a substitution of H^- by F^- anion in the hydride lattice and accordingly, a favorable thermodynamics adjustment. These results well explain the observed dehydriding performance associated with $\text{TiF}_3/\text{TiCl}_3$ -doping. More significantly, the coupled computational and experimental efforts allow us to put forward a “functional anion” concept. This renews the current mechanism understanding in the catalytically enhanced sodium alanate.

1. Introduction

Onboard hydrogen storage has been generally recognized as a key technical challenge in commercialization of hydrogen technology. The combined stringent requirements on energy density, operation conditions, discharging/recharging rates and reversibility for the onboard H-storage system have largely frustrated numerous efforts on various metal hydrides and nano-structured carbon materials.¹ In 1997, an investigation of Bogdanović and Schwickardi demonstrated that, upon doping with Ti-catalysts, NaAlH_4 might undergo reversible dehydrogenation under moderate temperature range.² This discovery sparked extensive research interests on various lightweight complex hydrides as potential H-storage medium.^{3–7}

With the aid of appropriate catalyst, the large amounts of covalently bonded hydrogen in complex metal hydrides may be available for practical hydrogen storage application. Therefore, understanding of the catalytic mechanism in the Ti- NaAlH_4 model system has been a subject of great interest. During the past decade, several hypotheses have been proposed to picture the nature of the active Ti-species.^{8–13} While being fundamentally different on the understanding of the nature of active Ti-species and their state in the hydride

matrix, the various opinions share a common feature—focusing attention only on Ti-cation and/or its derivatives while neglecting the simultaneously incorporated anions. In our recent investigation, however, we found that the variation of dopant precursor from TiCl_3 to TiF_3 resulted in a significantly different de-/hydriding performance.¹⁴ Moreover, structural investigations also demonstrated some substantial difference between the samples doped with different dopant precursors.^{14–16} These findings challenge the traditional belief about the state and role of anions of dopant precursors in the reversible dehydrogenation of the doped hydrides.

In this paper, we present a density functional theory (DFT) calculation on TiF_3 or TiCl_3 -doped Na_3AlH_6 . In consistence with the experimental observations,^{14–16} the theoretical calculation elucidates that differing substantially from Cl^- , F^- could be incorporated in the hydride(s) lattice during the reversible de-/hydriding cycle. In particular, it was found that the substitution of F^- for H^- rendered favorable thermodynamics modification.

2. Methods and computation details

Limited by the thermodynamic property, Na_3AlH_6 generally needs to be heated up to over 150 °C to achieve an acceptable decomposition rate, thus largely degrading the dehydriding performance of NaAlH_4 . Quite recently, we found that the utilization of TiF_3 as dopant precursor resulted in a more pronounced enhancement on the $\text{Na}_3\text{AlH}_6/\text{NaH} + \text{Al}$ decomposition step, compared with TiCl_3 .¹⁴ For simplicity, we therefore focus on this reaction step (eqn (1)) and construct

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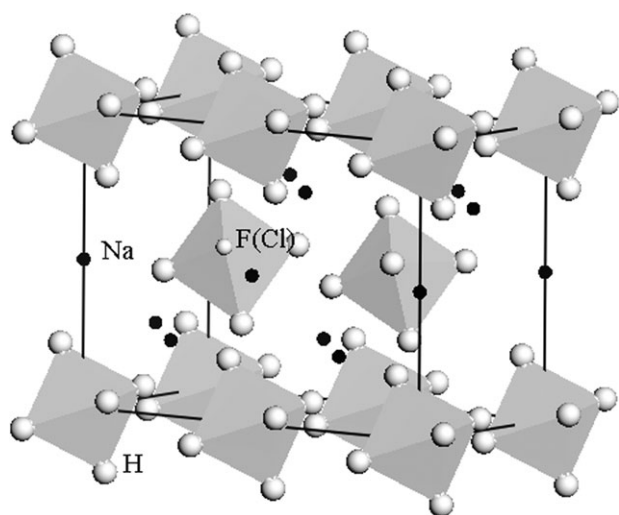


Fig. 1 Structure model of Na_3AlH_6 $1 \times 2 \times 1$ supercell, in which Na and H atoms are presented by black and white spheres, respectively. AlH_6 units centered at Al atoms are presented by grey octahedra. The smaller white sphere indicates the site where hydrogen is substituted by Cl or F atom.

a $1 \times 2 \times 1$ Na_3AlH_6 supercell consisting of 40 atoms ($\text{Na}_{12}\text{Al}_4\text{H}_{24}$) and a $3 \times 1 \times 1$ NaH supercell consisting of 24 atoms ($\text{Na}_{12}\text{H}_{12}$).



To model the substitution of F^- or Cl^- at H^- site, we used the $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{Cl}_1$ supercells (see Fig. 1). The calculations were performed within the generalized gradient approximation (GGA) to density functional theory (DFT)^{17,18} using projector augmented plane wave method (PAW),¹⁹ as implemented in VASP code.^{20,21} The pseudopotential configurations that yielded the minimum energies for all involved structures included: the $\{2s^2 2p^6 3s^1\}$ electrons for Na, the $\{3s^2 3p^1\}$ electrons for Al, the $\{1s^1\}$ electron for H, the $\{2s^2 2p^5\}$ electrons for F and the $\{3s^2 3p^5\}$ for Cl. The energy cutoff for the plane wave basis set is taken to be $E_{\text{cut}} = 600$ eV. In all calculations, the total energy convergence within 0.1 meV was achieved. During the calculation, the structure (ionic coordinates and unit cell vectors) was fully optimized by minimizing the Hellmann–Feynman forces on the atoms and stresses on the supercell, but without any symmetry constraint. The calculated cell parameters $a = 5.36$ Å, $b = 5.54$ Å, $c = 7.72$ Å and $\beta = 89.72^\circ$ of pure Na_3AlH_6 are highly consistent with the corresponding experimental values of 5.40 Å, 5.51 Å, 7.73 Å, and 89.86° , respectively.²² See the ESI for other details of calculations.†

3. Results and discussion

Experimentally, we have performed a systematic investigation on TiF_3 or TiCl_3 doped sodium alanates, and observed the property improvement arising upon changing the dopant precursor.¹⁴ In view of the identity of Ti cation and the similarity in chemical reactivity of the two dopant precursors, the observed property difference should clearly be associated

with the variation of halide anions. We therefore focus on the state and function of F^- and Cl^- anions in the present study.

To evaluate the favorability of the doping-induced incorporation of halide anions into Na_3AlH_6 host lattice, we first calculated the enthalpy of formation, ΔH_{form} , of the $\text{Na}_{12}\text{Al}_4\text{H}_{24}$, $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{Cl}_1$ supercells following eqn (2).

$$\begin{aligned} \Delta H_{\text{form}}(\text{Na}_{12}\text{Al}_4\text{H}_{24-x}\text{F}(\text{Cl})_x) \\ = \frac{E(\text{Na}_{12}\text{Al}_4\text{H}_{24-x}\text{F}(\text{Cl})_x) - (12E(\text{Na}) + 4E(\text{Al}) + \frac{24-x}{2}E(\text{H}_2) + \frac{x}{2}E(\text{F}(\text{Cl})_2))}{N_{\text{atom}}} \end{aligned} \quad (2)$$

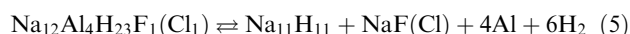
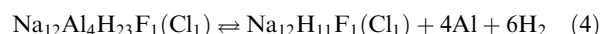
$$x = 0 \text{ or } 1$$

Here, to allow a reasonable approximation of the experimental conditions, a substitution ratio $\text{F}(\text{Cl}) : \text{H} = 1 : 23$ was selected, which corresponds to a near 3 mol% doping level of Ti(III) halides. In all cases, the enthalpy change was referenced to the energies of the stoichiometric equivalents of the constituent atoms in their standard state.¹² The calculated formation enthalpies of the three compounds are -17.2 , -29.0 and -21.8 kJ mol⁻¹, respectively. Accordingly, the enthalpies of substitution, ΔH_{subst} , of $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{Cl}_1$ were calculated to be -11.8 and -4.6 kJ mol⁻¹, respectively, following eqn (3).

$$\begin{aligned} \Delta H_{\text{subst}}(\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}(\text{Cl})_1) \\ = \frac{(E(\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}(\text{Cl})_1) + \frac{1}{2}E(\text{H}_2)) - E(\text{Na}_{12}\text{Al}_4\text{H}_{24}) - \frac{1}{2}E(\text{F}(\text{Cl})_2)}{N_{\text{atom}}} \end{aligned} \quad (3)$$

It should be noted that all the enthalpy values given here were divided by the number of atoms N_{atom} (kJ mol⁻¹ atom) in the substituted periodic cell. The negative (exothermic) ΔH_{subst} is indicative of a thermodynamically favorable substitution reaction. From an energetic point of view, it is therefore possible that both F^- and Cl^- anions are incorporated into the Na_3AlH_6 lattice and substitute for H^- anion. This should be quite understandable from the hydride–fluoride isostructure that has been well established in a range of hydrides–fluorides over a wide range of stoichiometries.^{23–26} For example, Na_3AlF_6 possesses same crystal structure and nearly identical lattice parameters to its counterpart, Na_3AlH_6 .²⁷ The following examination of the dehydriding reaction of the doped hydrides, however, reveals a substantial difference between F^- and Cl^- anions.

The incorporated halide anions have two possible destinations after dehydriding reaction, as given in eqns (4) and (5).



One is to be incorporated into NaH as a substitutional anion. The other is to combine with Na^+ cation to generate inactive sodium halide. Fig. 2 presents the calculated formation enthalpies and reaction enthalpies, which allow us to judge the reaction preference. In the case of $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{Cl}_1$, a much

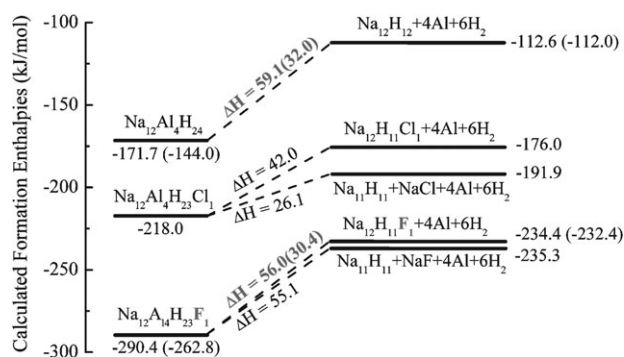


Fig. 2 Schematic representation of the calculated formation and reaction enthalpies. The calculated enthalpies after zero-point energies correction are given in brackets.

lower endothermic enthalpy (26.1 kJ mol^{-1}) following eqn (5), compared to the value (42.0 kJ mol^{-1}) following eqn (4), clearly indicates the preference of inactive NaCl formation. This result agrees well with the experimental observations, in which a generation of segregated NaCl crystal has been well established by XRD examination,^{14–16} while for $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$, the reaction enthalpies following eqns (4) and (5) were calculated to be 56.0 and 55.1 kJ mol^{-1} , respectively, with only a slight difference of 0.9 kJ mol^{-1} . From our thermochemical calculation results, it is difficult to judge the reaction preference of F^- -doped Na_3AlH_6 . While NaF phase has not yet been definitely experimentally identified in the TiF_3 -doped hydrides in both dehydrogenated and hydrogenated states,^{14–16} on the other hand, the substitution of F^- anion into NaH lattice has been experimentally validated by XRD examination. In this regard, our results agree well with those reported by Majzoub *et al.*²⁸ The lattice parameter of NaH decreases nearly linearly with increasing the TiF_3 doping level (the ionic radii of H^- and F^- are 2.08 and 1.36 \AA , respectively), and could be well fitted with the line connecting the parameters of NaH and NaF. Based on the combined experimental and theoretical results, it is reasonable to believe that F^- is, at least partially, incorporated in NaH lattice and substitutes for H^- anion after decomposition reaction of hexahydride. This means that F^- anion may retain its substitutional feature during de-/hydriding cycles, but under varied chemical environments.

Of particular interest, the calculation results show that the substitution of F^- for H^- anion in the Na_3AlH_6 lattice results in a favorable thermodynamic modification. As seen in Fig. 2, the decomposition enthalpy is reduced from 59.1 kJ mol^{-1} for the pure $\text{Na}_{12}\text{Al}_4\text{H}_{24}$ to 56.0 kJ mol^{-1} after substituting one H^- by F^- in $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$. A more careful examination found that the decreased reaction enthalpy was a combined effect of F^- substitution in Na_3AlH_6 and NaH lattices, respectively. Here, the formation enthalpies of bulk Al and gaseous H_2 were set as zero. For both F^- -doped structures, the formation enthalpies are much more negative than those of the pure counterparts. But the absolute value change arising from F^- substitution in $\text{Na}_{12}\text{H}_{12}$ ($121.8 \text{ kJ mol}^{-1}$) is larger than that arising from F^- substitution in $\text{Na}_{12}\text{Al}_4\text{H}_{24}$ ($118.7 \text{ kJ mol}^{-1}$), which gives a net decrease of 3.1 kJ mol^{-1} of the reaction enthalpy. The positive effect of F^- partial substitution was

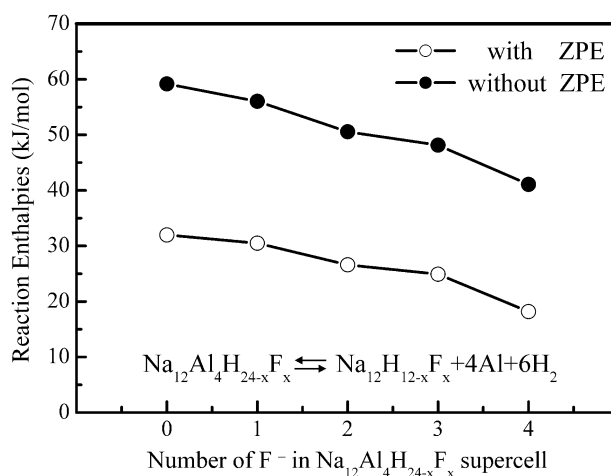


Fig. 3 Calculated reaction enthalpies with and without zero-point energies of F^- -doped Na_3AlH_6 with varied doping levels following the reaction $\text{Na}_3\text{AlH}_6 \rightleftharpoons 3\text{NaH} + \text{Al} + 3/2 \text{ H}_2$.

further examined by varying the $\text{F} : \text{H}$ ratio from $1 : 23$ to $4 : 20$ in the $\text{Na}_{12}\text{Al}_4\text{H}_{24-x}\text{F}_x$ supercell. As seen from Fig. 3, with increasing the F^- doping level, the thermodynamics of the decomposition reaction of Na_3AlH_6 becomes increasingly favorable. Here, it should be noted that the above results were obtained without taking into account the quantum-mechanical effect, mainly the zero-point energy (ZPE). To allow a more reliable evaluation of the effect of the F^- substitution, we have recalculated the reaction enthalpies by considering the ZPE correction. As seen in Fig. 2, after considering the ZPE correction, the decomposition enthalpies are 32.0 and 30.4 kJ mol^{-1} for pure $\text{Na}_{12}\text{Al}_4\text{H}_{24}$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$, respectively, which gives a smaller but still significant decrease of 1.6 kJ mol^{-1} . Moreover, as seen in Fig. 3, the calculated reaction enthalpies of F^- -doped Na_3AlH_6 with and without ZPE correction exhibit similar dependence on the F^- doping level.

Theoretically, it has been demonstrated that TiF_3 -doping may render a favorable thermodynamic modification at the $\text{Na}_3\text{AlH}_6/\text{NaH} + \text{Al}$ decomposition step. Experimentally, however, we encountered difficulty in directly measuring the reaction enthalpy using the synchronous TG/DSC technique. It was found that the endothermic effect associated with the decomposition of Na_3AlH_6 was always overlapped with an exothermic effect, which should be related to a phase transformation characteristic of the samples doped with Ti halides. Currently, time-consuming measurements of the plateau pressure are underway.

In our DFT calculation, we further examine the effect of F^- partial substitution on the decomposition behavior of the hydride by calculating the energy needed to remove a hydrogen atom from $\text{Na}_{12}\text{Al}_4\text{H}_{24}$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$ supercells. Again, the supercells were fully optimized as discussed previously. According to the calculation, the energies needed to remove a H atom from $\text{Na}_{12}\text{Al}_4\text{H}_{24}$ and $\text{Na}_{12}\text{Al}_4\text{H}_{23}\text{F}_1$ supercells are 136.7 and $130.1 \text{ kJ mol}^{-1}$, respectively, which gives a net energy decrease of 6.6 kJ mol^{-1} . The facilitated dehydriding process of Na_3AlH_6 , as well as the favorable thermodynamic modification, well explains the experimental observation that the variation of dopant precursor from TiCl_3

to TiF_3 led to a markedly improved dehydrogenating performance, especially at a moderate temperature range.¹⁴ More significantly, the finding of “functionality” of F^- anion renews our mechanism understanding that is currently confined to metal cations or their derivatives with suggested catalytic activity. Illustrational success has been achieved in fluoride-doped sodium aluminium hydride. Hopefully, further investigation of the functional anion(s) in other high H-capacity systems may lead to a new approach for developing viable onboard hydrogen storage systems.

4. Conclusion

In summary, our computational studies on the $\text{TiF}_3/\text{TiCl}_3$ -doped Na_3AlH_6 have elucidated the state and function of F^-/Cl^- anions in the de-/hydrogenated states of the hydride. From energetic and/or thermochemical points of view, these results well explain the experimental observations associated with $\text{TiF}_3/\text{TiCl}_3$ -doping. Furthermore, the coupled computational and experimental efforts allow us to put forward a “functional anion” concept. This renews the current mechanism understanding in the catalytically enhanced sodium alanate, and may pave a new way to pursuing further improved hydrogen storage performance of complex hydrides for onboard application.

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