Electronic Supplementary Material for PCCP

Supplementary Material for *B610257C---PCCP*

Functional Anion Concept: Effect of Fluorine Anion on Hydrogen Storage of Sodium Alanate

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Computational details and numerical results of calculations:

The cutoff energies of the plane-wave basis and augmentation charges used in our calculation for all involved structures are selected as 600 and 613.6 eV, respectively, which yields the convergence precision in the total energy achieving 0.1 meV. We considered all structures to be fully relaxed when the Hellmann-Feynman forces on the atoms are smaller than 0.01 eV/Å. The Brillouin zone was sampled using a Monkhorst-Pack sampling technique. The *k*-point grids used in our calculation for all considered periodical structures are listed in Table S1. Table S2 presents the original calculation data, including bond lengths (H_2, F_2 and Cl_2) and lattice parameters, total cohesive energies and zero points energies for all the phases.

Table S1: The *k*-point grids used for all considered periodical structures.

Structures	*k*-point grids
$Na_{12}Al_4H_{24-x}F(Cl)_x$, x = 0,1,2,3,4	5×3×5
$Na_{12}H_{12-x}F(Cl)_x$, x = 0,1,2,3,4	5×11×11
$Na_{12}Cl_{12}$ ($Na_{12}F_{12}$)	5×11×11
bcc Na (2 atoms)	21×21×21
fcc Al (4 atoms)	21×21×21

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Table S2: Numerical results of the calculations for all the involved phases.

Phase	Bond length (Å) & Lattice parameter (Å, degree)	Cohesive energy (eV)	Zero point energy (eV)
H_2	0.7510	-6.7733	0.2676
F_2	1.4237	-3.7208	0.0666
Cl_2	1.9926	-3.5747	
Bcc Na (2 atoms)	a = b = c = 4.1961	-2.6209	0.0247
Fcc Al (4 atoms)	a = b = c = 4.0379	-14.9787	0.1131
$Na_{12}H_{12}$	a = 14.4990, b = c = 4.8330	-61.0316	1.776
$Na_{12}Cl_{12}$	a = 17.0805, b = c = 5.6935	-81.3198	
$Na_{12}F_{12}$	a = 14.0928, b = c = 4.6976	-103.7555	
$Na_{12}H_{11}F_1$	a = 14.4842, b = c = 4.8282	-64.5551	1.74
$Na_{12}H_{10}F_2$	a = 14.4210, b = c = 4.8036	-68.0793	1.716
$Na_{12}H_9F_3$	a = 14.3689, b = c = 4.7896	-71.6010	1.656
$Na_{12}H_8F_4$	a = 14.3451, b = c = 4.7692	-75.1802	1.572
$Na_{12}Al_4H_{24}$	a = 5.3646, b = 11.0812, c = 7.7234, β = 89.722	-119.1027	4.622
$Na_{12}Al_4H_{23}F_1$	a = 5.3685, b = 11.1014, c = 7.7267, β = 89.744	-122.5153	4.536
$Na_{12}Al_4H_{22}F_2$	a = 5.3681, b = 11.1752, c = 7.7258, β = 89.926	-125.7937	4.428
$Na_{12}Al_4H_{21}F_3$	a = 5.3712, b = 11.2042, c = 7.7304, β = 89.960	-129.2526	4.336
$Na_{12}Al_4H_{20}F_4$	a = 5.3727, b = 11.2400, c = 7.7317, β = 90.002	-132.5979	4.24
$Na_{12}Al_4F_{24}$	a = 5.4720, b = 11.3460, c = 7.8770, β = 90.173	-201.4666	
$Na_{12}Al_4H_{23}Cl_1$	a = 5.4132, b = 11.4693, c = 7.7961, β = 90.066	-119.8894	
$Na_{12}H_{11}Cl_1$	a = 14.6514, b = c = 5.0242	-62.0606	