Chemical bonding of AlH$_3$ hydrogen storage material by electron energy loss spectroscopy and *ab-initio* calculation

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Aluminum trihydride (AlH$_3$, alane) has large gravimetric and volumetric hydrogen densities and has been intensively investigated for hydrogen storage applications [1-3]. Although its chemical bonding has been theoretically studied, there has been little experimental study on the chemical bonding directly coupled with *ab initio* calculations, except for ref. [4]. In this study, we examine the relationship between the Al-$L_{2,3}$ electron energy loss spectra (EELS) and the chemical bonding of the Al and its neighbor atoms in the hydride and other Al containing compounds.

The hydride sample was prepared by the chemical reaction between LiAlH$_4$ and AlCl$_3$ in an ether (99.5% purity Et$_2$O) solution. We observed the dehydrogenation process of the hydride particles by TEM with its electron dose carefully decreased to avoid their too fast decomposition [5,6] (Fig.1). The Al-$L_{2,3}$ ELNES of a hydride particle in the initial state and after the dehydrogenation were collected. The theoretical ELNES was calculated by the orthogonalized linear combination of atomic orbital (OLCAO) method. The theoretical intensities of relatively shallow inner shell excitation spectra such as Al-$L_{2,3}$ can be underestimated from the edge onset to ~10 eV. This intensity underestimation might be beyond the present theoretical approximation [7].

Figure 2 shows the Al-$L_{2,3}$ ELNES results for AlH$_3$ and other typical Al compounds. The experimental spectra clearly show that their onsets are shifted to the higher energy in the order of Al, AlH$_3$ and Al$_2$O$_3$. The theoretical chemical shifts are consistent with the experimental, as illustrated by the green, red and black vertical lines indicating the onset energy positions of Al, AlH$_3$ and Al$_2$O$_3$, respectively. The theoretical β-AlF$_3$ spectrum onset is further shifted.

Table 1 shows a theoretical band-gap energy, an Al effective charge and a sum of bond overlap population (BOP) for Al-X (X = Al, H, O, F) in the calculated Al compounds. The compounds are tabulated in ascending order of the Al-$L_{2,3}$ onset energy. This table indicates that the Al-X bonds show the stronger ionic bonding with the onset energy. Furthermore, for the spectral fine structures, metallic Al shows a number of small peaks successively. The number of fine peaks in AlH$_3$, Al$_2$O$_3$ and AlF$_3$ spectra, on the other hand, decreased in this order with the peak intensities and the peak distances increased. Therefore, the fine peak structure of the Al-$L_{2,3}$ spectra, as well as the chemical shift, can be experimental indicators for the degree of covalent bond strength in the Al compounds.

References

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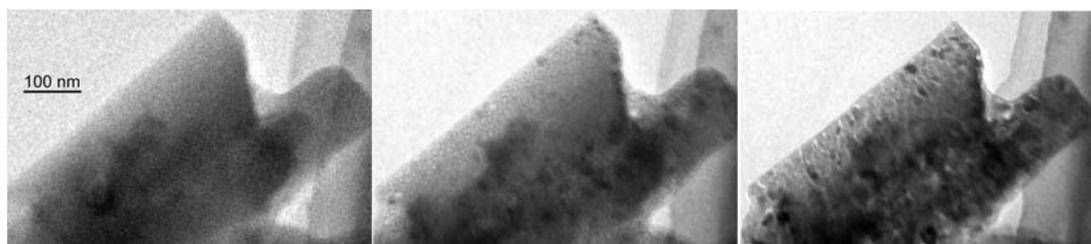[7] W. Olovsson et al., Phys. Rev. B (2011) 83 195206.

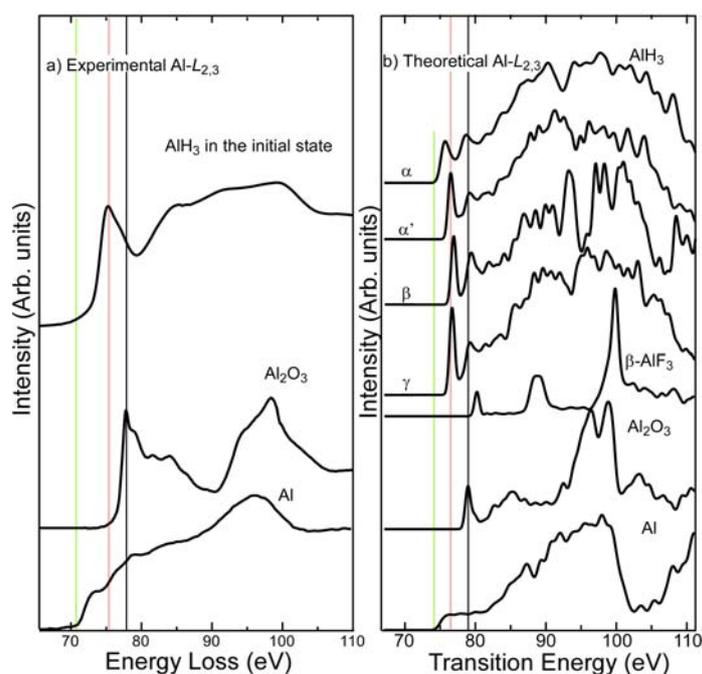FIG. 1. Low-dose TEM image of the dehydriding process of AlH_3 particle.

FIG. 2. Experimental and theoretical Al-$L_{2,3}$ spectra.

TABLE. 1. Calculated chemical bonding data among the Al containing compounds including AlH_3.

	Al	AlH_3 (α, α')	Al_2O_3	AlF_3
Band-gap (eV)	0.0	1.4, 2.1	5.9	7.2
Al effective charge	3.0	2.8, 2.8	2.1	1.8
Sum of BOP Al-X (1/Al atom)	3.6	2.9, 2.7	-0.2	1.0