Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Mechanisms of Reversible Hydrogen Storage in $NaBH_4$ Through NdF_3 Addition

Electronic and XRD supplementary information

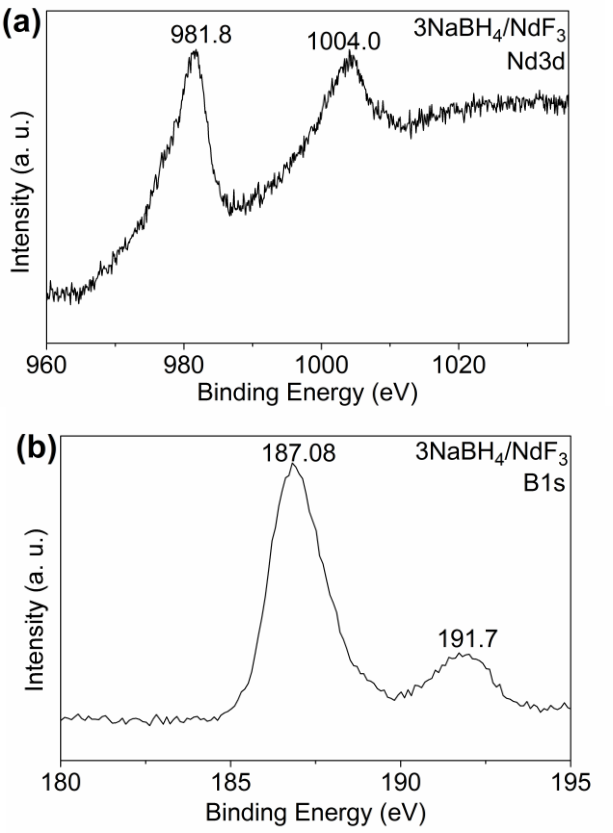

Fig. 1 Nd3d (a) and B1s (b) XPS spectra of the dehydrogenated $3NaBH_4/NdF_3$ composite

XPS is used for further identification of the existence and states of the elements B and Nd in the dehydrogenation sample of the $3NaBH_4/NdF_3$ composite. B1s and Nd3d photoemission peaks in the dehydrogenated sample of the $3NaBH_4/NdF_3$composite are shown in Fig. 1. The peaks in Fig. 1(a) reveal that the Nd3d spectrum can be resolved into two sets of $3d_{3/2}$ - $3d_{5/2}$ spin-orbit doublets at 981.8 and 1004.0 eV, respectively. The B1s peak shows two different chemical states as shown in Fig. 1(b). According to the literature,[1] the banding energies at 181.1 and 191.7eV are quite similar to the banding energies of NdB_6 and B_xO_y ($1.5 < x/y < 3$), respectively. The presence of B_xO_y may be due to the partial oxidation during the sample being taken out from the glove box and transferred to the XPS facility as well as the sputtering of oxygen during the XPS examination. The XPS results further demonstrate the formation of NdB_6 in the dehydrogenation process of the $3NaBH_4/NdF_3$ composite. Similar result has been reported [2] in the study of $LiBH_4$-CeH_2 system for which CeB_6 was formed during dehydrogenation. MB_6 type metal borides, such as CaB_6, have the CsCl-like cubic structure in which B_6 octahedral clusters occupy the place of the Cl^- ions.[3] The structure of CaB_6 is close to the polyhedral structure of $[B_{12}H_{12}]^{2-}$ ligand, so as NdB_6.[4] In addition, the bonding energy of B-M is lower than that of B-B.[5] Therefore, from both geometric and energy point of views, the appearance of NdB_6 makes the formation of $Na_2[B_{12}H_{12}]$ or $NaBH_4$ from the dehydrogenated products of $3NaBH_4/NdF_3$ composite easier than that from the dehydrogenated products of pure $NaBH_4$.

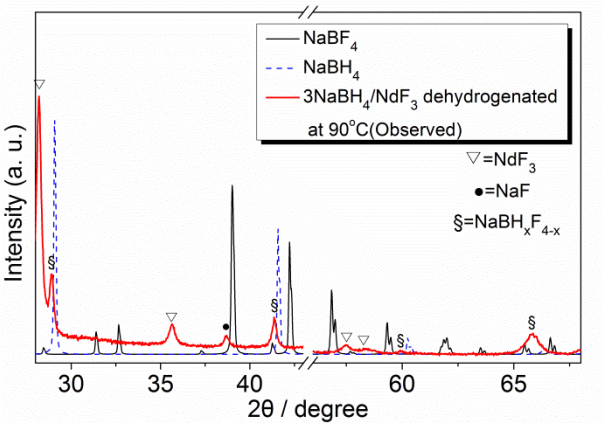

Fig. 2 Observed XRD pattern of a $3NaBH_4/NdF_3$ sample dehydrogenated at 90 °C in vacuum for 3.5h. Simulated patterns for $NaBH_4$ and $NaBF_4$ are also given for comparison.

In order to prove that the dehydriding reaction between $NaBH_4$ and NdF_3 can occur at low temperatures in vacuum, XRD analysis was carried out on a $3NaBH_4/NdF_3$ sample dehydrogenated at 90 °C in vacuum for 3.5 h. For comparison, the observed XRD pattern and simulated patterns for $NaBH_4$ (*F*-43*m*) and $NaBF_4$ (*Bbmm*) were all shown in Fig. 2. The peak located at 38.4° corresponds to the NaF (200) plane, indicating that the reaction between $NaBH_4$ and NdF_3 has already occurred at 90 °C in vacuum. As shown in Fig. 2, the observed diffraction peaks at 28.9°, 41.5°, 59.8° and 65.9° do have intensity between the simulated peaks of $NaBH_4$ and $NaBF_4$. This further confirmed the formation of the intermediate $NaBH_xF_{4-x}$ between $NaBH_4$ and $NaBF_4$ during the dehydrogenation process of the $3NaBH_4/NdF_3$ composite at low temperatures, which results from the interchange between F- and H-. Similar phenomenon was also observed in a 3NaF/Al system, for which the exchange of F- and H- resulted in the formation of intermediate phase $Na_3AlH_{6-x}F_x$.[6]

References

1. S. Patil, G. Adhikary, G. Balakrishnan and K. Maiti, *Solid state communications*, 2011, **151**, 326-328.
2. P. Mauron, M. Bielmann, A. Remhof, A. Zuttel, J. H. Shim and Y. W. Cho, *J. Phys. Chem. C*, 2010, **114**, 16801-16805.
3. F. A. Cotton, G. Wilkinson, Eds. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988, P167.
4. J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, in

Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, MN, 1992.

5. S. A. Jin, J. H. Shim, Y. W. Cho, K. W. Yi, O. Zabara and M. Fichtner, *Scr. Mater.*, 2008, **58**, 963-965.
6. H. W. Brinks, A. Fossdal and B. C. Hauback, *J. Phys. Chem. C*, 2008, **112**, 5658-5661.