Formation of Hydrides in $(Ti_{1-x}Zr_x)Co_{2.00}$ (0 < x < 1) Pseudobinary Alloys

H.-T. Kuo (郭慧通)[1], R.-S. Liu (劉如熹)[1], S. M. Filipek[2], R. Wierzbicki[2], R. Sato[2], C.-L. Chan (詹承濂)[3], H.-D. Yang (楊弘敦)[3], and J.-F. Lee (李志甫)[4]

[1]Department of Chemistry, National Taiwan University, Taipei, Taiwan
[2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland
[3]Department of Physics, National Sun Yat-Sen University, Kaoshiung, Taiwan
[4]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Hydrogen, in particular, is a promising clean energy carrier. The main limitation on its use is the need to store it in a safe and practical manner. Therefore, materials for storing hydrogen are essential to future clean energy systems. Hydrogen (H_2) can be stored in numerous forms and using various methods. It can be stored in H_2-absorbing alloys, as a chemical hydride compound, such as $NaBH_4$ or $NaAlH_4$, or in an organic hydride, such as methylcyclohexane or decalin. Several researchers have focused on the synthesis and characterization of alloys that can contain hydrogen under moderate or high pressures at their crystal interstitial sites. In particular, the RM2 (where R refers to a rare earth metal and M to a transition metal) group of Laves compounds are of interest because of not only their high H absorption but also their effect of hydrogen on their properties, including considerable volume expansion, and a change in their structural and magnetic properties. The effect of hydrogen absorption on the thermodynamic, structural and magnetic properties of RM_2 with Laves phase compounds has been extensively widely investigated. Our previous works have demonstrated that such titanium compounds as TiFe, TiCo and TiNi, all with CsCl-type structures, are well known to be good hydrogen absorbers whereas Ti-based alloys of $TiFe_2$ and $TiCo_2$ are supposed to be non-hydride forming. To prove that whether $TiCo_2$ can also be transformed into hydride at a sufficiently high hydrogen pressure, a series of pseudobinary $(Ti_{1-x}Zr_x)Co_{2.00}$ (0 < x < 1) alloys were investigated. In this study, $(Ti_{1-x}Zr_x)Co_{2.00}$ (0 < x < 1)-based hydrides were synthesized and characterized by such *in-situ* methods as X-ray absorption spectrum (XAS).

Figure 1 displays *in-situ* XAS spectra at the Co *K*-edge of $(Ti_{0.10}Zr_{0.90})Co_{2.00}$ hydride. The background was subtracted from all XAS spectra, which were then normalized with respect to the edge jump. In most related studies, the cobalt valence state is determined from the position of the absorption near-edge (as displayed in the inset), which increases as the valence state increases. We suggest that as the $(Ti_{0.10}Zr_{0.90})Co_{2.00}$ hydride sample is discharged, the free electron is extracted from its electronic band and combines with H^+ to form hydrogen and is thus released from the surface of the hydride sample; the valence state of the cobalt metal is thus shifted from low energy to high energy. Figure 1(a) depicts the details. To clarify the edge features, only a small energy range of the XAS is presented. Figure 1(b) plots the second derivative function of the Co *K*-edge of the $(Ti_{0.10}Zr_{0.90})Co_{2.00}$ hydride sample for various discharging times. The zero crossing of the main absorption features, indicated by the arrow in Fig. 1(b), representing the inflection point energy, was found to increase from 7708.4 to 7708.5 eV from 1 h to 4 h. The curve of the second derivative of the Co *K*-edge at various discharging times has a similar shape. Figure 1(b) also presents the zero crossing of the main absorption features, which suggests that the local structure is mostly maintained during discharge.

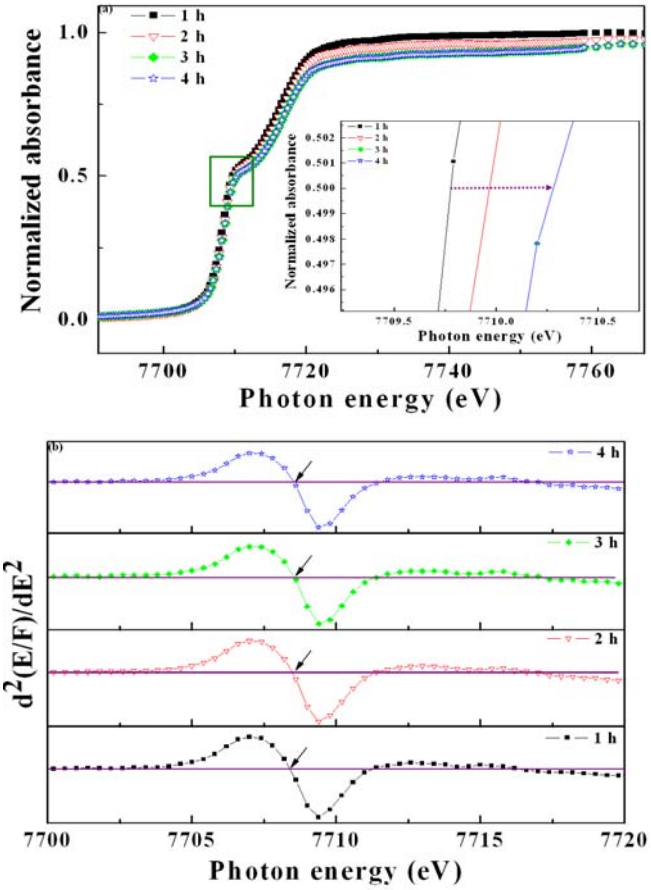

Fig. 1: (a) *In-situ* XAS patterns at Co *K*-edge of discharge process of $(Ti_{0.10}Zr_{0.90})Co_{2.00}$ hydride during exposure to ambient at 25 °C; near-edge region is shown in inset; (b) second derivatives of normalized Co *K*-edge XAS spectra.