Change in the Electronic Structure of MgH_2 after the Electrochemical Process

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Solid electrolytes that conduct hydride ions (H^-) have attracted considerable attention, and among these, rare-earth metal hydrides such as LaH_3 are known for their high H^- ion conductivity. Previous studies have reported that La-M-H compounds, in which cations with different valences are doped into the La site, exhibit high H^- ion conductivity even at room temperature[1]. Our group has also confirmed that similar ionic conductivity can be achieved using Ce in place of La[2]. By utilizing these H^- ion conductors, it is expected that hydrogenation and dehydrogenation of alkali and alkaline earth metals such as Li and Mg can proceed near room temperature, according to the following reaction equations.

(Anode) $MgH_2 + 2e^- \rightleftarrows Mg + 2H^-$

(Cathode) $2H^- \rightleftarrows 2H^0 + 2e^-$ (H^0 is adsorbed by Pd)

In this study, we investigated the electrochemical dehydrogenation behavior using MgH_2/$(La,Na)H_{3-x}$/Pd solid state cell and the electronic structure of the sample (MgH_2) after electrochemical reaction was evaluated using Mg K-edge XANES measurement.

$(La,Na)H_{3-x}$(LNH) was prepared by the ball milling of the mixtrue of LaH_3 and NaH (3 : 1 in molar ratio) at 500 rpm for 20 h. Then, MgH_2 + LNH + ketchen black(KB) / LNH / Pd pellet was prepared for the electrochemical test. The MgH_2, LNH and KB were mixed in the weight ratio of 1 : 6 : 1. Electrochemical MgH_2 dehydrogenation was tested by keeping the voltage 2V for 96 h as the MgH_2 is the counter electrode.

Electronic state of the sample before and after the electrochemical test was evaluated by Mg K-edge XAS at Rits SR center BL10. X-ray beam was irradiated to collect the XAS spectrum from the back side of MgH_2 the electrochemical cell.

Fig. 1(a) shows Mg K-edge XAS spectrum of the MgH_2 samples before and after electrochemical test and MgO, Mg and MgH_2 as references. Comparing with three reference samples, edge positions were clearly different from each other. Therefore, dehydrogenation or oxidation of the MgH_2 after the electrochemical test could be easily found by the XAS measurement.

The edge shift of XAS spectra of MgH_2 was not confirmed after the electrochemical test. Fig.1(b) shows the first derivative of the profiles in Fig. 1(a). The peak positions of the two samples were the same and no other small peak was detected. This indicates that the electrochemical dehydrogenation of the MgH_2 was not confirmed in this experiment. However, the dehydrogenation might be proceeded at the MgH_2/LNH interface where the X-ray could not reach in this experimental approach.

One possible reason why the Mg peak was not observed in this measurement is that the measurement was conducted from the back side of the electrode, rather than at the MgH_2/LNH interface where the reaction actually occurs. As a result, the reactive region may not have been detected. Assuming that all the current detected during the electrochemical test was due to the dehydrogenation reaction of MgH_2, it would imply that only half of the MgH_2 reacted. Even when using the fluorescence yield method, this measurement technique can only provide information to a depth of several micrometers. Given that the sample pellet is several hundred micrometers thick, it is likely that the reaction did not proceed throughout the entire sample.

Future challenges include developing a method to measure near the sample/electrolyte interface and fabricating samples with thin-film electrodes. Electrode fabrication using sputtering is being considered, and further measurement will be attempted.

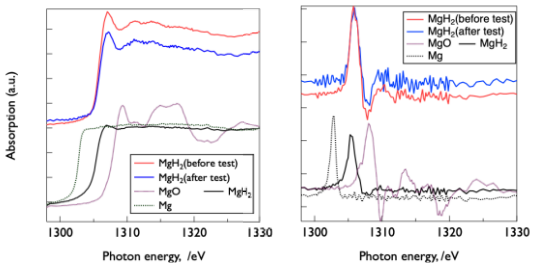

Fig. 1 (a) Mg K-edge XANES spectra of MgH_2 samples and the references and (b) the first derivative spectra of (a).

References

[1] Y. Izumi et.al., Advanced Energy Materials, 13 (2023) 2301993.
[2] R. Kataoka, et. al., 2025 annual spring meeting of JIMM (No. 74)