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Electrochemical charge and discharge properties for the formation of magnesium and aluminum hydrides

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ABSTRACT

The electrochemical properties of Mg + 2LiH and Al + 3LiH are investigated by applying a Li-ion insertion and extraction system to form magnesium and aluminum hydrides. For MgH_2 formation, the voltage–composition (VC) curve for Mg + 2LiH during charging exhibits a plateau voltage at 0.58 V, then the final composition is obtained with 1.05 mol Li extraction at 3.0 V. After the charging, the MgH_2 phase is observed by XRD measurement. Therefore, MgH_2 is produced from Mg and LiH by electrochemical charging. With respect to AlH_3 formation, Al + 3LiH is charged at a plateau voltage of 0.81 V, which corresponds to the reaction of Al with hydrogen in LiH to form AlH_3. And the final composition at 3.0 V is 0.6 mol Li. In the XRD profile after charging, the AlH_3 phase is not detected.

1. Introduction

Hydrogen is a secondary fuel source for obtaining energy in internal combustion engines and fuel cells, producing only water as a by-product. To use hydrogen in mobile applications, hydrogen storage in a solid medium is considered to be one of the most promising options rather than the use of compressed hydrogen gas or liquid hydrogen. Among the hydrogen storage materials considered, aluminum hydride is one of the most promising candidates because it possesses a high hydrogen capacity of 10.1 mass% and a low hydrogen desorption temperature of 150 °C [1–5]. However, because the enthalpy change of AlH_3 formation is small (-7.6 kJ/mol H_2) [6], the equilibrium H_2 fugacity for the formation of AlH_3 from Al and H_2 molecules is 26 GPa (equivalent to 0.6 GPa H_2 pressure) at 298 K [7]. The direct hydrogenation of Al has been reported at an extreme pressure (8.9 GPa) and temperature (600 °C) [8,9]. However, the typically used formation route is through the chemical reaction of lithium alanate with aluminum chloride in diethyl ether [5,10]. Furthermore, Zidan et al. have synthesized AlH_3 electrochemically, providing a synthetic route that closes a reversible cycle from a cathode material of Al plate and an electrolyte of sodium alanate in THF solvent [11]. Another promising candidate is magnesium hydride, which has a high hydrogen capacity of 7.6 mass%. However, it requires a high hydrogen desorption temperature of 300 °C, because the enthalpy of formation of MgH_2 is large (-75.3 kJ/mol H_2) [12]. Moreover, the reaction kinetics of hydrogen absorption and desorption are too slow for practical use. The improvement of hydrogen sorption kinetics by adding transition metals [13], metal fluorides [14,15] and metal oxides [16–19] as catalysts has been reported.

The Li-ion battery is a key component in the application of mobile power sources. For the anode of the battery, alloys [20], oxides [21] and various forms of carbon have been investigated to overcome capacity limit of the currently used graphite (372 mAh g^{-1}) [22,23]. Oumellal et al. have investigated the use of the metal hydride MgH_2 as an anode [24,25]. The MgH_2 electrode exhibits a large reversible capacity of 1480 mAh g^{-1} at an average voltage of 0.5 V versus Li^+/Li. It has been pointed out that the following reaction at the anode is not specific to MgH_2, as other metal hydrides (NaH and TiH_2) and intermetallic hydrides (Mg_2NiH_4 and $LaNi_5H_6$) exhibit similar electrochemical reactivity towards Li:

$$MH_x + xLi^+ + xe^- \rightarrow M + xLiH \quad (M = \text{metal, alloy}). \tag{1}$$

In this study, the electrochemical charge properties of Mg + 2LiH and Al + 3LiH are investigated by applying a Li-ion extraction system to form magnesium and aluminum hydrides through the following reactions:

$$\begin{array}{ll} \text{Cathode} & Mg + 2LiH \leftrightarrow MgH_2 + 2Li^+ + 2e^- \\ \text{Anode} & 2Li^+ + 2e^- \leftrightarrow 2Li \\ \text{Total} & Mg + 2LiH \leftrightarrow MgH_2 + 2Li \end{array} \tag{2}$$

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$$\begin{array}{lll} \text{Cathode} & Al + 3LiH \leftrightarrow AlH_3 + 3Li^+ + 3e^- & \\ \text{Anode} & 3Li^+ + 3e^- \leftrightarrow 3Li & (3) \\ \text{Total} & Al + 3LiH \leftrightarrow AlH_3 + 3Li. & \end{array}$$

Furthermore, the electrochemical discharge properties of MgH_2 and AlH_3 are investigated by applying a Li-ion insertion system to investigate the reversibility of the above reaction for the decomposition of magnesium hydride and aluminum hydride to the metal and lithium hydride phases.

2. Experimental methods

Lithium hydride (LiH) powder (95% purity) was purchased from Sigma–Aldrich Co. Magnesium (Mg) powder (99.9% purity) and aluminum (Al) powder (99.9% purity) were from Rare Metallic Co. The α phase of aluminum hydride (AlH_3) was synthesized from lithium alanate and aluminum chloride as described in the literature [3–5]. Three grams of Mg + 2LiH, Al + 3LiH or MgH_2 was placed in a zirconia vessel (250 cm^3 inner volume) together with 150 zirconia balls (8 mm in diameter) and the vessel was sealed in an argon-filled glovebox. Mg + 2LiH and Al + 3LiH were mechanically milled for 10 h (repetition of 1 h milling followed by 30 min rest) at 370 rpm using a planetary ball milling apparatus (Fritsch P6). MgH_2 was similarity mechanically milled for 20 h. The samples before and after ball milling were always handled in a glovebox filled with argon gas so as to minimize the oxidation of the samples.

To fabricate a cathode, the ball milled samples (Mg + 2LiH, Al + 3LiH and MgH_2) or as-prepared AlH_3 were mixed with 5 mass% acetylene black (Hohsen Co.) and 5 mass% PTFE (Hohsen Co.) using an agate mortar and pestle. The product was spread to ~500 μm thickness using a brass bar and punched to form a coin of 15 mm in diameter (an electrode of 40–50 mg of an electrode). A Cu current collector, a cathode, a separator (24 mm in diameter, glass fiber filter paper, GA-100, Toyo Glass Co.) and a Li metal disc (16 mm in diameter, Honjo Metal Co.) were placed in order with an electrolyte (EC/EMC (volume ratio of 1:1) + 1 M $LiPF_6$, Kishida Chemical Co.) in an experimental cell (Hohsen Co.). The cell was assembled in a glovebox filled with argon gas. The Li extraction (charge) and Li insertion (discharge) reactions were measured by an automatic cycling/data recording system (HJ1001SD8, Hokuto Denko Co.) in galvanostatic operating mode at a voltage between 0.001 and 3 V versus Li^+/Li and a current density of 0.11 mA/cm^2 at 30 °C. For structural characterization of the electrodes before and after charge–discharge measurements, X-ray diffraction (XRD) measurement was performed using a Rigaku RINT 2500 or Shimadzu XRD-6100 (Cu Kα radiation) diffractometer. To avoid the oxidation of the sample during the transfer and in the XRD measurement, the samples were protected with a transparent polyimide film of 8 μm thickness.

3. Results and discussion

3.1. Electrochemical properties of Mg + 2LiH and MgH_2

Fig. 1(a) shows the voltage–composition (VC) curve of the charging reaction for the cathode of Mg + 2LiH ball milled for 10 h. The VC curve has a plateau voltage at 0.58 V until 0.87 mol Li is extracted. This plateau voltage corresponds to a calculated equilibrium voltage of 0.52 V vs Li^+/Li for the total reaction of MgH_2 formation ($Mg + 2LiH \rightarrow MgH_2 + 2Li$; estimated from the standard Gibbs free energy changes of −35.9 kJ/mol for MgH_2 [12] and −68.3 kJ/mol for LiH [12] according to Nernst's equation $E^0 = -\Delta G^0/2F$). The VC curve in Fig. 1(a) increases to 3.0 V at the final composition of 1.05 mol Li, which is half the amount of Li extracted in the total reaction (2 mol). Fig. 2(a) shows the XRD profiles of Mg + 2LiH powder ball milled for 10 h before VC curve measurement. Phases of Mg and LiH are observed, which were the starting materials. The electrodes after the VC curve measurement exhibit peaks of MgH_2 along with peaks of Mg and LiH of reduced intensity. From these results, it is concluded that MgH_2 is produced electrochemically in the cathode from Mg and LiH at room temperature and atmospheric pressure by the reaction

$$Mg + 2LiH \rightarrow MgH_2 + 2Li^+ + 2e^-. \quad (4)$$

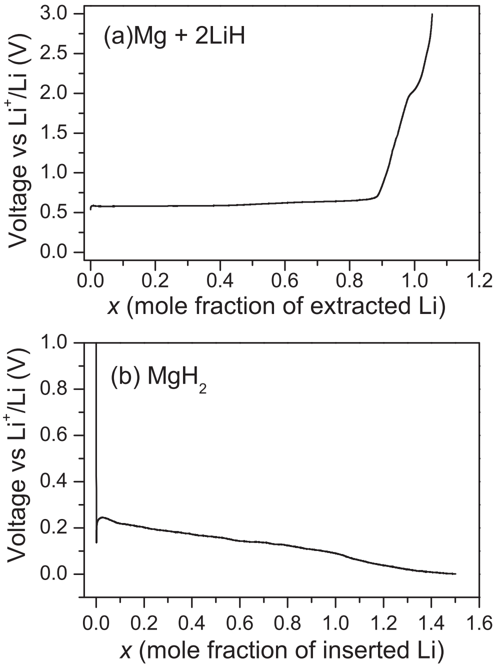

Fig. 1. VC curves of (a) Mg + 2LiH ball milled for 10 h for the charging reaction up to 3 V and (b) MgH_2 ball milled for 20 h for the discharging reaction down to 0.001 V.

Fig. 1(b) shows a VC curve of the discharge reaction for the cathode of MgH_2 ball milled for 20 h. Initially, the voltage in the VC curve drops to approximately 0.25 V then gradually decreases to 0.001 V. During the discharge reaction 1.5 mol Li enters in the cathode. As shown in Fig. 2(b), the ball milled MgH_2 before VC curve measurement shows broad peaks of β-MgH_2 together with γ-MgH_2 peaks; γ-MgH_2 is formed during ball milling [26]. After discharging, Mg and LiH peaks appear in the XRD profile along with peaks of MgH_2 with reduced intensity. Therefore, MgH_2 reacts with the provided Li ions by the reaction,

$$MgH_2 + 2Li^+ + 2e^- \rightarrow Mg + 2LiH. \quad (5)$$

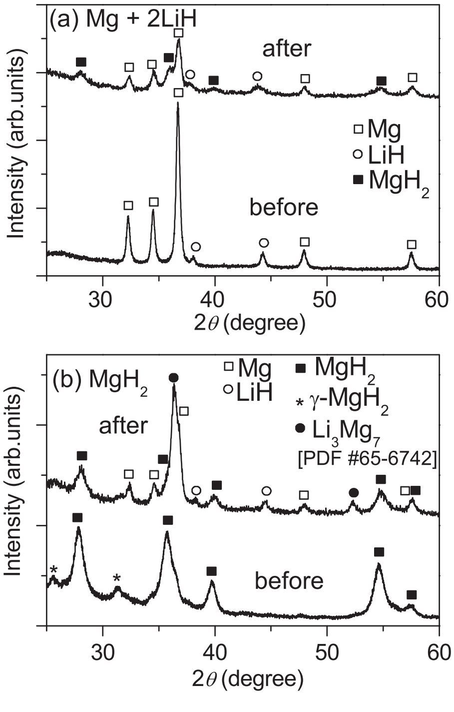

Fig. 2. XRD profiles of (a) Mg + 2LiH powder ball milled for 10 h before and after VC curve measurement and (b) MgH_2 powder ball milled for 20 h before and after VC curve measurement.

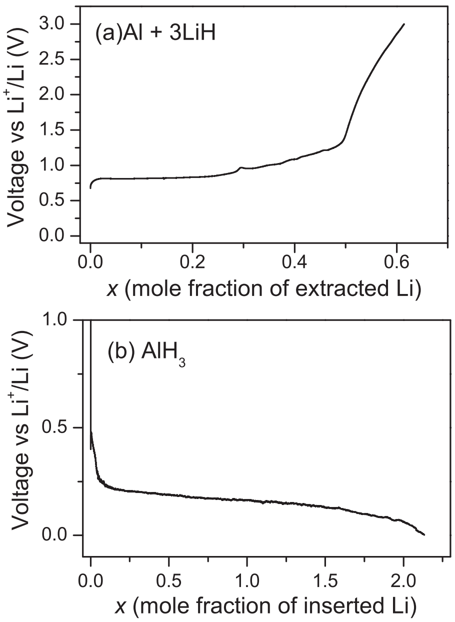

Fig. 3. VC curves of (a) Al + 3LiH ball milled for 10 h for the charging reaction up to 3 V and (b) as-prepared AlH_3 for the discharging reaction down to 0.001 V.

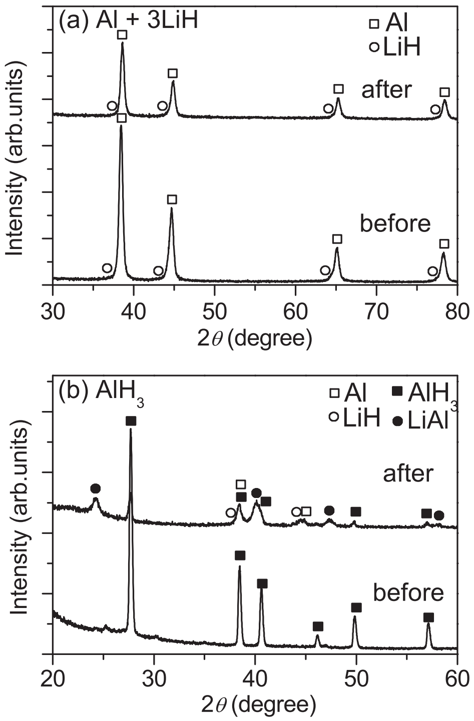

Fig. 4. XRD profiles of (a) electrodes of Al + 3LiH ball milled for 10 h before and after VC curve measurement and (b) AlH_3 powders before and after VC curve measurement.

Moreover, the Li_3Mg_7 phase is also observed in the XRD profile. The formation of Li–Mg alloy after charging agrees with the results reported by Oumellal et al. [24] The Mg produced further reacts with the provided Li ions to form Li_3Mg_7 alloy by the reaction

$$Mg + 3/7Li^+ + 3/7e^- \rightarrow 1/7Li_3Mg_7. \qquad (6)$$

This reaction corresponds to the region from 1.0 mol Li to 1.5 mol Li in the VC curve in Fig. 1(b), where slight change of gradient of the curve can be observed and the voltage is below 0.1 V.

Both the charging properties of Mg + 2LiH and the discharge properties of MgH_2 are similar to the results from Oumellal et al. [24,25], although the amount of Li that reacted and the plateau voltage during the reaction are slightly different because of the difference in the milling conditions used to prepare the samples and the method of fabricating the electrodes.

3.2. *Electrochemical properties of Al + 3LiH and AlH_3*

Fig. 3(a) shows the VC curve of the charge reaction for Al + 3LiH ball milled for 10 h. The VC curve exhibits a plateau voltage at 0.81 V until 0.3 mol Li has been extracted. This plateau voltage corresponds to the calculated equilibrium voltage of 0.87 V vs Li^+/Li for the total reaction $Al + 3LiH \leftrightarrow AlH_3 + 3Li$ (estimated from the standard Gibbs free energy changes; 46.5 kJ/mol for AlH_3 [6] and −68.3 kJ/mol for LiH [12] using $E = -\Delta G^0/3F$). Therefore, this correspondence indicates that the electrochemical reaction forming AlH_3 proceeds during the plateau voltage. The VC curve exhibits a gradual slope up to 0.5 mol Li after a small peak at 0.3 mol Li. The origin of the peak is not clear, although it is reproducible. Finally, the VC curve rises rapidly to 3.0 V at a composition of 0.6 mol Li, which is one-fifth of the 3 mol Li extracted during the total reaction of AlH_3 formation. Fig. 4(a) shows the XRD profiles for the electrode of ball milled Al + 3LiH before and after the VC curve measurement. Before charging, the Al and LiH phases of the starting materials are observed. After charging, Al and LiH peaks are still observed but without the AlH_3 peaks. The reason for the lack of AlH_3 peaks in the XRD profiles is speculated to be that the AlH_3 synthesized during the electrochemical reaction decomposes before the XRD measurement owning to its instability. Another possibility is that AlH_3 is formed in an amorphous state, therefore it is not detected in the XRD profiles. However, it is difficult to distinguish the halo pattern of the amorphous phase under our experimental conditions. Further investigation is needed to identify the Al compounds in the electrode.

Fig. 3(b) shows the VC curve of the discharge reaction for the cathode of as-prepared AlH_3. Initially, the voltage of the VC curve drops to approximately 0.5 V then gradually decreases to 0.001 V at a composition of 2.2 mol Li. As shown in Fig. 4(b), the as-prepared AlH_3 exhibits sharp peaks corresponding to the α-AlH_3 phase. After discharging, Al and LiH peaks appear. Because the peak positions of Al and LiH are quite close, it is difficult to distinguish them in the XRD profile. This result suggests that AlH_3 reacts with Li ions by the following reaction:

$$AlH_3 + 3Li^+ + 3e^- \rightarrow Al + 3LiH. \qquad (7)$$

Therefore, the reversibility of reaction (3), resulting in the electrochemical decomposition of AlH_3 to Al and LiH, is confirmed. Furthermore, LiAl peaks are also observed in the XRD profile. This means that Al decomposed from AlH_3 further reacts with the provided Li ions to form the LiAl phase following the reaction

$$Al + Li^+ + e^- \rightarrow LiAl. \qquad (8)$$

4. Conclusion

The electrochemical charge properties of Mg + 2LiH and Al + 3LiH were investigated to form magnesium and aluminum hydrides. In the case of MgH_2 formation, the VC curve of Mg + 2LiH ball milled for 10 h during charging exhibited the plateau voltage at 0.58 V, then 1.05 mol Li had been extracted at 3.0 V. After the charging, the MgH_2 phase was observed in the XRD profile. Therefore, MgH_2 was produced from Mg and LiH by electrochemical charging at room temperature. In the case of AlH_3 formation, Al + 3LiH ball milled for 10 h was charged at a plateau voltage of 0.81 V, which corresponds to the reaction between Al and LiH to form AlH_3, then the final composition was obtained with 0.6 mol Li extraction at

3.0 V. In the XRD profile after charging, the AlH_3 phase could not be detected. Furthermore, the electrochemical discharge properties of MgH_2 and AlH_3 during their decomposition were investigated. MgH_2 was discharged with the formation of LiH and Mg phases as a first step and a Li_3Mg_7 phase as a second step until a composition corresponding to 1.5 mol Li insertion was reached. On the other hand, AlH_3 was discharged with the formation of LiH and Al phases as a first step and a LiAl phase as a second step until a composition corresponding to 2.2 mol Li was reached. Therefore, it was confirmed that MgH_2 and AlH_3 electrochemically decompose to Mg and Al and LiH, respectively, in the Li-ion insertion system.

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