

Characteristics of the Dendrite Growth in the Electrochemical Alane Production Process

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Abstract. The electrochemical alane production process was proposed for a feasible production of alane. The operation of process was difficult because of short circuit by a dendrite growth in the reactor. Therefore, characteristics of the dendrite growth in the process were investigated. We conducted the electrochemical alane production process using Teflon block for inhibition of the dendrite growth. The obtained dendrite was characterized by XRD, SEM and ICP-AES. It was concluded that the dendrite growth was attributed to a melting and agglomeration of Al fine particles existed in the solution.

Keywords: Hydrogen storage, Energy storage system, Electrochemical, Alane, Dendrite

1 Introduction

Alane (aluminum hydride, AlH_3) is a metastable, crystalline solid with a very high hydrogen capacity (10 wt% H_2 of a gravimetric hydrogen density and $149 \text{ kg H}_2/\text{m}^3$ of a volumetric hydrogen density). The energy density (1200 Wh/L) of the AlH_3 -fuel cell system was higher four times than that of lithium battery system. The AlH_3 -fuel cell system has expected to apply the future energy storage system including the hydrogen fuel cell vehicle [1]. Therefore, AlH_3 is one of the promising candidate for development of the future hydrogen storage system [2,3].

The production of AlH_3 by a direct hydrogenation of aluminum (Al) is impracticable because it theoretically requires hydrogen pressure over 10^5 bar at room temperature. Zidan et al. recently proposed the AlH_3 production process including electrochemical method, which is close to a reversible cycle (Fig. 1) [4]. This process consists of two processes: (1) electrochemical process which produces AlH_3 and MH ($M=\text{Li}$ or Na) by electrochemical decomposition of MAIH_4 and (2) chemical process which regenerate the MAIH_4 by reacting hydrogen with Al and MH using catalysts.

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The continuous operation of reaction was difficult due to short circuit by a dendrite growth during the electrochemical AlH_3 production [5]. The problem of dendrite growth should be resolved to operate continuously the electrochemical AlH_3 production process. The studies for the mechanism of dendrite growth and the physicochemical method to inhibit the dendrite growth were not yet reported. Therefore, we identified the mechanism of dendrite growth to resolve the problem of dendrite growth. The electrochemical AlH_3 production was performed by using Al, Pd electrodes and LiAlH_4 -THF solution.

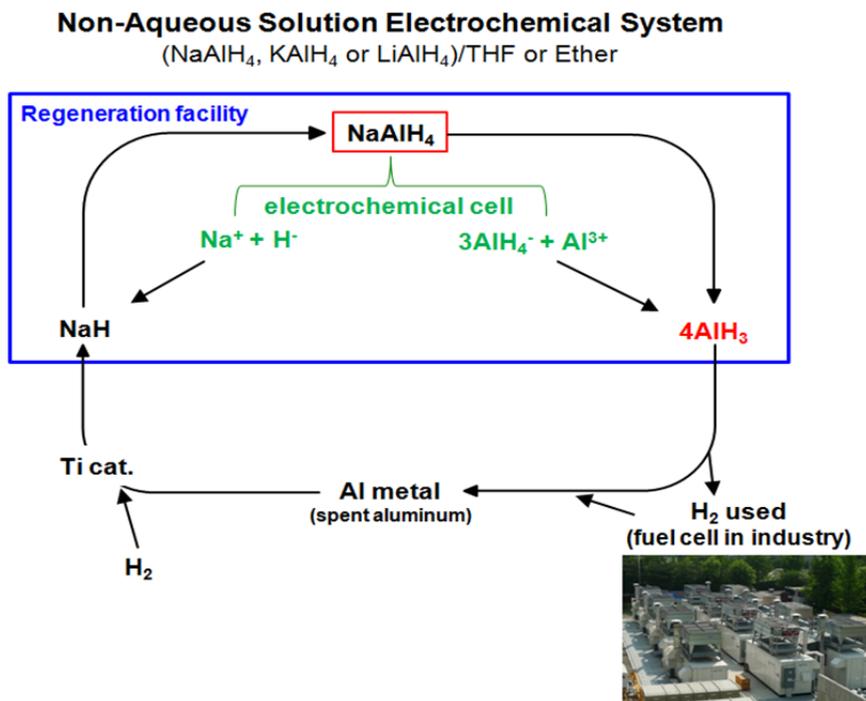


Fig. 1. Schematic diagram of the electrochemical AlH_3 production process [4].

2 Experimental

Experimental procedure was performed in an argon-filled glove box. The electrochemical AlH_3 production was conducted in the glass reactor with 400 mL in volume. The Al electrode was polished using sandpaper and rinsed with acetone to remove the oxide layer. The Al plate (13.25 cm^2) and Pd foil (13.25 cm^2) were used as the anode and cathode in the reactor, respectively. A 150 mL of 1 M LiAlH_4 -THF (Sigma Aldrich) was fed to the reactor. The DC power supply (E3615A, Agilent) was connected to the Al and Pd electrodes. The reaction proceeded by applying a constant voltage for 12 h.

The obtained dendrite was characterized by powder X-ray diffraction (XRD, D/MAX-2200), scanning electron microscopy (SEM, Hitachi S-4800) and inductively coupled plasma atomic emission spectrometry (ICP-AES, OPTIMA 7300 DV).

3 Results and Discussion

The Teflon block was installed in the reactor to inhibit the dendrite growth (Fig. 2(a)). The applied voltage was controlled at 5 V. The initial current density was measured at 11.32 mA/cm^2 . A large amount of dendrite grew up toward the Al electrode at 740 min of

reaction (Fig. 2(b)). Fig. 3 shows the variation of current density during the reaction. The current density increased after 500 min. This result was because the length between the dendrite formed at the cathode and the Al electrode decreased gradually. The final current density was achieved 24.91 mA/cm².

The XRD and SEM results of the dendrite were shown in Figs. 4 and 5, respectively. From the XRD result, the peaks of the dendrite were well agreed with that of aluminum. It was considered that the irregular particles of the dendrite were agglomerated each other at a microscopic level from the SEM images. We measured that the content of Li was 22.75 wt% in the dendrite by ICP-AES.

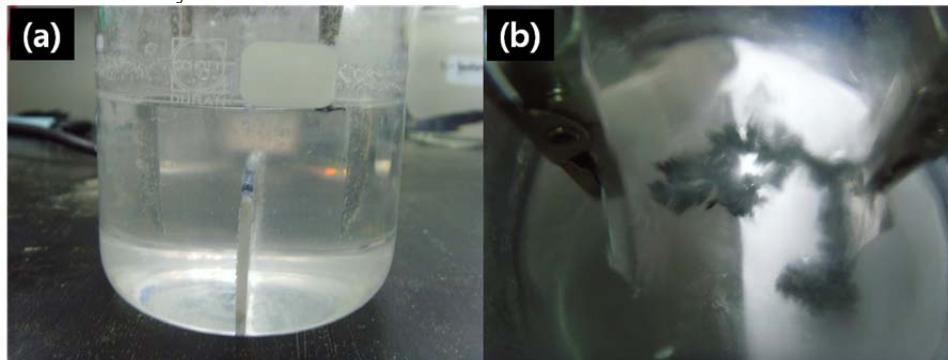


Fig. 2. (a) The reactor installed Teflon block in 1 M LiAlH₄-THF solution and (b) dendrite growth in the reactor; electrodes: Al plate and Pd foil.

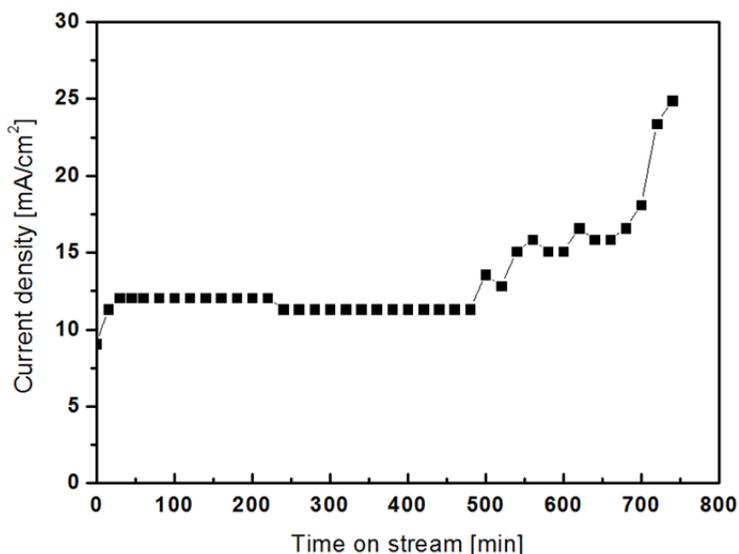


Fig. 3. Variation of current density in 1 M LiAlH₄-THF solution during the reaction; electrodes: Al plate and Pd foil.

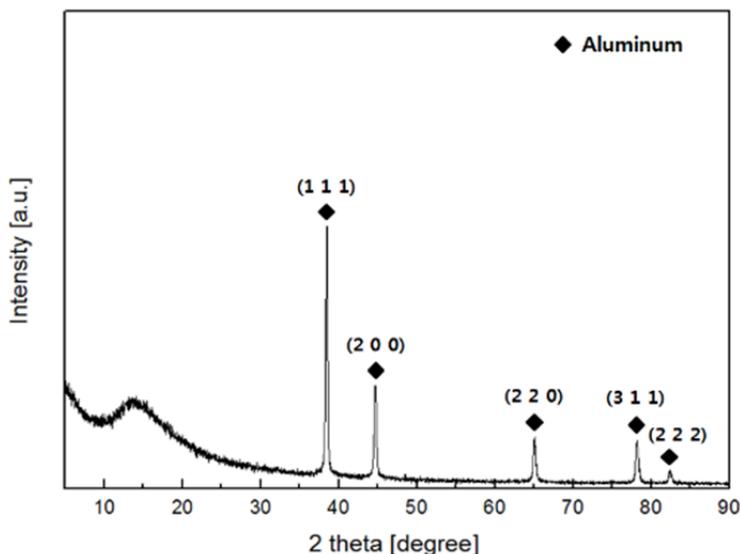


Fig. 4. XRD pattern of the dendrite obtained from electrochemical AlH_3 production.

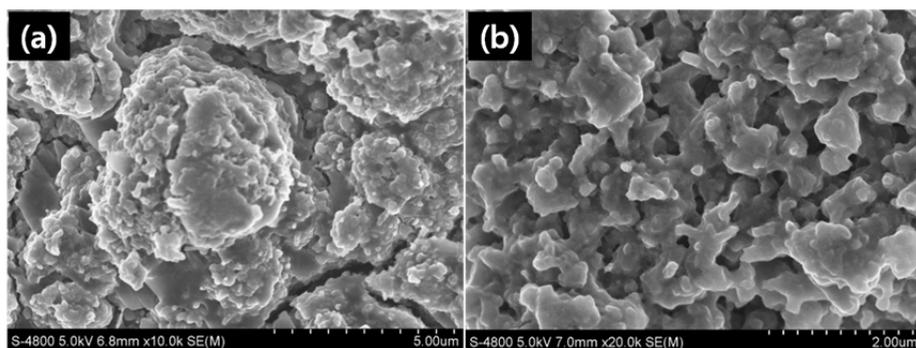
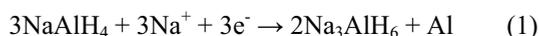


Fig. 5. SEM images of dendrite obtained from electrochemical AlH_3 production

On the other hand, we used the reactor of an H-cell type to inhibit the short circuit due to the contact between Al particles and dendrite. The applied voltage was controlled at 5 V. During the reaction for 6 h, it was not observed that the dendrite growth at the cathode and the gas emission at the anode, indicating that the reaction was difficult to proceed. This result was attributed to an increase in resistance due to decrease in the amount of LiAlH_4 -THF solution and the space between the electrodes.

Martínez-Rodríguez et al. reported that crystalline structure of dendrite consisted of Na_3AlH_6 and Al in the electrochemical AlH_3 production using NaAlH_4 -THF solution [6]. They explained that the dendrite consisting of Na_3AlH_6 and Al was formed by reacting with Na^+ and NaAlH_4 at the cathode when H^+ ions were not present (Eq. (1)). In addition, the dendrite could be formed with a similar procedure when LiAlH_4 was used instead of NaAlH_4 .



Although we did not observed the evidence of Li_3AlH_6 component in the XRD result, it was considered that the dendrite growth proceeded by the Li plating due to reduction of Li^+ at the surface of Pd electrode or by the Li_3AlH_6 component. The dendrite grew up rapidly by melting and agglomeration of Al fine particles that existed in the solution. From these

results, it was found that the consumption of Al electrode (Eq. (2)) and the formation of Al fine particles could not be avoided in the electrochemical AlH₃ production process. We also concluded that the dendrite growth was attributed to mainly the Al fine particles.



4 Conclusions

In this study, characteristics of the dendrite growth were investigated in the electrochemical AlH₃ production process. A series of experiments were performed in the reactor installed the Teflon block for inhibition of the dendrite growth. Major results were summarized as follows.

(1) A large amount of dendrite was obtained from the electrochemical AlH₃ production process. The XRD peaks of the dendrite were well agreed with that of aluminum. From the SEM images, it was considered that the irregular particles of the dendrite were agglomerated each other at a microscopic level. We measured that the content of Li was 22.75 wt% in the dendrite by ICP-AES. From these result, it was concluded that the structure of dendrite consisted of Al and Li components.

(2) The reactor of an H-cell type was not adequate for the electrochemical AlH₃ production process due to a high resistance. It was considered that the dendrite grew up by the Li plating due to reduction of Li⁺ at the surface of Pd electrode or by the Li₃AlH₆ component. The consumption of Al electrode and the formation of Al fine particles could not be avoided. The dendrite growth was attributed to mainly the Al fine particles.

Acknowledgements

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