

Short communication

Electrochemical reaction of lithium alanate dissolved in diethyl ether and tetrahydrofuran

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Abstract

We present electrochemical properties of lithium alanate (LiAlH_4) dissolved in aprotic ethers – diethyl ether (Et_2O) and tetrahydrofuran (THF) – under an Ar atmosphere of 1 atm at 298 K. Specific conductivities of both LiAlH_4 -THF and LiAlH_4 - Et_2O solutions are measured by AC four-terminal method. Cyclic voltammetry is performed with using a beaker-type electrochemical cell consisted of a Ni wire, Ni mesh and Li wire as a working, counter and reference electrode, respectively. In order to clarify the electrochemical behavior, anodic polarization of LiAlH_4 -THF solution is measured. The current density of 1.0 M LiAlH_4 -THF solution reaches to 1 A cm^{-2} , which is higher than the LiAlH_4 - Et_2O solution. Quantitative analysis of H_2 gas generated on the working electrode during the potentiostatic electrolysis tells that the number of electrons involved in the anodic reaction at the limiting current is one in case of the LiAlH_4 -THF solution. We propose conceivable electrochemical reactions of LiAlH_4 in the non-aqueous ethereal solutions.

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1. Introduction

To harness the chemical energy, hydrogen is the most attractive element because of the highest ratio of valence electrons to nucleons in the periodic table; namely, the energy released by a chemical reaction per weight can be very high when hydrogen is involved in the reaction. This is one of the reasons why hydrogen gas (H^0) is considered the most efficient energy source for fuel cell where the electrochemical oxidation to proton (H^+) takes place at the anode. Hydrogen can take another valence state, hydride ion (H^-). This two-electron state is stabilized by strong cation $\text{M} = \text{Li}^+$ or Na^+ in hydride salts, such as alkaline hydride (e.g. MH), borohydride (MBH_4) and alanate (MAIH_4) [1]. Hydride ion in these compounds is easily, or sometimes violently, oxidized by many protogenic substances; water, alcohol and so on. With this reducing ability, hydrides are utilized as reducing agents in synthetic chemistry [2]. As an electrochemi-

cal application of hydride ion, Brenner [3,4] developed in 1952 the “hydride bath” that consists of AlCl_3 and LiH (or LiAlH_4) in anhydrous ether whereby one can deposit metallic aluminum at room temperature. Numerous studies have been made for the electrodeposition of aluminum from organic solvents containing LiH or LiAlH_4 with AlCl_3 , since then [5–14]. Electrochemistry of hydride has been investigated also in ionic liquids. For example, Tsuda et al. [15] studied the anodic hydrogen electrode reaction in aluminum chloride-1-ethyl-3-methylimidazolium chloride (AlCl_3 -EtMeImCl) containing LiAlH_4 and reported the hydrogen generation on the electrode surface. LiAlH_4 in these solutions mixed with AlCl_3 forms other aluminate species such as AlHCl_2 , AlH_2Cl whose composition depends on the molar ratio of LiAlH_4 to AlCl_3 . For a hydride solution without AlCl_3 , the specific conductivity of LiAlH_4 solution is focused until now [5,7–12], whereas other electrochemical properties reported are limited to the measurement of linear sweep voltammetry [11,14]. A detailed study on LiAlH_4 itself in ethereal solution, especially the anodic reaction of AlH_4^- anion, is yet to be known.

In order to clarify the electrochemical properties of LiAlH_4 in organic solvents, we deal with LiAlH_4 solutions as elec-

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trolyte without other salt. As LiAlH_4 is liable to react not only with water, but also with protogenic solvents, such as alcohols, we studied LiAlH_4 in aprotic ethers, diethyl ether (Et_2O) and tetrahydrofuran (THF). Based on the electrochemical results derived from specific conductivity, cyclic voltammetry, polarization and potentiostatic electrolysis we speculate the mechanism of the hydrogen electrode reaction of AlH_4^- in the non-aqueous ethereal solutions.

2. Experimental

Preparation of the cell and electrochemical measurements was carried out under an Ar atmosphere. The temperature and pressure were 298 K and 1 atm, respectively. The Solartron Instruments model SI 1280B was used for all electrochemical measurements.

We used two solvents for LiAlH_4 in the present study. 1.0 M LiAlH_4 solutions in Et_2O ($\text{LiAlH}_4\text{-Et}_2\text{O}$ solution) and in THF ($\text{LiAlH}_4\text{-THF}$ solution) purchased from Aldrich were used as received. Concentration of LiAlH_4 was determined based on the method proposed by Krynskiy et al. [16]. Diluted LiAlH_4 solutions were prepared by diluting above solutions with adding each solvent (Kishida Chemical) purified by the distillation with using Na metal and benzophenone.

Beaker-type conductivity cell sealed with Teflon[®] is shown in Fig. 1(a). The electrodes consist of two bright Pt plates ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$, Nilaco, 99.98%), which are for current, and of two Pt wires ($\text{Ø}0.5\text{ mm}$), which are for the measurement of voltage; the latter pair is placed with 5 mm intervals. The conductivity of the solutions was measured by AC four-terminal method. Impedance spectra were recorded using commercial software (ZPLOT 2). The cell constant was determined with using 0.1 M KCl aqueous solution, within an error of 10%.

Fig. 1(b) shows the electrochemical cell for measurement of cyclic voltammogram and polarization curve. About 7.5 ml

of each solution is placed in Pyrex glass cell with stirring of 400 rpm. Ni wire ($\text{Ø}0.5\text{ mm}$, Nilaco, 99.9%) sealed in glass is used as working electrode (WE). Prior to the measurement, the surface of Ni wire is polished with $1\text{ }\mu\text{m}$ diamond powder and buffered with $0.05\text{ }\mu\text{m}$ alumina powder. The current density in the present study is calculated with respect to the geometric area of the working electrode. Counter electrode (CE) was Ni sheet (80 mesh, $10\text{ mm} \times 40\text{ mm}$). They are washed by ethanol in an ultrasonic bath for several minutes and dried in vacuo at 353 K. The reference electrode (RE) is Li–Al–H composite prepared by immersing Li wire ($\text{Ø}2\text{ mm}$, Aldrich, 99.9%) in the LiAlH_4 solution for several hours, which is placed 5 mm from the working electrode. We confirmed that the Li–Al–H composite electrode was stable as a reference by immersing a pair of thus prepared electrodes in the solution and by observing that the potential difference between two electrodes fluctuated within a few millivolts. The potential of this reference electrode is calibrated every time prior to the measurement of LiAlH_4 solutions with referring to Li^+/Li electrode prepared by electrodepositing Li metal on a Ni wire.

The electrochemical cell for electrolysis as shown in Fig. 1(c) has two compartments: one compartment has a working electrode of Ni sheet (80 mesh, $10\text{ mm} \times 10\text{ mm}$) and the reference electrode, and the other has a counter electrode of Ni sheet ($20\text{ mm} \times 20\text{ mm}$). The gas burette is connected to the cell to measure the amount of H_2 gas generated on the working electrode. To avoid the leakage of H_2 gas the system is comprised of tightly sealed stainless steel and glass. In order to measure the amount of H_2 gas accurately, water in the gas burette is saturated with H_2 by bubbling before the measurement. Additionally other factors, such as the vapor pressure of the solvent from cell without electrolysis are eliminated in calculation. Internal pressure of the cell is kept at atmospheric pressure all through the electrolysis.

3. Results

3.1. Specific conductivity of LiAlH_4 solution

Fig. 2 shows specific conductivities of $\text{LiAlH}_4\text{-Et}_2\text{O}$ and $\text{LiAlH}_4\text{-THF}$ solutions. The values of 0.1 and 0.2 M $\text{LiAlH}_4\text{-THF}$ solutions at 298 K are consistent with those reported at 293 K [9], suggesting the validity of the present measurement. The conductivities of both solutions increase gradually with increasing the concentration. The value of 1.0 M $\text{LiAlH}_4\text{-THF}$ solution is comparable to that of 0.1 M KCl aqueous solution, or that of representative electrolyte for the Li secondary batteries [17]. As Ishibashi et al. [8] pointed out, the conductivity of $\text{LiAlH}_4\text{-THF}$ solution is higher about two orders of magnitude than that of $\text{LiAlH}_4\text{-Et}_2\text{O}$ solution. In general, specific conductivity is proportional to the ionic mobility and the concentration of ions. Whereas high viscosity of solvent lowers the ionic mobility, high dielectric constant of solvent increases the concentration of ions by dissociating the salt into ions. According to the literature [18], both viscosity and dielectric constant of THF are higher than Et_2O . The fact that the THF solution of LiAlH_4 has higher conductivity than the Et_2O solu-

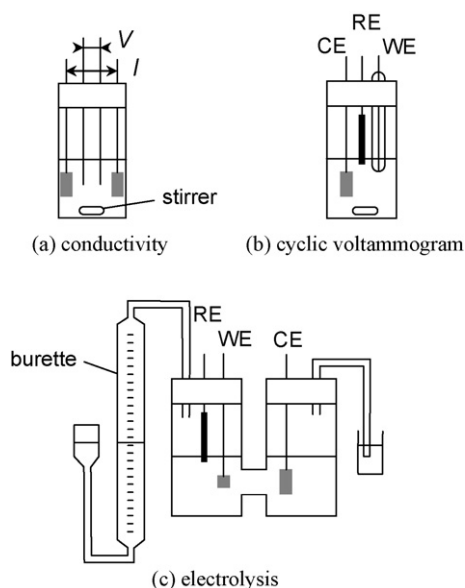


Fig. 1. Electrochemical cell for measuring: (a) conductivity, (b) cyclic voltammogram and (c) electrolysis.

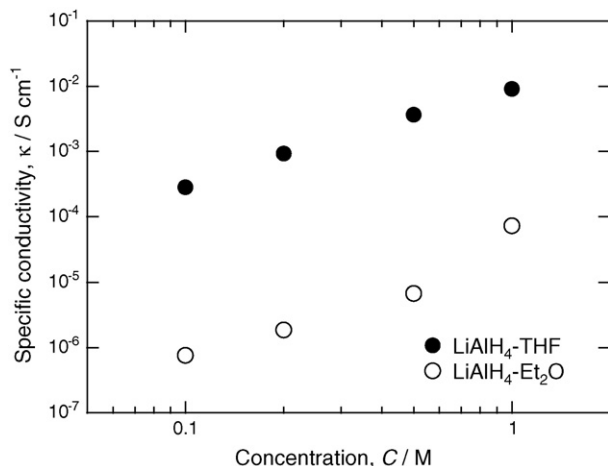


Fig. 2. Specific conductivities of LiAlH₄ dissolved in diethyl ether (LiAlH₄-Et₂O) and tetrahydrofuran (LiAlH₄-THF).

tion means that the positive influence on the conductivity from the dielectric constant overwhelms the negative one from the viscosity in the LiAlH₄-THF solution.

3.2. Cyclic voltammetry of LiAlH₄ solution

Cyclic voltammogram (CV) of LiAlH₄-Et₂O solution is shown in Fig. 3. The CV at 1.0 M LiAlH₄-Et₂O solution shows that one oxidation peak is present during anodic sweep while no characteristic peak appears during the cathodic sweep. The current density increases gradually with increasing the cycle number (Fig. 3(b)). Interestingly the oxidation peak during anodic sweep becomes recognizable only after the first cycle. None of the CV signal shown in Fig. 3 is attributed to the electrochemical decomposition of Et₂O because the decomposition potential [19] is far from the potential range measured in this study. We also confirmed that the impurities of LiAlH₄ solutions, such as Li₂O, LiOH and Al₂O₃, which can be produced by the reaction with trace amount of air remaining in the

Ar atmosphere, have no significant influence on the CV signal. Moreover, we found that the shape of the anodic peak is influenced by at which potential the cathodic sweep is reversed; that is, the more negative cathodic potential is applied, the bigger the anodic peak becomes. This observation suggests that the reaction, which undergoes the oxidation during the anodic sweep from 0 to +0.3 V, is subjected to the reduction during the cathodic sweep from 0 to -0.3 V. Considering that this redox reaction takes place around 0 V versus Li⁺/Li, the oxidation and reduction in this potential range can be respectively attributed to the dissolution and deposition of Li metal. Similar phenomenon has been observed in the Li metal-solvent systems [20]. The anodic sweep at higher potential shows that above 0.5 V the current density increases drastically with increasing the potential. The *E*-*i* relation is close to linear up to 4.0 V without hysteresis and no apparent peaks appear even at the scan rate of 5.0 V s⁻¹. With decreasing the concentration the current density plummets drastically (Fig. 3(a)). About 0.1 M LiAlH₄-Et₂O solution no longer shows a clear voltammogram probably due to the low ionic conductivity.

Fig. 4 shows the cyclic voltammograms of LiAlH₄-THF solution. The voltammograms taken with using Ni electrode is similar to that with using Au electrode reported by Lefebvre and Conway [14]. Comparing to the case of LiAlH₄-Et₂O solution in Fig. 3, one finds that the current density (*i*) is larger in the case of LiAlH₄-THF solution similarly to the ionic conductivity. The CV signal in the range of -0.3 to +0.3 V corresponds to the redox reaction of Li⁺/Li in the same manner as LiAlH₄-Et₂O solution. The anodic current increases gradually in the first several cycles; subsequently it reaches a stationary state (Fig. 4(b)). At high potential we observe spiky signals in the CV caused by gas formation on the electrode, which is hardly observed in the case of LiAlH₄-Et₂O solution. Lefebvre and Conway [14] have reported that the current arise at high potentials is the decomposition of solvent. However, we consider that the signal is attributed to the anodic reaction of AlH₄⁻ anion, not to the reaction of THF, because we confirmed the stability of THF in this potential range. According to the data reported previously [21], the

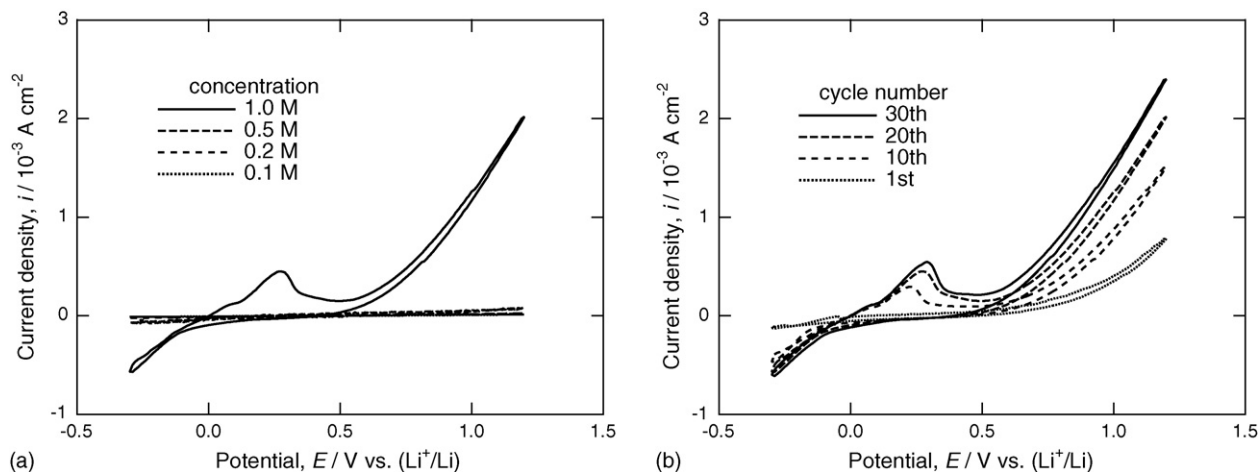


Fig. 3. Cyclic voltammograms of LiAlH₄ dissolved in diethyl ether: (a) at various concentrations after 20 cycles, (b) after various cycles at 1.0 M solution. Scan rate: 20 mV s⁻¹.

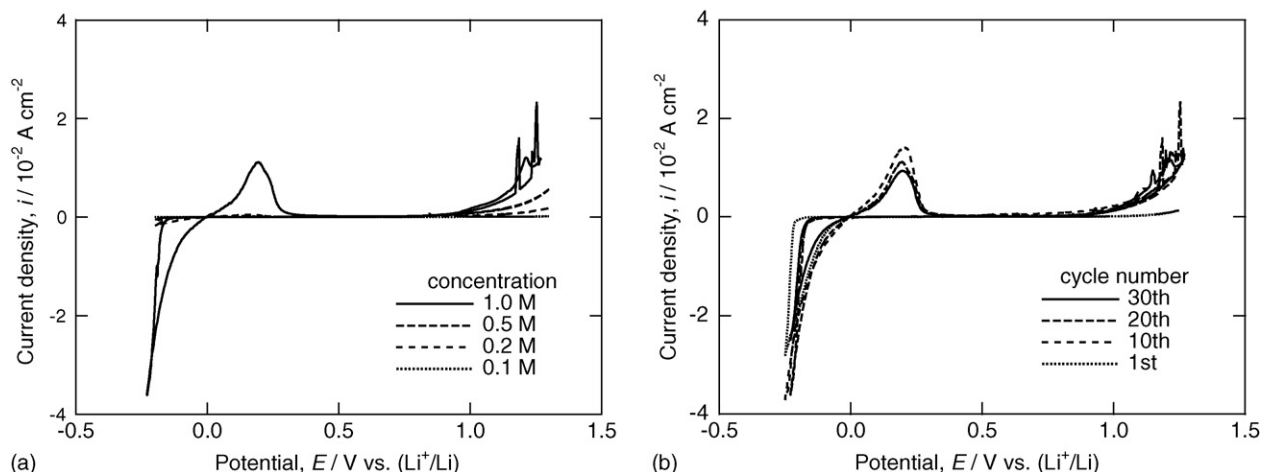


Fig. 4. Cyclic voltammograms of LiAlH_4 dissolved in tetrahydrofuran: (a) at various concentrations after 20 cycles, (b) after various cycles at 1.0 M solution. Scan rate: 20 mV s^{-1} .

anodic potential of THF is 4.7 V versus Li^+/Li . Qualitative analysis by means of the mass spectrometer tells that the gas generated at high potentials is composed only of hydrogen with a trace amount of the solvent THF, which is consistent with the results in AlCl_3 -related ionic liquids reported by Tsuda et al. [15].

3.3. Anodic polarization of AlH_4^- anion

Let us focus on the electrochemical reaction of AlH_4^- anion. Fig. 5 shows the polarization curves above 0.4 V where no redox peak of Li^+/Li appears. As can be seen in the figure, symmetric anodic and cathodic current branches are not observed; the anodic current is probably due to the anodic reaction of AlH_4^- anion while another reaction may proceed on the cathodic polarization. This suggests the irreversible electrochemical reaction of AlH_4^- anion. The linear relationship between potential and logarithmic current density from 0.65 to 0.95 V (solid line in Fig. 5) follows the Tafel equation ($\eta = a_a + b_a \log i$: subscript denotes the anodic polarization), suggesting that the charge-transfer process is the rate-determining step in the anodic reac-

tion of AlH_4^- anion. The b_a factor of the Tafel plot estimated from the straight line is ca. $120 \text{ mV decade}^{-1}$, which agrees with the value of cathodic polarization on Ni electrode for hydrogen generation reaction in 1.0 M NaOH aqueous solution at 298 K [22]. Based on the relation, $b_a = 2.303RT/\alpha_a nF$, we obtain that the transfer coefficient of anodic reaction α_a as 0.5 by assuming the number of electrons n in the reaction to be unity. This is not consistent with the value (0.65) at high LiAlH_4 content in $\text{LiAlH}_4\text{-AlCl}_3\text{-THF}$ solutions [14], indicating the different reaction mechanism of the $\text{LiAlH}_4\text{-THF}$ solution.

Above 1.0 V the current density asymptotically reaches to the limiting current density, indicating the reaction rate is diffusion-controlled. The limiting current density at 1 A cm^{-2} of $\text{LiAlH}_4\text{-THF}$ solution is higher about two orders of magnitude than that of $\text{LiAlH}_4\text{-Et}_2\text{O}$ solution. A vigorous H_2 gas generation on the working electrode is observed in this potential range for the THF solution. To evaluate the charge efficiency during the H_2 generation, the potentiostatic electrolysis was conducted. Fig. 6 shows the correlation between the quantity of electricity imposed at 1.2 V and amount of H_2 gas generated on the working

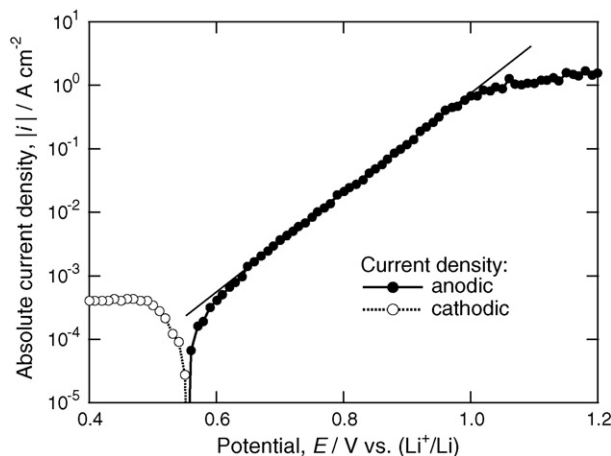


Fig. 5. Polarization curves of 1.0 M LiAlH_4 dissolved in tetrahydrofuran after 50 cycles between -0.25 and 1.25 V at 20 mV s^{-1} . iR correction was made by the current interrupt method.

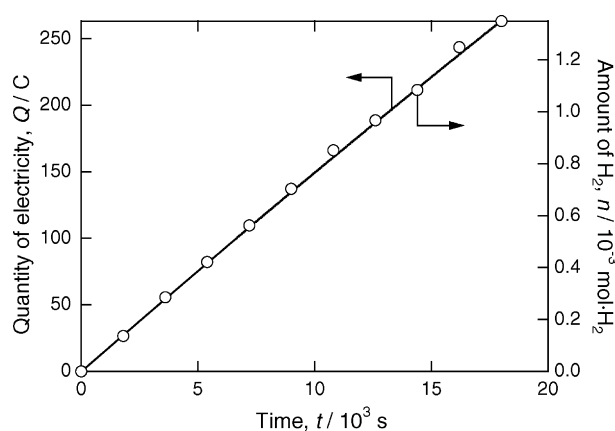


Fig. 6. Relation between the quantity of electricity and the amount of H_2 gas generated during the potentiostatic electrolysis of 1.0 M LiAlH_4 dissolved in tetrahydrofuran. Potential of working electrode was maintained at 1.2 V vs. (Li^+/Li) .

Table 1
Conceivable reactions of LiAlH₄ in solution

Dissociation reaction	Electrochemical reaction	E^* (V)
(1)	$\text{LiAlH}_4 \rightleftharpoons \text{Li}^+ + \text{Al} + 2\text{H}_2 + \text{e}^-$	+0.50
(2)	$\text{LiAlH}_4 \rightleftharpoons \text{Li}^+ + \text{AlH}_3 + 0.5\text{H}_2 + \text{e}^-$	+0.98
(3) $\text{LiAlH}_4 \rightleftharpoons \text{LiH} + \text{Al} + 1.5\text{H}_2$	$\text{LiH} + \text{Al} + 1.5\text{H}_2 \rightleftharpoons \text{Li}^+ + \text{Al} + 2\text{H}_2 + \text{e}^-$	+0.71
(4) $\text{LiAlH}_4 \rightleftharpoons \text{LiH} + \text{AlH}_3$	$\text{LiH} + \text{AlH}_3 \rightleftharpoons \text{Li}^+ + \text{AlH}_3 + 0.5\text{H}_2 + \text{e}^-$	+0.71

E^* : equilibrium potential vs. Li⁺/Li estimated from thermodynamic data [18,23].

electrode. The correlation tells that 0.5 mol of H₂ gas is evolved per 1 F of electricity. We tried to determine the ratio of the quantity of electricity to that of evolved H₂ gas also in the potential range where the Tafel relation is satisfied (0.65 < E (V) < 0.95). But, the miniscule rate of gas generation due to the small current density defied us.

4. Discussion

Now let us speculate what electrochemical reactions are taking place. In Table 1, we list some conceivable one-electron reactions. Reactions in which more than two electrons are involved are excluded from the consideration because the equilibrium potentials of multi-electron reactions are calculated to be higher than the potential range of the present study. Reaction Eqs. (1) and (2) indicate direct anodic reaction of AlH₄[−] anion while Eqs. (3) and (4) are two-step reaction; the first step is non-electrochemical dissociation of LiAlH₄ or the self-decomposition reaction and the second step is electrochemical reaction. If the reaction (3) were the case, the gas generation must be observed even without electric field. We confirmed this is not the case. The reaction (4) is also unlikely: Although Graef [11], suggested that there is equilibrium in THF:



where the equilibrium constant is $\log K = 13.45$. Considering the fact that the solubility of LiH in THF is very small, together with the above equilibrium constant, we can exclude as well the possibility that LiAlH₄ decomposes to LiH and AlH₃ spontaneously (reaction (4)). In effect, there is no characteristic signal corresponding to the anodic reaction of LiH at around 0.71 V in Fig. 5, which is predicted based on the thermodynamic data [18,23].

Reactions (1) and (2) are the direct anodic reaction of AlH₄[−] anion in solutions. The products are Al metal with 2 mol of H₂ gas in Eq. (1) and AlH₃ with 0.5 mol of H₂ in Eq. (2). The theoretical equilibrium potentials calculated from the molar enthalpy and entropy at 298 K at standard state are 0.50 and 0.98 V versus (Li⁺/Li) in reactions (1) and (2), respectively. Fig. 5 tells that the x -intercept is close to the value predicted for reaction (1). We speculate that in the potential range below 1.0 V the AlH₄[−] anion is electrochemically oxidized with one electron transfer and forms Al as indicated in reaction (1), although in this potential range some other electrochemical reactions such as the deposition of Al metal may overlap (see below). In the limiting current range above 1.0 V versus (Li⁺/Li), on the other hand, it is possible that reaction (2) is taking place as we observed 0.5 mol of H₂ generation per 1 F of electricity. The fact that the E - i relation

deviates from the Tafel polarization and reaches to the limiting current at around 1.0 V implies that the reaction switches at this potential from reaction (1), whose rate-determining step is the charge transfer process, to reaction (2), which is diffusion controlled, because this value is close to the predicted one for reaction (2) (see Table 1). However, an excess amount of the product AlH₃ gives rise to the instability of AlH₃ in THF [11]. In this case, the following reaction:



can occur slowly when the solution is left to stand still.

Several phenomena such as redox reaction of aluminate species formed by the anodic reaction of AlH₄[−] anion, etherification and association of LiAlH₄ should be taken into account in order to clarify the reaction mechanism of AlH₄[−] anion comprehensively. Furthermore, experiments to investigate in detail the electrochemical reactions of ethereal solution of AlH₄[−] are currently under progress in our laboratory, e.g. qualitative analysis of the substances in the solution and on the surface of electrodes, determination of the gas amount and electricity in the wider potential range, and so on.

5. Conclusion

The electrochemical characteristics of LiAlH₄ were studied in two organic solvents around room temperature. Solvation of LiAlH₄ by Et₂O and THF seems to explain the large differences in the ionic conductivity and the current density. Anodic polarization of LiAlH₄-THF solution shows that from 0.65 to 0.95 V versus Li⁺/Li the anodic reaction of AlH₄[−] anion follows the Tafel equation, suggesting that the charge-transfer process is the rate-determining step. At higher potential the current density reaches asymptotically to the limiting current indicating the diffusion is rate determining. At this limiting current, the ratio between the number of electrons and the number of H₂ molecules generated on the working electrode is 1:0.5. Further electrons can be released by the anodic reaction of the H₂ gas to proton. This suggests that LiAlH₄ can be an active anode material with high voltage and capacity with high reactivity.

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