수소저장합금을 이용한 신개념의 알칼라인 연료전지의 특성에 관한 연구

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The Characterization of New Type of Alkaline Fuel Cell using Hydrogen Storage Alloys

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ABSTRACT

본 연구는 Chemical hydride 형태의 수소발생제를 포함한 액체연료를 이용한 신개념의 알칼라인 연료전지[1,2]의 특성을 분석하였다. Chemical hydride는 연료전지의 수소공급원으로써 사용될 수 있으며, 본 연구팀은 KOH 전해질에 수소발생제인 Sodium Borohydride (NaBH₄)를 첨가하여 제조된 액체연료를 알칼라인 연료전지에 공급함으로서 상온에서 매운 우수한 전기화학적 성능결과를 얻을 수 있었다. 이때 음극 활물질로 $ZrCr_{0.8}Ni_{1.2}$ 수소저장합금이 사용되었으며, 양극은 방수처리된 카본지 위에 분산된 Pt/C 가 사용되었고, air가 1atm으로 양극에 공급되었다. 음극에 대한 XRD 분석결과 음극에서의 산화에 의해 Sodium Borohydride (NaBH₄)가 분해되어 수소가 발생되며, 연속적으로 액체연료가 주입되어도 전지가 작동하는 것을 확인할 수 있었다. 이때 에너지밀도는 6,000 Ah/kg (for NaBH₄ or KBH₄)이다.

주요기술용어 : Alkaline fuel cell(알칼라인 연료전지), Chemical hydride(화학적수소발생제), Metal hydride(수소저장합금), Sodium borohydride(NaBH₄)(소듐보로하이드라이드), Alkaline solution(염기성 용액), Hydrogen fuel (수소연료)

1. Introduction

Fuel cells produce the electric current directly by the electrochemical reaction of hydrogen with atmospheric oxygen[3-5]. Generally, fuel cells whose anode is directly supplied with

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hydrogen gas as a fuel have been utilized because the electrochemical reaction can also occur at a normal temperature and its efficiency is very high. However, the hydrogen fuels have the disadvantages that their storage density is lower than that of other fuels, and thus their economical efficiency is low.

In the meantime, the studies of fuel cells of the type which employ a hydrogen-containing hydrocarbon compound such as methane, propane, methanol, hydrazine, ammonia, and the like in place of the hydrogen gas in the solution of electrolyte, or of the type which supplies hydrogen reformed from such a compound for the anode, have been developed[6~9]. However, these fuel cells have the disadvantages that they require high temperature (e.g., 100-300℃) for effective oxidation/reduction reactions of hydrogen/oxygen and that the reaction rate is slower. Thus, the reaction efficiency is degraded as compared with cells using hydrogen gas.

As a new fueling concept, it can be suggested that the chemical hydrides act as new fuel media supplying hydrogen at normal temperature. Chemical hydrides ($NaBH_4$, LiH, NaH, etc.) are very reactive with water, which results in releasing a large amount of H_2. Generally, to minimize the hydrolysis, the borohydride ion should be stabilized by hydroxide ions ([OH-] > 5 M), which is confirmed by empirical rule[10]. The solution can release hydrogen gas if catalyzed or acidified. Therefore, in battery application, gas-releasing conditions are to be avoided. Release of hydrogen gas is undesirable because it can reduce the energy available and causes a variety of other undesirable characteristics for the cell. The chemical hydride, reducing agent,

plays a role in reducing a metal hydride in alkaline solution through producing the hydrogen atom in the oxidation/reduction reaction.

As a representative example, C. Iwakura et al have suggested that KBH_4 acts as a reducing agent for improving the activation properties of MH electrode[11]

They have also found that the lattice volume of alloy was expanded due to the absorption of hydrogen atoms released from BH_4^- into the alloy particles and the formation of the new electroactive surfaces. It has been suggested that a key factor in modification by a reducing agent for improving the characteristics of MH electrodes is due to both the electrons and atomic hydrogen released.

S. Wakao et al have also investigated the behavior of Zr-based hydrogen storage material in the alkaline solution containing the reducing agent such as hydrazine (N_2H_4)[12]. When these alloys were immersed into the hydrazine solution, they rapidly extracted and absorbed hydrogen from hydrazine molecule until they were saturated by hydrogen. As a result of the extraction of hydrogen, the evolution of nitrogen gas occurred. Immersing hydrogen-absorbing alloys into the hydrazine solution is one of the interesting techniques of hydriding. Eventually, as a similar concept, to know MH electrode characteristics of the cell reaction in borohydride solution is important to its application to the electrode of a borohydride fuel cell.
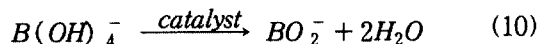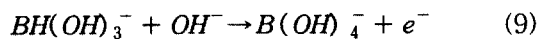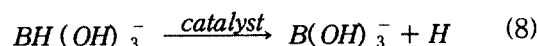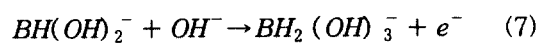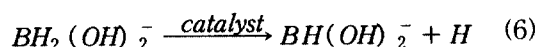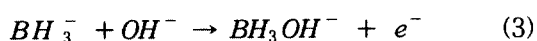
In this work, the approaches for overcoming these disadvantages of prior art are reported. As a result, it was examined that when a hydrogen-releasing agent, $NaBH_4$, is added to an aqueous alkaline solution of electrolyte as

hydrogen fuel, the electrochemical reaction rate is higher at a normal temperature than that of cells containing other hydrogen fuels.

2. Theoretical backgrounds

According to the present work, an alkaline fuel cell is provided which contains a hydrogen-releasing agent (chemical hydride) selected from the group consisting of NaBH₄, KBH₄, LiAlH₄, KH and NaH. The reactions at the electrodes of the alkaline fuel cell containing the hydrogen-releasing agent are as mentioned below.

First, the added hydrogen-releasing agent releases hydrogen and electron in the aqueous solution of electrolyte through an electrochemical decomposition and oxidation by the hydrogen storage alloy catalyst. Where the hydrogen-releasing agent is NaBH₄, the following reactions will occur:

$$NaBH_4 \rightarrow Na^+ + BH_4^- \qquad (1)$$

$$BH_4^- \xrightarrow{catalyst} BH_3^- + H \qquad (2)$$

$$BH_3^- + OH^- \rightarrow BH_3OH^- + e^- \qquad (3)$$

$$BH_3OH^- \xrightarrow{catalyst} BH_2OH^- + H \qquad (4)$$

$$BH_2OH^- + OH^- \rightarrow BH_2(OH)_2^- + e^- \qquad (5)$$

$$BH_2(OH)_2^- \xrightarrow{catalyst} BH(OH)_2^- + H \qquad (6)$$

$$BH(OH)_2^- + OH^- \rightarrow BH_2(OH)_3^- + e^- \qquad (7)$$

$$BH(OH)_3^- \xrightarrow{catalyst} B(OH)_3^- + H \qquad (8)$$

$$BH(OH)_3^- + OH^- \rightarrow B(OH)_4^- + e^- \qquad (9)$$

$$B(OH)_4^- \xrightarrow{catalyst} BO_2^- + 2H_2O \qquad (10)$$

The above equations (2) to (10) can be represented by the following single equation:

$$BH_4^- + 4OH^- \rightarrow \quad BO_2^- + 2H_2O \\ + 4H + 4e^- \qquad (11)$$
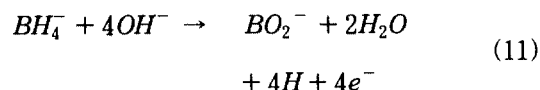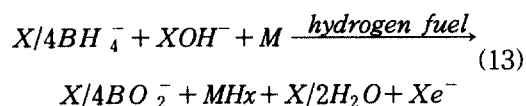
Where the hydrogen-releasing agent is KBH₄ or the others, similar decomposition reactions to the equations (2) to (10) will occur in the aqueous solution of electrolyte to produce hydrogen in the solution.

Hydrogen, which is generated by the above hydrogen-releasing agent, is stored in a hydrogen storage alloy anode as a hydrogen storage material, e.g., metal hydrides to supply the hydrogen fuel. The reaction involved can be represented by the equation:

$$M + XH \xleftrightarrow{reversible} MHx + Q(cal) \qquad (12)$$

wherein M represents a metal or an intermetallic compound (hydrogen storage alloy), and MHX represents a metal hydride.
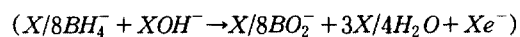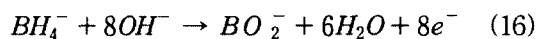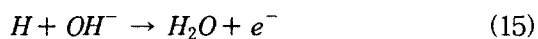
Thus, the generation of hydrogen and electron in the alkaline solution containing a hydrogen-releasing agent, and the subsequent storage of the hydrogen in the hydrogen storage alloy can be represented by the equation

$$X/4BH_4^- + XOH^- + M \xrightarrow{hydrogen \ fuel} \\ X/4BO_2^- + MHx + X/2H_2O + Xe^- \qquad (13)$$

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Hydrogen, which has been stored in MH electrode, produces electrons by dehydrogenation, i.e., oxidation of the hydrogen storage alloy at the anode, as in the anode of nickel/metal hydride (Ni/MH) cell [see Equation (14)].

$$MHx + XOH^- \xleftrightarrow{reversible} M + XH_2O + Xe^- \quad (14)$$
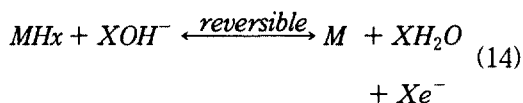
In addition, the reduction reaction of hydrogen released from the hydrogen-releasing agent as shown in the following equation (15), and the electron-releasing reaction as in the following equation (16) can occur in the alkaline solution of electrolyte.

$$H + OH^- \rightarrow H_2O + e^- \quad (15)$$

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (16)$$

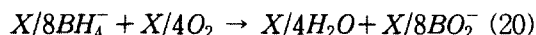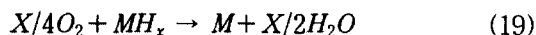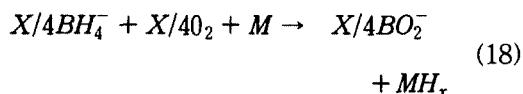$$(X/8BH_4^- + XOH^- \rightarrow X/8BO_2^- + 3X/4H_2O + Xe^-)$$

In the meantime, atmospheric oxygen fuel is supplied for the oxygen cathode to cause the reduction reaction of the following equation (17) at the interfaces between the electrode and the aqueous solution of electrolyte, and thus electrons are consumed.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (17)$$

$$(X/4O_2 + X/2H_2O + Xe^- \rightarrow XOH^-)$$
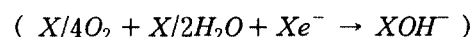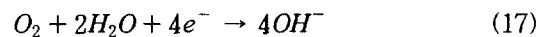
Thus, where the hydrogen-releasing agent is either $NaBH_4$ or KBH_4, the overall reaction of atmosphere/hydrogen storage alloy cell containing the hydrogen-releasing agent can produce electric energy by the following three-electrochemical oxidation/reduction reactions.

$$X/4BH_4^- + X/4O_2 + M \rightarrow X/4BO_2^- + MH_x \quad (18)$$

$$X/4O_2 + MH_x \rightarrow M + X/2H_2O \quad (19)$$

$$X/8BH_4^- + X/4O_2 \rightarrow X/4H_2O + X/8BO_2^- \quad (20)$$

The key half reaction which defines the fuel side (anode; negative electrode) of the cell is based on borohydride ions. Equation (18) is written for an aqueous system but is not limited to such a system. The new type of fuel cell use as air electrode to provide the other half-cell reaction (equation (17)) required to make a complete cell. The theoretical voltage for net reaction of the cell is 1.64V.

3. Experimental details

An aqueous solution containing 1g of $NaBH_4$ in 500cc of 6M KOH was used. A $ZrCr_{0.8}Ni_{1.2}$ alloy was used as an anode. The hydrogen storage alloy electrode was prepared by melting the weighed amount of each pure metal under an argon atmosphere, mechanically pulverizing, and then mixing with an appropriate amount of copper or nickel powder and TEFLON powder. The resulting mixture was pressure-molded. The hydrogen storage alloy electrode was made in disc form, and has a size of 1 cm in diameter and 1 mm in thickness. The weight of the disc alloy electrode was 0.24 g. A platinum-dispersed carbon electrode (Pt/C) was used as a cathode. The Pt/C electrode was made by dispersing 5% by weight of platinum in VULCAN XC-72. The hydrophobic/hydrophilic

1. Cell case,   2. KOH electrolyte
3. Separator,   4. Air electrode(cathode)
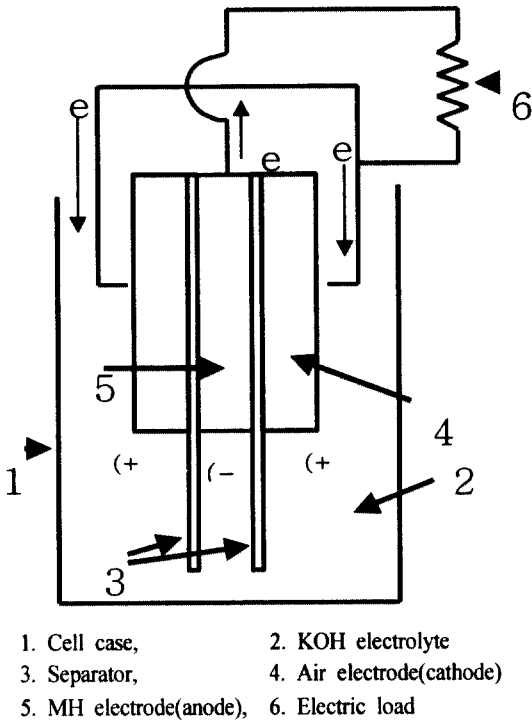5. MH electrode(anode),   6. Electric load

Fig. 1. A schematic structure of developed fuel cell.

treatment was carried out as follows. The Pt/C powder and polytetrafluoroethylene were mixed in weight ratios of 70/30 for the hydrophilic side of the electrode, and 60/40 for the hydrophobic of the electrode.   The mixed powder were intimately mixed in distilled water by ultrasonic agitation, and rolled in a carbon paper.   The rolled powder was covered by a carbon paper which was made by dispersing and coating 20 % by weight of platinum in VULCAN XC-72 at a laboratory, and the moisture was removed by pressing, followed by drying at 120 ℃ in a nitrogen atmosphere.   The reaction layer was attached with the carbon paper by pressing and calcining at the melting point of PTFE, i.e. 300 ℃ for one hour to obtain a specimen. The final pressure had a diameter of 15 mm and a thickness of 0.2 mm.   In order to increase the

ionic conductivity of the electrolyte 2, for example, LiOH may be added to the alkaline solution of electrolyte in an amount of 0.01 to 0.1% by weight.

4. Results and discussion

The developed fuel cell will be further illustrated with reference to Fig. 1.   The electrolyte which can be employed in this work is an alkaline electrolyte at pH>12, for example, KOH, NaOH, etc. $NaBH_4$ containing solution is stabilized in alkaline one, retarding the evolution rate of hydrogen gas.   A hydrogen-releasing agent was selected from the group consisting of $NaBH_4$, KBH_4, $LiAlH_4$, KH, and NaH.   The $NaBH_4$ has the highest specific hydrogen storage capacity of all hydrogen-releasing agents.   The hydrogen-releasing agent should be used in an amount of 0.01 to 50.00% by weight on the basis of the total weight of the alkaline solution of electrolyte.   When the amount of hydrogen-releasing agent used is less than the lower limit of the range, the amount of hydrogen to be released will be lowered.   This degrades the efficiency of the cell.   When the amount of hydrogen-releasing agent used is more than the upper limit of range, the hydrogen-releasing agent is not dissolved in the alkaline solution, resulting in the formation of solid precipitates.   This also degrades its utility and efficiency. Oxygen electrodes are made of materials which oxygen can be easily engaged in an oxidation/reduction reaction on its surface.   For example, such electrodes may include carbon electrodes, platinum-dispersed carbon electrodes, nickel electrodes, and the like which have a double or triple structure consisting of a hydrophilic side
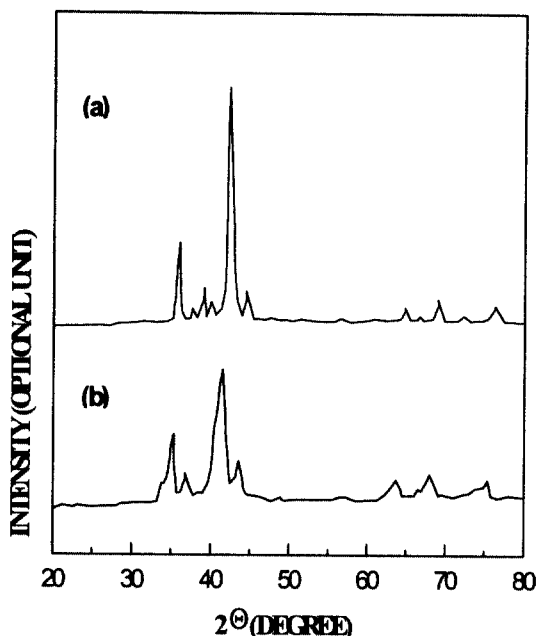
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Fig. 2. X-ray diffraction pattern of a pressure-molded hydrogen storage alloy electrode, (a) is not exposed to the alkaline solution of electrolyte, (b) (a) after the electrode is impregnated in the alkaline solution of electrolyte.

from an intermetallic compound to a metal hydride by the action of the hydrogen-releasing agent added. It can be seen from Fig. 2(a), (b) that the hydrogen fuel could be supplied to the hydrogen storage alloy electrode without any treatment.

After the hydrogen storage alloy absorbed hydrogen, the cell was discharged at 10 mA with measuring of its discharge voltage. The results are indicated by a discharge curve in Fig. 3. It can be seen that the discharge voltage is about 0.7 V and that the overpotential of about 0.3 V is generated. Such overpotential is mostly generated from the oxygen cathode. However, if pure oxygen gas, not air, is supplied to the oxygen cathode and the volume of oxygen to be supplied is increased, the overpotential decreases as shown in Table 1. A glass tube for gas feeding was inserted into the rear side of the oxygen electrode, and the tube

interfaced with electrolyte and a hydrophobic side interfaced with atmosphere. The preferable hydrogen storage alloy is one, which can reversibly absorb and release hydrogen irrespective of the hydrogen storage capacity. It should reveal the properties of a fast hydrogenation reaction rate, and a good stability in the electrolyte. The aqueous electrolyte solution provides an electrode/electrolyte interface by means of capillary action through the separator. It also acts as an ion conductor between the electrodes. It was observed by an X-ray diffraction analysis that upon exposing the hydrogen storage alloy anode to the solution of electrolyte containing the hydrogen-releasing agent without ant external treatment, the reaction at the alloy electrode caused a change
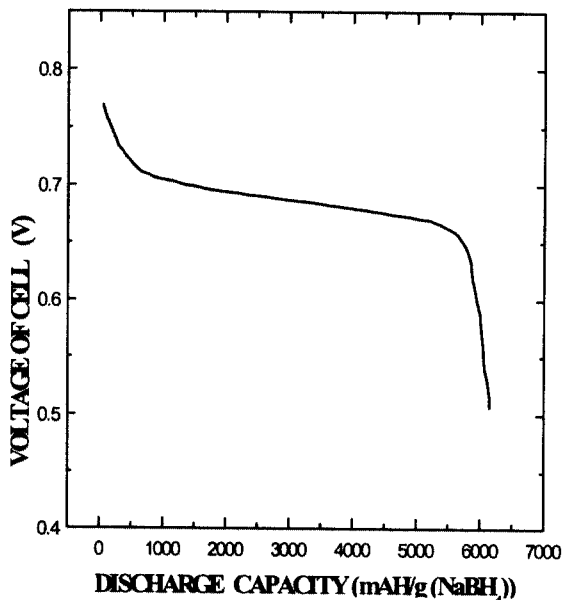

Fig. 3. A current discharge curve of a fuel cell containing a hydrogen-releasing agent.

Table 1. Discharge voltage of the cell depending on the flow rate of either oxygen gas or air

Flow rate of air (liter/min)	Discharge voltage (V)	Flow rate of oxygen (liter/min)	Discharge voltage (V)
0	0.71	0	0.8
0.1	0.73	0.1	0.84
0.2	0.78	0.2	0.88
0.5	0.85	0.5	0.95

was connected with the pressurized oxygen cylinder. The flow rate of oxygen (or air) was controlled by a valve or a ventilator. Table 1 below shows the discharge voltage of the cell depending on the flow rate of either oxygen gas or air.

Consequently, the developed cell has a higher electro-chemical reaction rate than those of the prior art fuel cells. It can operate at a normal temperature and produce a large amount of

Fig. 4. A current discharge curve of a fuel cell, where the hydrogen-releasing agent is intermittently added to the fuel cell.

energy due to its high energy density of 6,000 Ah/kg or more (for $NaBH_4$ or KBH_4).

Whenever the discharge voltage of the cell decreased to below 0.5 V, 1 g of $NaBH_4$ as a hydrogen fuel source was supplied for the solution electrolyte, the continuous generation of current was monitored. Continuously, the continuous generation of current was monitored.

It can be shown in Fig. 4 that the fuel cell continuously generates current when the hydrogen-releasing agent is added to the electrolyte solution. That is, the fuel cell (electrochemical oxidation /reduction reaction) continuously operates as long as oxygen and hydrogen fuel are supplied.
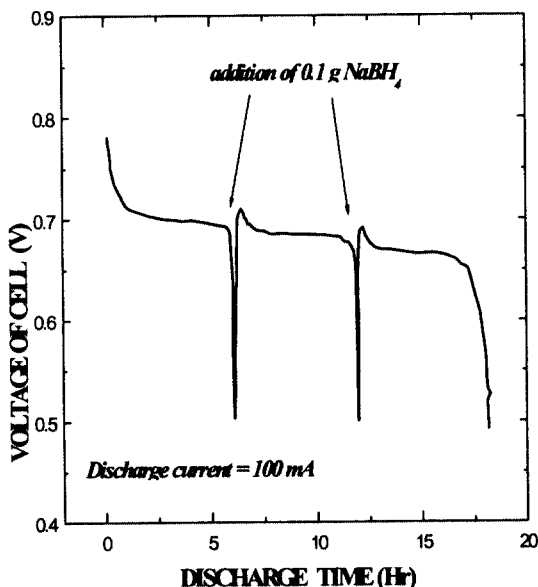
5. Conclusion

The present work has been described to provide a fuel cell having a high electrochemical reaction efficiency and a good discharge capacity, which comprises an aqueous alkaline .solution of electrolyte containing a hydrogen-releasing agent selected from the group consisting of $NaBH_4$, KBH_4, $LiAlH_4$, KH and NaH, a hydrogen storage alloy electrode as an anode, and an oxygen electrode as a cathode.

If air is supplied to the oxygen electrode and the hydrogen-releasing agent is fed to the

alkaline solution of electrolyte, the cell can produce electric current continuously. Therefore, it can operate at a normal temperature and produce a large amount of energy due to its high energy density of 6,000 Ah/kg or more (for $NaBH_4$ or KBH_4).

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