



Short communication

A fundamental study on electrochemical hydrogen generation from borohydrides

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ABSTRACT

Borohydrides (LiBH₄, NaBH₄, KBH₄, etc.) are the most attractive materials for hydrogen storage due to their high-volumetric and -gravimetric hydrogen density as well as safety issues. Although H₂ for fuel cells is generated by the hydrolysis of borohydrides, it is very difficult to control the rate of H₂ generation due to the nature of the catalytic reaction. In addition, the change in enthalpy (ΔH) of the reaction is directly wasted as heat generation. We propose a method for the electrochemical generation of hydrogen, in which a borohydride in an alkaline solution is oxidized at the anode while water is reduced at the cathode to generate H₂ gas. The cell has a cation exchange polymer electrolyte membrane between a precious metal anode and a Pt cathode to inhibit the crossover of BH₄⁻ anion. The open circuit voltage of the cell is positive, which raises the possibility of spontaneous operation with electrical generation as an alternative to the heat generation in hydrolysis. At the cathode, the rate of H₂ generation coincides well with the current density, indicating that H₂ generation from borohydrides can be electrochemically controlled by means of this hydrogen generator.

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1. Introduction

Fuel cells such as a polymer electrolyte fuel cell (PEFC) have attracted attention for application in portable electronic devices because of their high-fuel efficiency. Hydrogen has been stored in a compressed tank or as liquefied H₂, in hydrogen storage alloys and so on [1]. Borohydrides (LiBH₄, NaBH₄, KBH₄, etc.) are the most attractive materials for hydrogen storage due to their high-volumetric and -gravimetric hydrogen density as well as safety issues. Hydrogen gas is generated by the hydrolysis of borohydride in the presence of a suitable catalyst at room temperature [2]:



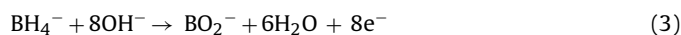
Although this reaction is simple and suitable for a high rate of H₂ supply, it is difficult to control the rate of H₂ generation due to the catalytic reaction of hydrolysis. However, some fuel cells, especially those intended for portable electronic devices, demand instant start-stop and change in the rate of hydrogen supply. In addition, the change in enthalpy of the reaction ($\Delta H = -248.9 \text{ kJ mol}^{-1}$) is directly wasted as heat generation in H₂ generation by the catalytic hydrolysis reaction.

Electrochemical hydrogen generation offers the advantage of instant start-stop and change in the rate of hydrogen supply because the reaction rate can be controlled by the current. In an

alkaline solution, the hydrogen evolution reaction occurs at the cathode as



Electrochemically, the anodic oxidation of borohydrides proceeds at the anode [3]:



which is used in a direct borohydride fuel cell (DBFC) [4,5]. As estimated from thermodynamic data [6] the standard electrode potential of borohydrides in Eq. (3) (-1.241 V vs. SHE) is lower than that of water in Eq. (2) (-0.828 V), which raises the possibility of spontaneous H₂ generation accompanied by electrical generation by coupling both equations. The overall reaction is given by



The standard cell voltage (E_{cell}^0) calculated from the Gibbs free energy ($\Delta G = -318.9 \text{ kJ mol}^{-1}$) is 0.413 V . The electrical generation (ΔG) is greater than the heat generation in hydrolysis (ΔH) from borohydrides, i.e., the theoretical efficiency exceeds 100%.

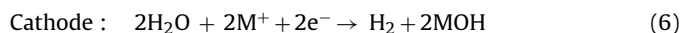
We propose here a device for the electrochemical generation of hydrogen using a solid polymer electrolyte membrane, in which borohydride is oxidized at the anode while water is reduced at the cathode. H₂ generation is electrochemically controlled at the cathode. Hydrogen generators which use polymer electrolyte water electrolysis are well known and commercially available [7,8]. Polymer electrolyte water electrolysis consumes electric power and requires an applied voltage of greater than 1.23 V at 25°C . On the

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other hand, this proposed H₂ generation from borohydrides may theoretically be capable of spontaneous operation without the consumption of electricity, as mentioned above. The H₂ produced can be supplied as a fuel for hydrogen–air fuel cells. Although a DBFC is a much simpler system than a system composed of this proposed H₂ generator and a fuel cell, a serious problem with DBFC is the deposition of alkali metal carbonates at the air cathode, which prevents the long-term generation of electricity by the DBFC. Since a borohydride solution is alkaline, an alkali metal cation (M⁺) reaches the cathode through the cation exchange membrane, reacts with carbon dioxide in the air and causes the same problem as in alkaline fuel cells, which cannot be used with an air cathode. Although the fuel cell system composed of the H₂ generator and a fuel cell is more complicated, the system is capable of long-term operation with borohydride as an energy source because water in the place of the air is delivered to the cathode of the H₂ generator under an alkaline condition, which prevents the formation of cathode depositions of alkali metal carbonates. In this paper we describe a device for the electrochemical generation of hydrogen using a polymer electrolyte membrane and survey the problems that must be solved for the development of this H₂ generator. This work provides some evidence regarding the characteristics and possibility of this new electrochemical device.

2. Concept

A schematic representation of H₂ generation is shown in Fig. 1. The cell has a membrane electrode assembly (MEA) that is obtained by sandwiching a polymer electrolyte membrane between an anode and cathode. A cation exchange polymer electrolyte membrane (Nafion[®]) was used as the electrolyte to prevent the crossover of BH₄⁻ anion, leading to the controllable generation of hydrogen at the cathode. When alkali metal cation is used as a counter cation, the anodic oxidation of borohydrides in Eq. (3) and the cathodic reduction of water in Eq. (2) can be rewritten using an electric charge carrier, M⁺, in the membrane as



During operation, both M⁺ conduction and water permeation from the anode to the cathode occur in the membrane, and subsequently H₂ is generated at the cathode with the formation of MOH. Since the MOH at the cathode can be recycled to the anode, MOH is not consumed in H₂ generation. The overall reaction and thermodynamic cell voltage (E_{cell}) are given by

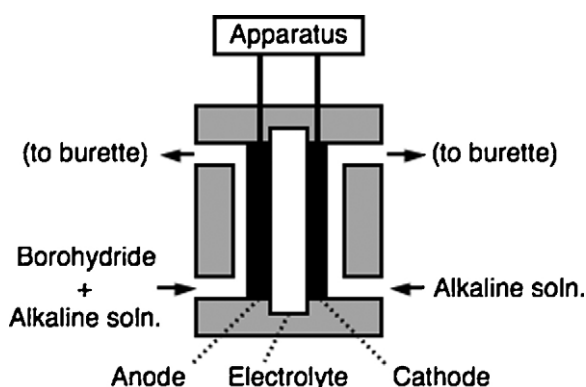
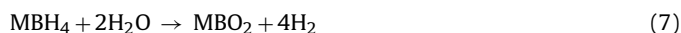


Fig. 1. Schematic representation of the electrochemical generation of hydrogen.

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{a_{\text{BO}_2^-} p_{\text{H}_2}^4}{a_{\text{BH}_4^-} a_{\text{H}_2\text{O}}^2} \quad (8)$$

where R , T , n and F are, respectively, the gas constant, absolute temperature, number of electrons in the overall reaction ($=8$) and the Faraday constant; $a_{\text{BH}_4^-}$, $a_{\text{BO}_2^-}$ and $a_{\text{H}_2\text{O}}$ are the activities of BH₄⁻ anion, BO₂⁻ anion and water in the alkaline solution, respectively; and p_{H_2} is the hydrogen pressure at the cathode. E_{cell} increases with an increase in the activity of MBH₄ in MOH aqueous solution, which is accomplished by increasing the concentration of MBH₄.

3. Experimental

Pt black (Johnson-Matthey, HiSPECTM 1000, 20 m² g⁻¹) was used as an electrocatalyst of MEA. It was suspended in Nafion[®] solution as a binder (Aldrich, 5 wt% solution in lower aliphatic alcohols and water). The slurry was spread on a PTFE sheet and subsequently dried in a vacuum at 80 °C for 1 h. The obtained layer with Pt black (2.4 mg cm⁻²) was used for the cathode and anode unless otherwise noted. Au powder (Ishifuku, SA05, 0.6 m² g⁻¹) was also used as an electrocatalyst for the anode.

Cation exchange polymer electrolyte membrane (DuPont, Nafion[®] 117, equivalent weight: 1100 g equiv.⁻¹) was pretreated with H₂O₂ and H₂SO₄ and washed with water by the conventional method [9]. MEAs were prepared by decal transfer [10] of the electrode layers onto both sides of a Nafion[®] membrane. MEAs were sandwiched between two carbon cloths (E-TEK, B-1A) used as gas-diffusion media [9]. A single cell with a geometric electrode area of 10 cm² was constructed.

Borohydrides dissolved in an alkaline hydroxide aqueous solution were prepared as reported previously [11]. In most experiments in this report, Li⁺ was used as a typical of counter cation, since LiBH₄ has a higher volumetric and gravimetric hydrogen density than NaBH₄ and KBH₄, and the conductivity of Li⁺ in Nafion[®] stays a higher value over a wide concentration range [12]. The cell performance is hardly affected by the kind of alkali metal cation, as noted in Section 4.3. Unless otherwise stated, 1 M LiOH solution containing 0.1 M LiBH₄ was delivered to the anode at 0.1 ml s⁻¹, while LiOH solution with the same concentration was delivered to the cathode at the same flow rate to reduce the effect of the difference in the concentration of alkali metal cation between the anode and cathode.

All electrochemical measurements were conducted using a Solartron Instruments model SI 1280B at room temperature (ca. 25 °C) and atmospheric pressure. The current was measured after a steady state was reached (1000 s). Both anode and cathode potentials were determined vs. a standard hydrogen electrode (RHE) connected to the periphery of the cathode side, as shown previously [13]. The rate of H₂ generation was determined by averaging the amount of H₂ generated from the outlet of the cell for 1000 s.

4. Results and discussion

4.1. Polarization of anode and cathode

The electrochemical properties of each electrode were determined prior to cell operation. Fig. 2 shows the anodic polarization of borohydride oxidation and the cathodic polarization of water reduction. The open circuit potential of the cathode is close to 0 V vs. RHE and a potential–current relation based on the Butler–Volmer equation [14] is observed, suggesting that the cathodic reduction of water is primarily due to the charge-transfer on the electrode surface. In the case of the anode, the observed open circuit potential is less than that of the cathode. Although the slope of the

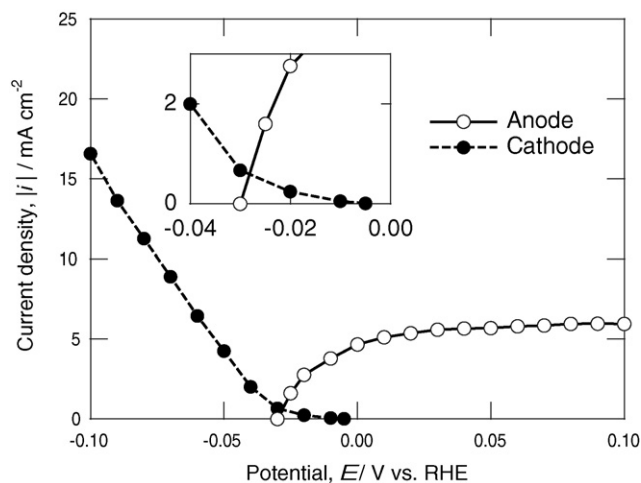


Fig. 2. Polarization curves for the anode and cathode of the cell.

potential–current relation is positive below 0 V vs. RHE, the anodic current density is almost independent of the potential above 0 V. This indicates that the diffusion of BH_4^- in the solution rather than the charge-transfer and membrane resistance by cation conduction dominates the anodic current density in this region. The experimental results also confirmed that the current density is influenced by the flow rate of the solution.

4.2. H_2 generation during cell operation

The relation between cell voltage and current density is shown in Fig. 3. At any time, the cell shows a stable current density under potentiostatic operation. When the alkaline solution containing BH_4^- is delivered to the anode and the alkaline solution is delivered to the cathode, the open circuit voltage is 23 ± 8 mV, which indicates the spontaneous generation of hydrogen without the application of voltage. The current density increases with a decrease in the cell voltage and is 1.5 mA cm^{-2} at 0 V. Fig. 4 shows the detailed properties of electrical generation. A plot of the current density against the cell voltage is almost linear. The power density of the cell reaches $6.3 \pm 1.8 \mu\text{W cm}^{-2}$ at 0.01 V. This result actually shows that H_2 generation can spontaneously occur with simultaneous electrical generation although this is limited to a region of very low-current density. As shown in Fig. 3, a further increase in

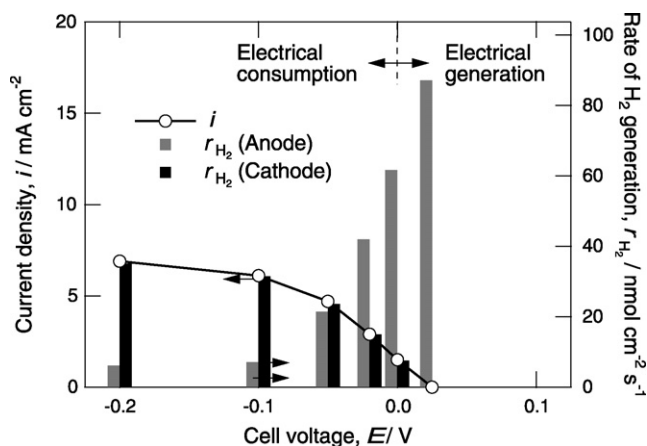


Fig. 3. Rates of H_2 generation at the anode and cathode and the relation between cell voltage and current density. The rate of H_2 generation on the right axis corresponds to the current density on the left axis.

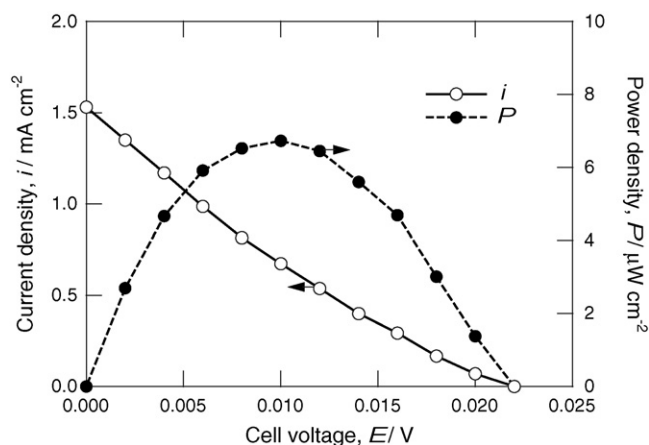
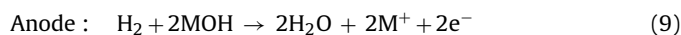


Fig. 4. Current density and power density as a function of cell voltage.

the current density is accomplished by applying voltage to the cell (negative cell voltage). The current density is close to the limiting current density of the anodic polarization, as shown in Fig. 2, suggesting that cell performance is attributed to the diffusion of BH_4^- to the anode at the applied cell voltage in this condition.

In the cell, H_2 is continuously generated by the catalytic hydrolysis of BH_4^- , while at the cathode it is generated by the cathodic reduction of water. The rates of H_2 generation at both the anode and cathode are also shown in Fig. 3. At the anode, the rate of H_2 generation by hydrolysis at the open circuit voltage is ca. $90 \text{ nmol cm}^{-2} \text{ s}^{-1}$, indicating that approximately 2% of BH_4^- delivered to the anode is decomposed by hydrolysis. This catalytic hydrolysis is a serious problem for controlling H_2 generation. A drastic decrease in the rate of H_2 generation is observed with a decrease in the cell voltage, in contrast to the current density. This suggests that BH_4^- is consumed by anodic oxidation rather than hydrolysis. When the potential of the anode is positive, H_2 generated by the hydrolysis of BH_4^- is possibly oxidized as follows:



As a result, the cell might act partially as a chemical pump for H_2 from the anode to the cathode at a large current density.

In contrast to the situation at the anode, very little H_2 generation is observed at the cathode at the open circuit voltage, which suggests that H_2 permeation from the anode to the cathode due to the difference in partial pressure and the crossover of BH_4^- due to the difference in concentration in the membrane are negligibly small. The rate of H_2 generation at the cathode increases with a decrease in the cell voltage. In any case, this value coincides well with the current density, suggesting that the coulomb efficiency of H_2 generation by the cathodic reduction of water (Eq. (6)) reaches almost 100%.

4.3. Effect of anolyte on the cell performance

Fig. 5 shows the influence of alkali metal cation on the cell performance. The cell performance of LiBH_4 in LiOH solution is in good agreement with those of NaBH_4 in NaOH solution and KBH_4 in KOH solution, which shows that cell performance is barely affected by the kind of alkali metal cation that is completely dissociated in the solution.

The cell performance at various BH_4^- concentrations is summarized in Fig. 6. The open circuit voltage of the cell increases with an increase in the BH_4^- concentration, as mentioned in Section 2, although it is smaller than the theoretical value (0.413 V) in all cases. Above 0 V, i.e., in the region of spontaneous electrical gen-

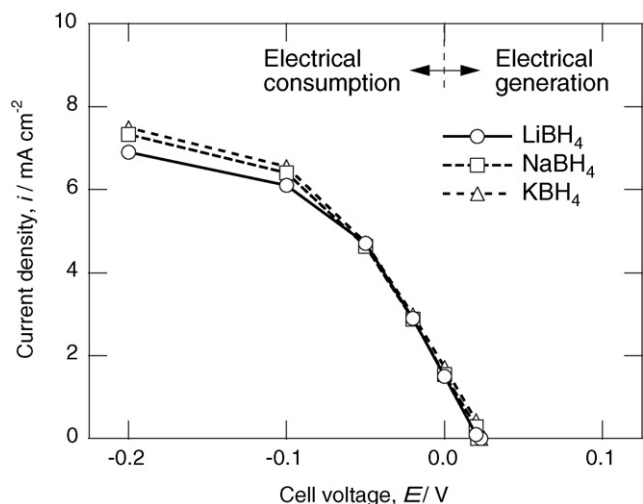


Fig. 5. Relation between current density and cell voltage. Analyte: 1 M MOH solution containing 0.1 M MBH_4 ($M = \text{Li, Na, and K}$). Catholyte: 1 M MOH solution.

eration, the slope between the cell voltage and the current density is somewhat inclined due to the increase in the BH_4^- concentration, which leads to a large current density at 0V. The limiting current density at applied cell voltage is also strongly influenced by the BH_4^- concentration. The hydrogen-generation current density could be increased to about 20 mA cm^{-2} at applied voltage of 0.2 V. A high- BH_4^- concentration leads to a large current density, i.e., large H_2 generation although the catalytic hydrolysis of BH_4^- on Pt is a serious problem.

4.4. Suppression of hydrolysis by using Au as anode

When the anode uses Pt for electrocatalysis, the catalytic hydrolysis of BH_4^- (Eq. (1)) proceeds, and this reduces the ability to control hydrogen generation. The hydrolysis depends markedly on the nature of the anode materials. Au is an effective catalyst for the anodic oxidation of borohydrides but not for the hydrolysis of borohydrides [5,15].

To suppress hydrolysis at the anode, Au powder was used as an anode electrocatalyst instead of Pt. Fig. 7 shows the cell performance when Au (24 mg cm^{-2}) was used at the anode. Compared

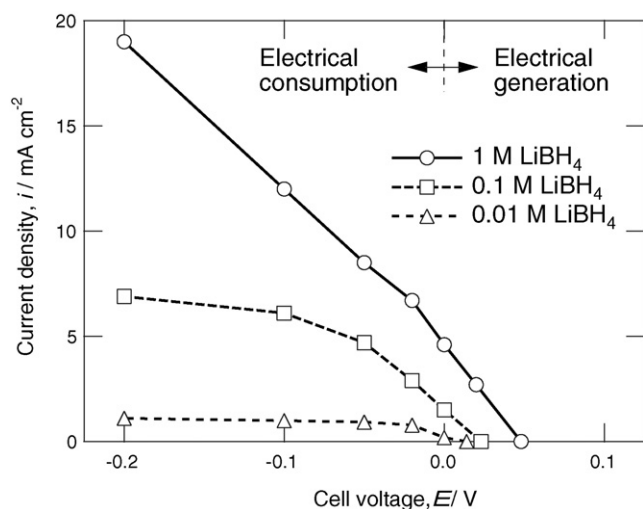


Fig. 6. Relation between current density and cell voltage. Analyte: 1 M LiOH solution containing 0.01, 0.1 and 1 M LiBH_4 . Catholyte: 1 M LiOH solution.

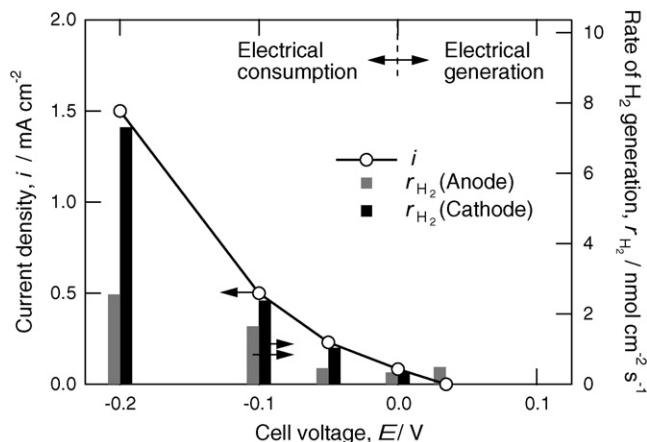


Fig. 7. Rates of H_2 generation at the anode and cathode and the relation between cell voltage and current density. The electrocatalyst at the anode is Au powder. The rate of H_2 generation on the right axis corresponds to the current density on the left axis.

with Pt (Fig. 3), H_2 generation at the anode is drastically suppressed. In contrast, the rate of H_2 generation at the cathode is in good agreement with the current density. With Au, the OCV was greater than with Pt because of the reduction of hydrogen generation at the anode. As in the cell with a Pt anode, the cell with a Au anode simultaneously generates H_2 and electricity at a low-current density. Fig. 8 shows the power generation of the cell with Au. The slope between the cell voltage and the current density is also linear. The power density of the cell reaches $1.7 \pm 0.7 \mu\text{W cm}^{-2}$ at 17 mV. Although the power density with Au is apparently lower than that with Pt, the actual power density per Au surface ($120 \pm 30 \mu\text{W m}^{-2}$ Au) is comparable to that per Pt surface ($130 \pm 40 \mu\text{W m}^{-2}$ Pt). However, H_2 generation by hydrolysis per Au surface is less than ca. one-fiftieth of that per Pt surface. Since Pt is active for both Eqs. (2) and (3), the catalytic hydrolysis of BH_4^- occurs easily. Therefore an anode catalyst should be selective for Eq. (3). Au is a better catalyst in this regard and catalytic hydrolysis could be remarkably suppressed with the use of Au as an anode catalyst, but the activity of borohydride oxidation is not sufficient for the practical electrochemical generation of hydrogen.

To realize the practical electrochemical generation of hydrogen, several problems must be addressed, including the suppression of hydrolysis at the anode catalyst, the reduction of overpo-

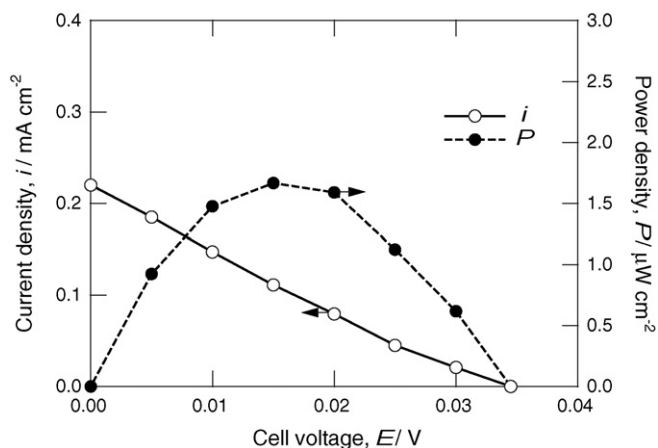


Fig. 8. Current density and power density as a function of cell voltage. The electrocatalyst at the anode is Au powder.

tential for the anodic oxidation of BH_4^- , increase in the BH_4^- concentration in the alkaline solution without decomposition. The development of a highly active and selective anode catalyst is the most important goal for improving the ability of the system to generate H_2 . The present results have raised the possibility of spontaneous H_2 generation without the need to apply voltage. Moreover, the coproduction of hydrogen and electricity may be realized by using the full chemical energy of borohydride with the development of a high-performance anode catalyst.

5. Conclusions

The H_2 -generation properties and cell performance of an electrochemical device using a Nafion[®] membrane were presented. This device spontaneously generated hydrogen along with electricity, although this was limited to the region of very low-current density. When Pt black was used as an electrocatalyst of both the anode and cathode, the open circuit voltage and the maximum power density were 0.023 ± 0.008 V and $6.3 \pm 1.8 \mu\text{W cm}^{-2}$, respectively. The slight H_2 generation at the cathode at the open circuit voltage indicates the inhibition of the crossover of BH_4^- anion. A further increase in H_2 generation is achieved by applying voltage to the cell although the current density is affected by the diffusion of BH_4^- . The cell performance was scarcely affected by the kind of alkali metal cation. Au powder instead of Pt black suppresses H_2 generation by hydrolysis at the anode without lowering the specific power density in electrical generation.

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