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Fabrication of a three-electrode battery using hydrogen-storage materials

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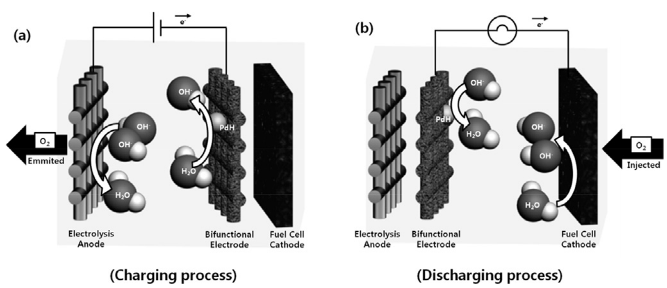
HIGHLIGHTS

- We design new-concept three-electrode battery using hydrogen as energy carrier.
- Charging process is electrolysis of alkaline electrolyte.
- Discharging process is operation of alkaline fuel cell.
- Hydrogen is stored at bifunctional electrode as metal hydride with charging process.
- Bifunctional electrode acts as electrolysis cathode and fuel cell anode at same time.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an energy storage device using a three-electrode battery is fabricated. The charging process takes place during electrolysis of the alkaline electrolyte where hydrogen is stored at the palladium bifunctional electrode. Upon discharging, power is generated by operating the alkaline fuel cell using hydrogen which is accumulated in the palladium hydride bifunctional electrode during the charging process. The bifunctional palladium electrode is prepared by electrodeposition using a hydrogen bubble template followed by a galvanic displacement reaction of platinum in order to functionalize the electrode to work not only as a hydrogen storage material but also as an anode in a fuel cell. This bifunctional electrode has a sufficiently high surface area and the platinum catalyst populates at the surface of electrode to operate the fuel cell. The charging and discharging performance of the three-electrode battery are characterized. In addition, the cycle stability is investigated.

1. Introduction

Recently, along with high-edge technologies for portable electric devices, energy storage systems with a high volumetric energy density are highly demanded. Currently, electric energy is generally stored in secondary batteries or capacitors. Whereas capacitors have lower volumetric energy densities than secondary batteries as well as somewhat unsuitable discharge characteristics for portable electronic devices, secondary batteries possess slightly more suitable discharge characteristics and higher volumetric energy densities [1]. Therefore, secondary batteries are more advantageous than capacitors for configuring small scale energy storage systems.

Among secondary batteries, Li-ion batteries are currently the most commonly used for energy storage applications. However, in

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the case of thin film lithium ion batteries which have a small volume, it has been found that there is a stability issue which limits increasing the film thickness because of the increased channel distance through which Li ions come in and out. As a result, it is hard to form a structure thicker than a few μm [2]. On the other hand, in the case of metal hydride, hydrogen atoms penetrate into the metal lattice structure, which is much larger than the size of the hydrogen atoms being stored. Therefore, the channels for hydrogen atoms are not plugged so that there are fewer limitations concerning the electrode thickness. In addition, metal hydride can theoretically have a volumetric energy density of 2000 Wh/l or higher, which is larger than that of thin film Li-ion batteries [1].

Metal hydrides can be utilized in fuel cell (FC) type secondary batteries. In this FC-type battery, the oxidation of hydrogen stored as a hydride, and the reduction of oxygen occur in an alkaline electrolyte in the discharging process. In this case, an active type fuel cell, into which pure oxygen is injected, as well as a passive type fuel cell, to which oxygen in air is supplied through a breathing process, can be formed for discharging. This FC-type secondary battery which employs a metal hydride has many advantages. The fuels are only hydrogen and oxygen which are nontoxic and completely environmentally friendly. In addition, the electrolyte is an aqueous alkaline solution instead of an explosive organic solution. Also, it charges faster or requires no charging time, has a longer service life as well as a lack of self-discharge [3]. As a result, FC-type secondary batteries are considered as a good alternative secondary battery and diverse studies of these battery systems have been carried out. For example, G. Erdler and C. Bretthauser [4–7] et al. designed chip integrated FC-type secondary batteries using polymer electrolyte membranes.

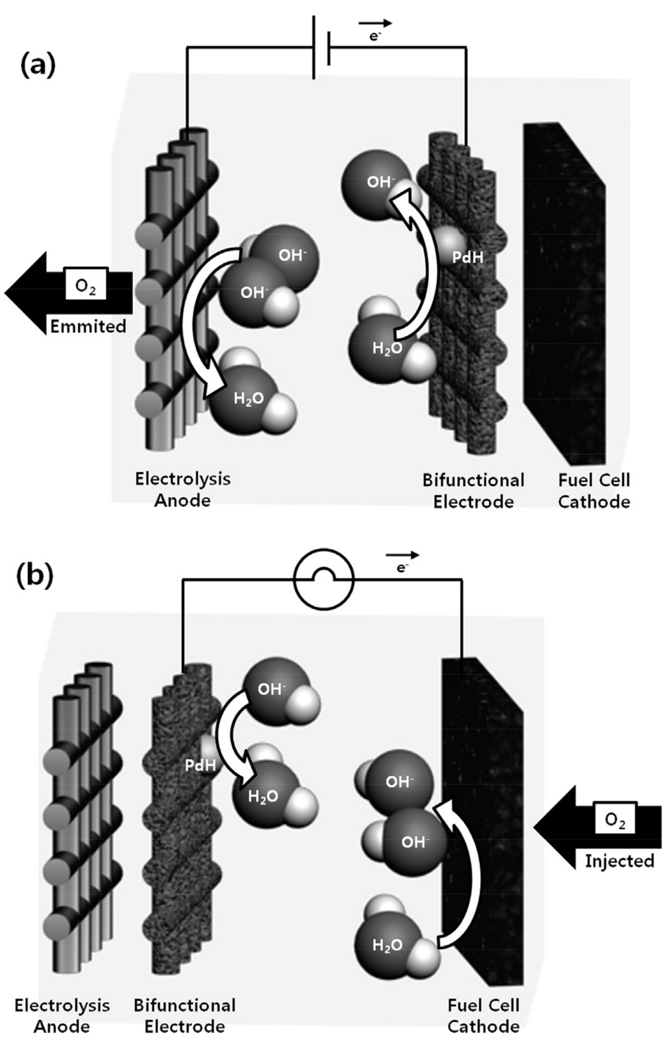

Fig. 1. Schematic diagram of the (a) charging and (b) discharging processes of the 3-electrode battery. In the charging process, protons are stored as palladium hydride (PdH_x) in the bifunctional electrode. In the discharging process, hydrogen atoms stored in the form of PdH_x meet OH^- ions to become water and discharge electrons.

In this study, based on these recent technical trends, we designed a 3-electrode battery, as shown in Fig. 1, and adopted palladium as hydrogen storage materials among the many potential hydrogen storage metals and alloys. Since the present study focuses on the performance of batteries in relation to the structure of the metal hydride electrodes, palladium, which is easy to handle and possesses excellent ability for hydrogen storage at ambient condition [8,9], is a suitable material.

The batteries designed in the present study are in the form of three electrodes immersed in an alkali electrolyte solution, as shown in Fig. 1. The electrodes are an electrolysis anode, a bifunctional electrode, and a fuel cell cathode. Fig. 1(a) shows a mimetic diagram of the operation of the charging process used to store hydrogen in the bifunctional electrode. In this hydrogen charging process, protons meet equivalent electrons at the bifunctional electrode and are stored as palladium hydride (PdH_x) while water is electrolyzed and O_2 is evolved at the electrolysis anode. The chemical reactions of this process are as follows.

$$\text{Anode (electrolysis anode)}: \chi OH^- \rightarrow \frac{\chi}{2}H_2O + \frac{\chi}{4}O_2 + \chi e^- \tag{1}$$

$$\text{Cathode (bifunctional electrode)} : Pd + \chi H_2O + \chi e^- \rightarrow PdH_\chi + \chi OH^- \tag{2}$$

$$\text{Overall reaction} : Pd + \frac{\chi}{2}H_2O \rightarrow \frac{\chi}{4}O_2 + PdH_\chi \tag{3}$$

Fig. 1(b) shows the discharging process which utilizes the oxidation reaction of the hydrogen stored in the bifunctional electrode. In this hydrogen discharging process, the fuel cell is operated and each hydrogen atom stored in the form of palladium hydride meets an OH^- ion to form a water molecule and discharge one electron. As a result, an electric current flows in this process. The process can be expressed by the following chemical formulas.

$$\text{Anode (bifunctional electrode)} : \chi OH^- + PdH_\chi \rightarrow \chi H_2O + Pd + \chi e^- \tag{4}$$

$$\text{Cathode (fuel cell cathode)} : \frac{\chi}{2}H_2O + \frac{\chi}{4}O_2 + \chi e^- \rightarrow \chi OH^- \tag{5}$$

$$\text{Overall reaction} : PdH_\chi + \frac{\chi}{4}O_2 \rightarrow \frac{\chi}{2}H_2O + Pd \tag{6}$$

The characteristics of the individual electrodes of the 3-electrode batteries developed using this concept were analyzed by SEM (scanning electron microscope), EDS (energy-dispersive X-ray spectroscopy), and ICP–AES (inductively coupled plasma–atomic emission spectroscopy). In addition, the charge–discharge characteristics and cycling stability of the fabricated 3-electrode batteries were analyzed through electrochemical experiments.