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Power generation/energy storage by a fuel cell/battery system: Regeneration of the MnO_2 positive electrode with gaseous oxygen

Bokkyu Choi, Sunmook Lee, Chihiro Fushimi, Atsushi Tsutsumi*

Collaborative Research Center for Energy Engineering, Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

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ABSTRACT

Fuel cell/battery (FCB) systems are promising power generation/energy storage systems because of their bi-functionality as fuel cells and as secondary batteries. We investigated the required charging after the discharged manganese dioxide (MnOOH) by oxygen gas under the rest condition and during the fuel cell operation mode using manganese dioxide as a positive electrode for the FCB system. Electrochemical characterization was performed using cyclic voltammetry and galvanostatic measurements. Additionally, changes in the crystal structure and the chemical functional groups during the electrode reactions were monitored by X-ray diffractometry and Fourier transform infrared spectroscopy. The results indicated that MnOOH formed via the electrochemical discharge of manganese dioxide (MnO_2) and that the oxyhydroxide can be chemically transformed back to MnO_2 with gaseous oxygen (O_2). The recharged MnO_2 can be used as the cathode in a fuel cell with an O_2 supply and it can also be electrochemically discharged without an O_2 supply. In addition, we confirmed that MnO_2 does not convert to Mn_3O_4 during the charge/discharge cycles if the redox reaction is maintained within a restricted range where a homogeneous process exists between MnO_2 and MnOOH. The results in this study suggest that the FCB system can be constructed using MnO_2 as the positive electrode and a metal hydride (MH) as the negative electrode, which can be rapidly charged to more than 70% of the theoretical capacity within 10 min using pressurized H_2 and electrochemically discharged, in an alkaline electrolyte. This system possesses a high-power generation efficiency, a high-energy density and a high load-following capability.

1. Introduction

To date, a large portion of the total primary energy supply has relied on fossil fuels such as coal/peat, oil and natural gas [1]. However, the use of fossil fuels has raised significant worldwide concern about carbon dioxide (CO_2) emissions, which has led to research on the use of renewable energy such as solar and wind power. Although a great deal of research is still underway, the intermittency and variability of the power produced by renewable energy still remains a major problem [2].

Secondary batteries have been widely used as the main power source in automobiles and portable devices. In addition, they are also expected to function as a major energy storage system to ensure a stable energy supply from renewable energy resources [3]. However, a massive amount of electrode materials are necessary to obtain a large enough energy storage capacity because the capacity of a battery is determined by the total amount of the electrode active materials. This increases the cost of the battery because most of the electrode materials are expensive metals [4].

In contrast, a fuel cell has no energy storage capability but has a higher energy density than secondary batteries because they convert chemical energy (e.g. hydrogen gas) into electrical energy at electrodes. However, the fuel cell reactions are restricted to three-phase (solid/liquid/gas) boundaries, which lead to a lack of load-following capability. This results in fuel cells with a low power density [5]. Moreover, fuel cells such as alkaline fuel cells (AFCs) and proton-exchange membrane fuel cells (PEFCs) are not very attractive from an economic point of view because they require expensive catalysts such as platinum to react with high efficiency.

In this context, novel fuel cell/battery (FCB) systems are expected to offer new opportunities [6–9]. The FCB system can function both as a fuel cell (power generation) and as a secondary battery (energy storage) by following the operating principle schematically illustrated in Fig. 1 [6]. In this system, power is generated by the following fuel cell reactions [6].

Negative electrode:

$$2M + H_2 \rightarrow 2MH \quad (1)$$

$$2MH + 2OH^- \rightarrow 2M + 2H_2O + 2e^- \quad (2)$$

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* Corresponding author. Tel.: +81 3 5452 6727; fax: +81 3 5452 6728.
E-mail address: a-tsu2mi@iis.u-tokyo.ac.jp (A. Tsutsumi).

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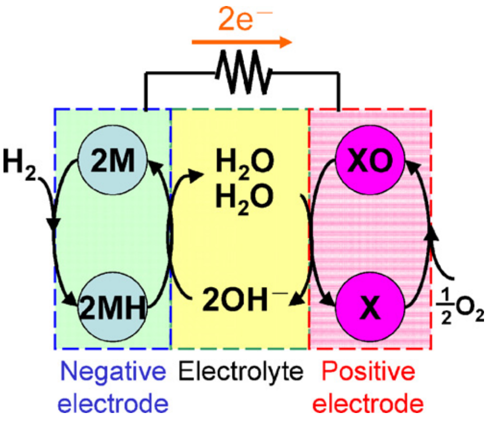

Fig. 1. Conceptual fuel cell/battery system [6].

Positive electrode:

$$X + \frac{1}{2}O_2 \rightarrow XO \tag{3}$$

$$XO + H_2O + 2e^- \rightarrow X + 2OH^- \tag{4}$$

Overall:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{5}$$

where M is a metal and XO a metallic oxide. This system can also store and generate power as the following secondary battery reactions [6].Negative electrode:

$$2MH + 2OH^- \leftrightarrow 2M + 2H_2O + 2e^- \tag{6}$$

Positive electrode:

$$XO + H_2O + 2e^- \leftrightarrow X + 2OH^- \tag{7}$$

Overall:

$$2MH + XO \leftrightarrow 2M + X + 2H_2O \tag{8}$$

(→: discharge, ←: charge)

As shown in Fig. 1 and above description, the FCB system is able to be recharged by the supply of electric power and also by the supply of gaseous hydrogen and oxygen to the negative and positive electrodes, respectively. Moreover, they can also function as a fuel cell by feeding hydrogen and oxygen to the negative and positive electrodes, respectively. Therefore, the FCB system can deliver high-capacity energy storage (i) via the active electrode materials and (ii) by storing the hydrogen gas generated by the water electrolysis of the electrolyte. In addition, this system can be charged by storing gaseous hydrogen and oxygen in the electrodes even during fuel cell mode operation. To construct this type of novel bi-functional FCB system, the electrode materials are required to possess the following characteristics: (i) the negative electrode materials should be reduced by hydrogen gas (gaseous charging) and be oxidized during electrochemical reactions and (ii) the positive electrode materials should be oxidized by oxygen gas (gaseous charging) and be able to be reduced electrochemically [8]. Metal hydrides (MHs) are well suited for the negative electrode of the FCB system because they adsorb gaseous hydrogen [7,10–16] and have been used as active materials in NiMH secondary batteries [15–21] as well as in air-metal batteries [11,22–23]. It has been reported that MH can be rapidly charged to more than 70% of its theoretical capacity within 10 min by pressurized (0.3 and 0.5 MPa) gaseous hydrogen and that the charged MH can be electrochemically discharged by the reactions shown below [7]:

$$M + \frac{1}{2}H_2 \rightarrow MH \tag{9}$$

$$MH + OH^- \leftrightarrow M + H_2O + e^- \tag{10}$$

For the positive electrode of the FCB system, we tested a mixture of nickel hydroxide ($Ni(OH)_2$) and a small amount of manganese dioxide (MnO_2) (9:1, w/w) and found that it can function as a secondary battery and as a fuel cell [8,9]. However, this positive electrode cannot be charged by oxygen like the air-metal batteries.

It is known that the reduction of oxygen with MnOOH (Eq. (12)) occurs after the homogeneous electrochemical reduction of MnO_2 (Eq. (11)).

The electrochemical discharge of electrodeposited manganese dioxide (EMD) can be represented as follows [24–43]:

$$\gamma\text{-}MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^- \tag{11}$$

and the reduction of oxygen with MnOOH is [40–43]:

$$MnOOH + \frac{1}{4}O_2 \rightarrow MnO_2 + \frac{1}{2}H_2O \tag{12}$$

These promising characteristics of MnO_2 are expected to provide excellent rechargeability via two recharging processes: (i) the regeneration of MnOOH by a one-electron reaction of MnO_2 (reverse reaction of Eq. (11)), and (ii) the reoxidation of MnOOH to MnO_2 by contact with gaseous oxygen (Eq. (12)). We thus expect that MnO_2 would satisfy the requirements for the positive electrode of the FCB system as it can be charged by oxygen gas and by the supply of electric power.

Many papers have reported rechargeable manganese dioxide electrodes in aqueous solutions by restricting the depth of discharge [25,26,42], by adding metals [26–35,42] and by oxygen-regeneration of the discharged manganese dioxide electrodes (MnOOH) [40–43]. However, few studies exist describing the gaseous charging of discharged manganese dioxide (MnOOH) by oxygen. Therefore, we investigated charging the discharged manganese dioxide (MnOOH) by a specific amount of charge using oxygen gas under a rest condition and we investigated charging the discharged manganese dioxide (MnOOH) by gaseous oxygen during fuel cell mode operation.

2. Experimental

2.1. Fabrication of electrodes

The electrodes that were used to evaluate FCB performance consisted of an active electrode layer of electrodeposited manganese dioxide (EMD; FMH, ~10 μm in diameter, Tosoh Corp.), carbon black (CB; #3050B, 50 nm average diameter, Mitsubishi Chemical Corp.) and poly(tetrafluoroethylene) (PTFE; Aldrich) at a mass ratio of 10:3:1. The total weight was approximately 150 mg. The gas diffusion layer consisted of EMD, CB and PTFE at a mass ratio of 4:5:5 and the total weight was approximately 250 mg, which is necessary for easy gas diffusion into the paste electrode with increasing amounts of CB and PTFE. These mixtures were rolled onto both sides of nickel foam and this was followed by baking the foam in an oven at 110 °C for 30 min. These foams and carbon paper (EC-TP1-060T, Toray Industries) were then pressed together under 6 MPa for 10 min. The total thickness of the electrode was approximately 1.5 mm and the surface area was 3.14 cm^2. To activate the electrode, one discharge/charge cycle was conducted in 6 M aqueous KOH solution with a cut-off potential of −0.5 V.

The electrodes used to test battery performance were composed of EMD, CB and PTFE at a mass ratio of 10:3:1. The total weight was approximately 150 mg while the surface area and thickness of the fabricated electrodes were 3.14 cm^2 and 0.6 mm, respectively.