



Chemical Charging on a MnO₂ Electrode of a Fuel Cell/Battery System in a Highly O₂-Dissolved Electrolyte



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ARTICLE INFO

Article history:

Received 25 November 2014
Received in revised form 3 February 2015
Accepted 3 February 2015
Available online 7 February 2015

Keywords:

Dissolved oxygen
Manganese dioxide
Fuel cell/battery system
Alkaline electrolyte

ABSTRACT

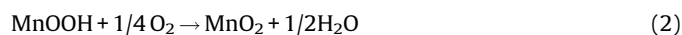
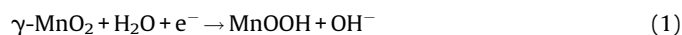
To improve the chemical reaction rate of oxygen charging on a manganese dioxide electrode of a fuel cell/battery system, we used highly dissolved oxygen in an electrolyte. For this chemical reaction, a discharged electrode was placed in a pressure-resistant chamber containing an electrolyte and then oxygen was supplied at 0.5, 1.0, 1.5, and 2.0 MPa to the electrolyte for 20, 40, and 60 min. Electrochemical characterization and X-ray diffraction were carried out to measure the amount of charge and the changes in the crystal structure before and after the chemical charging process. The results obtained from the chemical charge/electrochemical discharge experiments indicate that the dissolved oxygen in the alkaline solution can chemically charge the discharged electrode. The charge rate and amount were found to increase with O₂ partial pressure and supply time. Additionally, X-ray diffraction confirmed that the chemical charging process with dissolved oxygen is accompanied by a crystal structure change with the emission of protons and electrons from MnOOH in the same manner as in the electrochemical charging process.

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1. Introduction

Recently, rechargeable batteries such as lithium ion batteries and nickel-metal hydride batteries have attracted much attention and are used widely in information technology devices, power tools, electric vehicles, and energy storage systems [1–3]. These devices and systems are typically operated in a low current density range during normal use but they require a high current density for several minutes during transient conditions such as start-up and acceleration. Electric vehicles, for example, require a brief pulse of current for a minute during acceleration [4,5]. Energy storage systems should thus have high energy density as well as instantaneous high power so that they can be operated within several minutes. Taking this fact into account, novel electrochemical systems with a dual function of power generation and energy storage, referred to as fuel cell/battery (FCB) systems, have been suggested [6–11]. In FCB systems, the active materials of the negative and positive electrodes can store hydrogen and oxygen gases, respectively, by chemical reactions and this leads to an electrochemical charging process. The charged cell can emit electrons from the electrode by electrochemical redox reactions

without an external supply of gases. These reactions occur at the two-phase regions; i.e., the solid/gas (chemical reaction) and solid/liquid (electrochemical reaction) interfaces. This implies a unique advantage in obtaining high power compared with metal-air batteries or fuel cells that have a reaction area at the three-phase (solid/liquid/gas) boundary. Thus, FCB systems are expected to be preferred candidates for the applications demanding high-energy and high-power-density energy storage such as power tools and electric vehicles. Metal hydride (MH) and manganese dioxide (MnO₂) have been found to be suitable materials for the negative and positive electrodes of FCB systems, respectively [7,10,11]. MH can be quickly charged within 10 min by externally supplied hydrogen gas at 0.5 MPa [7]. The oxidation reaction between MnOOH and oxygen gas occurs slowly and 13% of the theoretical capacity can be recharged in an hour at 0.2 MPa [10]. Electrodes with a high surface area have been fabricated by the electrodeposition of materials on carbon fibers to investigate oxygen gas charging performance [11]. Unfortunately, their performance did not improve because of water generation on the electrode surface as shown below:



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Nomenclature

a	Specific interfacial area (m^{-1})
b	Langmuir parameter (–)
C	Oxygen concentration in the electrolyte (mol/L)
C_0	Oxygen concentration in the electrolyte at $t=0$ (mol/L)
C_{KOH}	KOH concentration (mol/L)
C^*	Oxygen solubility in the electrolyte (mol/L)
k_{H}	Constant with the dimensions of pressure divided by concentration (L atm/mol)
k_{L}	Liquid side mass transfer coefficient (m/s)
$k_{\text{L}a}$	Volumetric liquid side mass transfer coefficient (s^{-1})
$[\text{O}_2^*]$	Surface concentration of oxygen (mol/L)
P	Partial pressure of oxygen gas (atm)
t	time (s)
V_{ch}	Charging rate (mAh/g min)

The water generated after the oxygen reduction reaction with MnOOH (Eq. (2)) covered the surface of the active material because of the hydrophilic nature of the surface. This interrupted the subsequent reaction with oxygen gas. The prompt removal of this water from the electrode surface is important for further reactions. However, it is difficult to remove this water at ambient temperature. It is thus desirable to find an alternative approach for the regeneration of the MnO₂ electrode with oxygen gas. The reaction should be fast and not hindered by the water generated on the electrode surface.

Oxygen dissolved in an electrolyte has been used as a reactant in electrochemical devices such as metal-air batteries and microbial fuel cells [12,13]. Therefore, the MnO₂ electrode can be reversibly oxidized by dissolved oxygen in an aqueous solution if enough oxygen is present around the MnO₂/MnOOH active materials. The amount and chemical potential of dissolved oxygen increases linearly with an increase in oxygen partial pressure as described by Henry's law [14]. Therefore, the possibility of a reaction between MnOOH and dissolved oxygen will increase under a higher partial pressure. In this paper, the reactivity between dissolved oxygen and MnOOH at various oxygen partial pressures was investigated.

2. Experimental

2.1. Fabrication of the electrodes

The slurry used to fabricate the electrode was prepared by mixing electrodeposited manganese dioxide (EMD; Tosoh Corp., Japan, ~10 μm in diameter), carbon black (CB; Mitsubishi Chemical Corp., Japan, 50-nm average diameter), and ethylene vinyl acetate (EVA; Tosoh Corp., Japan) as a binder at a mass ratio of 100:30:10 or 100:15:10 in xylene. The slurry was heated at 120 °C for 30 min. This slurry was coated onto both sides of nickel foam (electrode area: 20 mm \times 30 mm) and then the foam was dried at 85 °C for 30 min and pressed at 40 MPa for 10 min. The amount of EMD on the electrode was approximately 30–40 mg.

2.2. Experimental apparatus and electrochemical measurements

2.2.1. Electrochemical discharge

A three-electrode cell was used to measure the electrochemical performance of the EMD electrode. Ag/AgCl/saturated KCl (RE-1C; BAS Inc. Japan) and nickel foam (electrode area: 40 mm \times 30 mm) were used as reference and counter electrodes, respectively. A 6 M KOH aqueous solution was used as the electrolyte. This experimental cell was used for the initial activation of the electrode as

well as to confirm the charging capacity of the electrodes that were regenerated with the oxygen gas-dissolved electrolyte. The galvanostatic performance was measured with a 1480 Multistat (Solartron Analytical, United Kingdom). Five charge/discharge cycles were carried out at 0.2 C (where C is a unit of relative current for batteries. 1 C is the current at which the battery is fully charged within an hour). The electrodes were discharged to a -0.5 V (vs. Ag/AgCl) cut-off potential to retain the one-electron reaction (Eq. (1)).

2.2.2. Chemical charging reaction with highly compressed oxygen gas

The fully discharged electrodes from the one-electron reaction were chemically charged by supplying highly compressed oxygen gas to the electrolyte. The experimental apparatus is shown in Fig. 1. The volume of the pressure-resistant container (TPS-1, SUS316; Taiatsu Techno, Japan) was 150 mL and the container was filled with approximately 50 mL of 6 M KOH aqueous solution. A ϕ 0.8-mm stainless tube was introduced to directly supply oxygen gas to the electrolyte. The discharged electrode was inserted into the container and oxygen gas pressurized at 0.5, 1.0, 1.5, and 2.0 MPa was supplied to the electrolyte over different time durations such as 20, 40, and 60 min. The electrodes were then discharged to a -0.5 V (vs. Ag/AgCl) cut-off potential at a current density of 0.2 C.

2.3. Characterization

Scanning electron microscope (SEM; Miniscope TM3030, Hitachi, Japan) images were recorded for the manganese dioxide electrodes before and after the test and the crystal structures of the charged and discharged manganese dioxide electrodes were observed by X-ray diffraction (XRD; XRD miniflex, Rigaku Corp., Japan) at a scan rate of 5°min^{-1} within a 2θ of $40\text{--}60^\circ$.

3. Results and discussion

3.1. Electrochemical redox reaction of EMD

To confirm the electrochemical properties of EMD, the first charge/discharge was conducted in a 6 M KOH aqueous solution. For this experiment, the electrode was composed of an active material, CB, and a binder at a mass ratio of 100:15:10. Fig. 2 shows the results of the first charge/discharge profiles with a current density of 0.1 C. The differential charge/discharge capacity (dQ/dV) curves were derived from the first charge/discharge profiles. The cut-off potential for the discharge was set to -0.5 V for the one-electron reaction and the electrode was charged to a state of charge (SOC) of 110%. The discharge capacity was approximately 220 mAh/g, which amounts to 71.4% of the theoretical capacity of manganese dioxide (i.e., 308 mAh/g for the one-electron

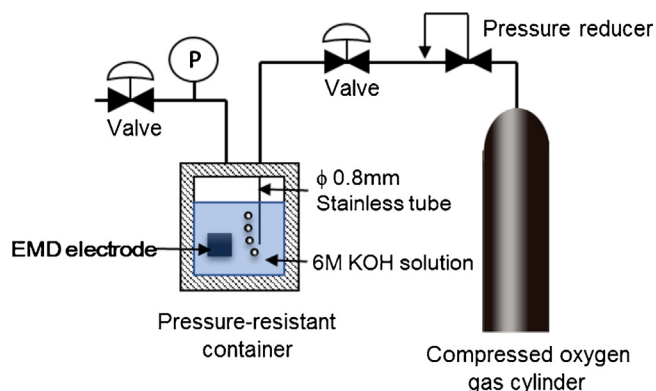


Fig. 1. Schematic of experimental apparatus for chemical charging by compressed oxygen gas.

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