



Short communication

Stability of carbon electrodes for aqueous lithium-air secondary batteries[☆]



Hirokazu Ohkuma, Ichiro Uechi, Masaki Matsui, Yasuo Takeda, Osamu Yamamoto*, Nobuyuki Imanishi

Graduate School of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu, Mie 514-8507, Japan

H I G H L I G H T S

- Air electrodes of carbon materials were examined in saturated LiOH with 10 M LiCl.
- The lowest over-potential was observed for Ketjen black.
- CO was detected after polarization for the oxygen evolution reaction.

A R T I C L E I N F O

Article history:

Received 23 April 2013

Received in revised form

30 May 2013

Accepted 26 June 2013

Available online 16 July 2013

Keywords:

Aqueous lithium-air battery

Oxygen electrode

Carbon electrode

High energy density battery

A B S T R A C T

The air electrode performance of various carbon materials, such as Ketjen black (KB), acetylene black (AB and AB-S), Vulcan XC-72R (VX), and vapor grown carbon fiber (VGCF) with and without $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) catalyst were examined in an aqueous solution of saturated LiOH with 10 M LiCl in the current density range 0.2–2.0 mA cm^{-2} . The best performance for oxygen reduction and evolution reactions was observed for the KB electrode, which has the highest surface area among the carbon materials examined. A steady over-potential of 0.2 V was obtained for the oxygen reduction reaction using the KB electrode without the catalyst, while the over-potential was 0.15 V for KB with the LSCF catalyst at 2.0 mA cm^{-2} . The over-potentials for the oxygen evolution reaction were slightly higher than those for the oxygen reduction reaction, and gradually increased with the polarization period. Analysis of the gas in the cell after polarization above 0.4 V revealed the evolution of a small amount of CO during the oxygen evolution reaction by the decomposition of carbon in the electrode. The amount of CO evolved was significantly decreased by the addition of LSCF to the carbon electrode.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

1. Introduction

Lithium-air secondary batteries consist of lithium metal as the anode active material and oxygen as the cathode active material have high potential for electric vehicle applications because they have an extremely high theoretical energy density. The rechargeable lithium–oxygen battery was first reported in 1996 by Abraham and Jiang [1], which was comprised of a lithium ion conductive gel-type polymer electrolyte, a lithium metal anode, and a carbon electrode with cobalt phthalocyanine as the catalyst. Kuboki et al.

[2] reported an extremely high discharge capacity of 5360 mAh g^{-1} (based on carbon mass) for a primary lithium-air cell with a hydrophobic ionic liquid electrolyte. Bruce et al. [3,4] presented more attractive results for a rechargeable lithium–oxygen cell using an organic electrolyte of 1 M LiPF_6 in propylene carbonate and a carbon black air electrode with a MnO_2 catalyst, in which a high charge and discharge capacity of 600 mAh g^{-1} (based on carbon mass) was achieved after 50 cycles. More recently, Scrosati and colleagues [5] reported a lithium–oxygen rechargeable battery that consisted of a tetra (ethylene) glycol dimethyl ether- LiCF_3SO_3 electrolyte and an air electrode with Super P carbon and carbon paper, which was operated over 30 cycles with a high capacity of 5000 mAh g^{-1} (based on carbon mass). However, such rechargeable lithium–oxygen batteries with non-aqueous electrolytes have many problems that must be addressed, such as the reaction of the electrolyte and lithium with water from the atmosphere, lithium dendrite formation on the lithium electrode during the charge process, and high polarization during the charge and discharge processes.

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial-No Derivative Works License, which permits non-commercial use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author. Tel.: +81 59 231 9420.

E-mail addresses: Yamamoto@chem.mie-u.ac.jp, osyamamo@alles.or.jp (O. Yamamoto).

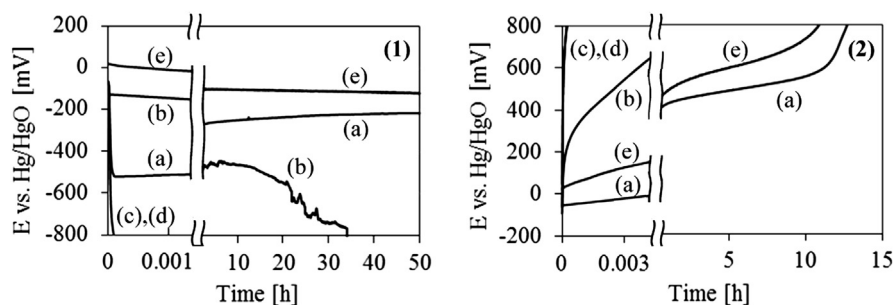
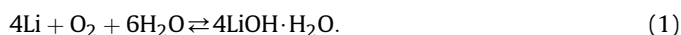


Fig. 1. Electrode potentials vs. time at 0.5 mA cm^{-2} for (1) ORR and (2) OER with (a) KB, (b) Vx, (c) VGCF, (d) AB, and (e) AB-S at room temperature.

Some of the problems observed in non-aqueous systems could be removed by employing an aqueous system. An aqueous lithium-air battery system could be constructed using a water-stable lithium-conducting solid electrolyte of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) as a protective layer between the lithium metal anode and aqueous electrolyte [6–10]. The reaction mechanism for aqueous lithium-air batteries is different from that for non-aqueous lithium-air batteries. In the case of the aqueous system, the cell reaction is:



The discharge product of $\text{LiOH} \cdot \text{H}_2\text{O}$ is soluble in the aqueous electrolyte. For the aqueous system, water molecules are involved in the redox reaction at the air cathode and the theoretical energy density of 1910 Wh kg^{-1} is lower than that for the non-aqueous system at 3457 Wh kg^{-1} . We have previously reported the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in an aqueous solution of saturated LiOH with 10 M LiCl at a carbon air electrode with various perovskite-type oxides as the catalyst component [11]. The aqueous electrolyte of saturated LiOH with 10 M LiCl was used for the stability of LATP, because LATP is unstable in saturated LiOH aqueous solution [9], but is stable in saturated LiOH with 10 M LiCl [12]. The over-potentials for the ORR and OER in saturated LiOH with 10 M LiCl were considerably lower than those in the non-aqueous electrolyte. However, the long term stability of the carbon air electrode was not examined in the previous study. In this study, we examine the long term performance of various types of carbon electrodes with and without $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) as a catalyst for the ORR and OER in the aqueous electrolyte of saturated LiOH with 10 M LiCl.

2. Experimental

The perovskite-type oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) was purchased from Seimi Chemical Co. The specific surface area was measured to be $1.79 \text{ m}^2 \text{ g}^{-1}$. Ketjen Black EC-600JD (KB; Lion Co.), acetylene carbon black (AB; Strem Chemicals), high surface area acetylene carbon black (AB-S), Vulcan XC-72R (VX; Cabot Co.), and vapor grown carbon fiber (VGCF; Showa Denko) were used for the air electrodes.

The air electrodes consisted of a reaction layer and an air diffusion layer. The reaction layer was prepared by mixing the carbon substrate, LSCF, and polytetrafluoroethylene (PTFE) in water with a surfactant of poly(oxyethylene)-octylphenyl ether using ultrasonication. The weight ratio of carbon:LSCF:PTFE was 55:30:15, and the carbon:PTFE ratio was 85:15 for the electrode without LSCF. The mixture was dried at 90°C and heated at 280°C to fix the PTFE onto a Ti mesh (100 mesh) with the diffusion layer under pressure at 64 MPa. The air diffusion layer was prepared by mixing AB and PTFE (7:3 weight ratio). The air electrodes were tested in an aqueous solution of saturated LiOH with 10 M LiCl. The

test cell was a beaker cell equipped with a working electrode (active area of 0.64 cm^2), a platinum plate with platinum black as a counter electrode, and a Hg/HgO or platinum plate/platinum black reference electrode. Experiments were conducted at room temperature and under a CO_2 -free air atmosphere. The electrode potentials were measured using a potentiostat/galvanostat (Hokuto Denko, HJ-1001SD8) and the electrode impedance was measured using a multichannel potentiostat/galvanostat (Biologic VMP 3). The gas evolved under the ORR and OER was analyzed using a gas chromatograph (GL Science, GC-3200). The working electrode, platinum counter electrode, and Hg/HgO reference electrode were set in a closed cell with a small hole for gas collection.

The surface area and pore distribution of the carbon materials were measured using a gas adsorption analyzer (Shimadzu Co., Tristar 3000). The contact angles of the carbons were measured using a contact angle meter (Kyowa Interface Science DMS-400), where the aqueous solution of saturated LiOH with 10 M LiCl was dropped on the surface of carbon pellets.

3. Results and discussion

Fig. 1 shows the changes in electrode potential with polarization period at 0.5 mA cm^{-2} for the various carbon materials without the LSCF catalyst, where the thickness of the reaction layer and gas diffusion layer were both approximately 0.2 mm. The over-potentials for the ORR on AB and VGCF quickly decreased with the polarization period. The current densities at $-0.4 \text{ V vs. Hg/HgO}$ for the AB and VGCF electrodes were 0.04 and 0.12 mA cm^{-2} , respectively. In contrast, the KB, AB-S, and VX electrodes exhibited more steady polarization behavior and the current densities at $-0.4 \text{ V vs. Hg/HgO}$ were 11.9 , 13.2 , and 0.26 mA cm^{-2} , respectively. The KB and AB-S electrode have a steady electrode potential for 50 h, whereas that for the VX electrode decreased gradually with the polarization period. The AB and VGCF electrodes, as well as the VX electrode, had high over-potentials for the OER, but the KB and AB-S electrode showed a steady potential for approximately 10 h after which the potential increased significantly with the polarization period. The physical properties of these carbon materials

Table 1

Current densities at $-0.4 \text{ V vs. Hg/HgO}$ for ORR (I_R) and at 0.6 V vs. Hg/HgO for OER (I_E) and physical properties of the carbon materials.

	KB	AB-S	VX	AB	VGCF
I_R at $-0.4 \text{ V vs. Hg/HgO}$ (mA cm^{-2})	11.9	13.2	0.26	0.04	0.12
I_E at 0.6 V vs. Hg/HgO (mA cm^{-2})	22.6	12.6	0.12	0.06	0.10
Surface area ($\text{m}^2 \text{ g}^{-1}$)	1292	829	215	87	13
Pore volume (mL g^{-1})	1.36		0.64	0.41	0.06
Crystallite ^a (I_D/I_G)	1.128	2.00	0.813	1.25	0.065
Contact angle ($^\circ$) ^b	128	121	48	108	135

^a Intensity ratios of D and G bands in Raman spectra from Refs. [13] and [14].

^b Measured using aqueous solution of saturated LiOH with 10 M LiCl.

Download English Version:

<https://daneshyari.com/en/article/7739432>

Download Persian Version:

<https://daneshyari.com/article/7739432>

[Daneshyari.com](https://daneshyari.com)