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Short communication

Rechargeable aqueous lithium–air batteries with an auxiliary electrode for the oxygen evolution

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HIGHLIGHTS

- Cyclic performance of Li/EC–DEC–$LiClO_4$/LTAP/saturated LiOH with 10 M LiCl/KB/air cell was examined.
- The 3rd oxygen evolution electrode was useful to obtain an excellent cycling performance.
- The specific energy density was calculated to be 810 Wh kg^{-1}.

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ABSTRACT

A rechargeable aqueous lithium–air cell with a third auxiliary electrode for the oxygen evolution reaction was developed. The cell consists of a lithium metal anode, a lithium conducting solid electrolyte of $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$, a carbon black oxygen reduction air electrode, a RuO_2 oxygen evolution electrode, and a saturated aqueous solution of LiOH with 10 M LiCl. The cell was successfully operated for several cycles at 0.64 mA cm^{-2} and 25 °C under air, where the capacity of air electrode was 2000 mAh $g_{cathode}^{-1}$. The cell performance was degraded gradually by cycling under open air. The degradation was reduced under CO_2-free air and pure oxygen. The specific energy density was calculated to be 810 Wh kg^{-1} from the weight of water, lithium, oxygen, and carbon in the air electrode.

1. Introduction

Rechargeable lithium–air batteries have potential application as a power source for electric vehicles (EV), because of their high energy density and lower material cost than conventional lithium-ion batteries. At present, two types of rechargeable lithium–air batteries have been developed; non-aqueous [1] and aqueous systems [2]. The specific energy density of the non-aqueous system (3460 Wh kg^{-1}) is higher than that of the aqueous system (1910 Wh kg^{-1}). However, the non-aqueous system has serious problems to be solved, such as the decomposition of aprotic electrolytes [3], high overpotentials for the oxygen reduction and evolution reactions [4], protection of the lithium metal electrode from water and carbon dioxide in the air [5], and carbon decomposition of the air electrode during the charge process [6]. These problems observed for the non-aqueous system could be removed for the aqueous system. One of the major advantages of the aqueous lithium–air system is that the reaction product of LiOH is soluble in the electrolyte. Protection of the lithium metal electrode from water is the most critical point for the aqueous system. The aqueous lithium–air battery system was proposed by Visco et al. [7] using a water stable NASICON-type lithium conducting solid electrolyte of $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$ (LATP). The water permeation-free dense LATP plate has a lithium-ion conductivity of 1×10^{-4} S cm^{-1} at room temperature. However, LATP is unstable in contact with lithium metal [8,9]. Visco et al. [7] and Zhang et al. [10] used Li_3N and polyethylene oxide (PEO) with $Li(CF_3SO_2)_2N$ (LiTFSI) as the interlayer between lithium metal and LATP, respectively. Li_3N and the polymer electrolyte are stable in contact with lithium metal, but unstable in aqueous solutions. Zhou et al. also reported the use of an organic electrolyte between lithium metal and LATP [11].

Rechargeable lithium–air batteries require a bifunctional air electrode for the oxygen reduction (ORR) and oxygen evolution reactions (OER). The development of rechargeable zinc–air

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batteries with a concentrated alkaline solution began in the middle of 1960s [12]. There have been many reports on ORR in alkaline solution; however, there are few reports on OER [13]. When an air electrode is used for oxygen evolution, it is exposed to a highly corrosive potential. The bifunctional electrodes for rechargeable zinc–air batteries have very complicated multilayer designs and compositions, but all of them have insufficient lifetime of the oxygen reduction catalyst at high oxygen reduction potentials (*ca.* 2.1 V *vs.* Zn/Zn^{2+}). Arai et al. [14] examined a carbon black electrode for ORR and OER in aqueous 8 M KOH and observed electrode deterioration during OER, which they claimed due to a loss of the electrochemically active surface area of the electrode, mainly due to carbon corrosion. Recently, Ohkuma et al. [15] reported the electrode performance for ORR and OER on carbon air electrodes for the aqueous lithium–air cell, where a saturated aqueous solution of LiOH with 10 M LiCl was used as the electrolyte, because the LATP protective layer for the water-stable lithium metal electrode is unstable in saturated LiOH aqueous solution [9]. Steady electrode performance for ORR was observed on high surface area carbon black (Ketjen black) at 2.0 mA cm^{-1} and at room temperature. The overpotential for OER was slightly higher than that for ORR and gradually increased with the polarization period. Analysis of the gas in the cell after polarization above *ca.* 0.4 V *vs.* NHE revealed the evolution of a small amount of CO during OER by the decomposition of carbon in the electrode. Decomposition of carbon during the charging process was also observed for the non-aqueous lithium–air cell [6]. Thus, suppression of carbon decomposition during the discharge process is one of the most important issues to develop an acceptable rechargeable lithium–air battery for EV. Stevens et al. [16,17] proposed the use of a third auxiliary electrode for OER made from a metallic grid for aqueous lithium–air batteries. The cell exhibited good cycling behavior for a short discharge and charge period at 2.0 mA cm^{-2}. Visco [18] has demonstrated large discharge capacity in a primary aqueous lithium–air cell. It is important to examine the possibility for oxidation of the reaction product of $LiOH \cdot H_2O$ on the carbon air electrode after deep discharge using the third electrode. The solubility of LiOH in water is 22.6 g in 100 g of water at 20 °C and the reaction product of LiOH is precipitated in the electrolyte and/or on the carbon electrode at 5% discharge depth. Stevens et al. [17] proposed to use an anion exchange membrane to precipitate the reaction product in the electrolyte. In this study, we investigate the deep charge and discharge performance of an aqueous lithium–air cell with an OER electrode, where a high surface area carbon black air electrode without a catalyst was discharged to 2000 mAh $g^{-1}_{cathode}$ in the aqueous electrolyte with saturated LiOH with 10 M LiCl, and charged using the 3rd electrode for OER.

2. Experimental

The air electrodes consist of a reaction layer and an air diffusion layer. The reaction layer was prepared by mixing Ketjen black (KB; EC600JD, Akzo Noble; specific surface area of 1400 m^2 g^{-1}) and polytetrafluoroethylene (PTFE) in water using ultrasonication. The weight ratio of KB:PTFE was 85:15. The mixture was dried at 80 °C and pressed onto a Ti mesh (100 mesh) with a carbon paper gas diffusion layer of 0.3 mm thick (Sigracet, SGL Co. Germany) under pressure at 64 MPa. The amount of KB was about 30 mg for the cell with a limited amount of water, and about 5 mg for the cycling test cell with excess water. The oxygen evolution electrode was prepared by pressing RuO_2 powder (Wako Chemicals, Japan; particle size of 1–3 μm) onto the Ti mesh (100 mesh) under pressure at 128 MPa. The thickness of the electrode was about 0.45 mm. LATP plates (19 mm diameter and 0.15 mm thick) were purchased from Ohara Inc., Japan.

Fig. 1 shows a schematic diagram of the aqueous lithium–air test cell with the oxygen evolution electrode. The diameters of the air electrode and the oxygen evolution electrode were 12 mm and 10 mm, respectively. The contact area of the air electrode with the electrolyte was 0.5 cm^2 or 1.13 cm^2. LATP was used as the protective layer of the lithium electrode. A conventional non-aqueous electrolyte consisting of a mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 v/v) with $LiClO_4$ was used as the interlayer to prevent the direct contact of lithium metal with LATP, because LATP is unstable in contact with lithium metal. The amount of the electrolyte used was *ca.* 2 mL and the distance between the lithium metal and LATP was 2.0 cm to prevent direct contact and lithium dendrite growth toward LATP. Sufficient air was supplied using an air pump with a flow rate of 70 mL min^{-1}. In some cases, air passed through a CO_2 absorber (soda lime) or pure oxygen were used.

The electrode potentials at a constant current drain were measured using a potentiostat/galvanostat (Hokuto Denko, HJ-10015D8), where a platinum plate with a platinum black or Hg/HgO was used as the reference electrode. The cell impedances were measured using an impedance/grain phase analyzer (Solartron, 1260) in the frequency range from 0.1 Hz to 1 MHz. Linear sweep voltammetry (LSV) was conducted using a potentiostat/galvanostat (Solatron 1287). The reaction product was examined by X-ray diffraction analysis (XRD, Rigaku, RINT 2500) with Cu Kα radiation.

3. Results and discussion

Fig. 2 shows an air electrode polarization curve of the Li/1 M $LiClO_4$ in EC–DEC/LATP/saturated LiOH with 10 M LiCl aqueous solution/KB/air cell at 0.88 mA cm^{-2} and 25 °C under an atmospheric air flow, where the mass of KB and water were 0.0255 g and 1.54 g, respectively. The air electrode potentials were measured using a platinum plate with a platinum black reference electrode. A steady electrode potential was obtained for 240 h and then decreased gradually with the polarization period. Considering that the capacity of the lithium–air batteries is always proportional to the area of the air electrode exposed to air, the capacity of the lithium–air batteries is proportional to both the specific capacity per gram of carbon (mAh g^{-1}_{carbon}) and the carbon loading per area (g_{carbon} cm^{-2}). Therefore, the product of these two parameters (*i.e.* area specific capacity mAh cm^{-2}) can be used as a more practical parameter to optimize the performance of the air electrode used in practical lithium–air cells [19]. The area specific capacity was calculated to be 204 mAh cm^{-2} from the carbon weight capacity of 8000 mAh $g^{-1}_{cathode}$ and the carbon loading of 0.0255 g_{carbon} cm^{-2}. The area specific capacity is one order higher than that of the KB oxygen electrode of the non-aqueous lithium–oxygen cell with EC–propylene carbonate (PC)–$LiPF_6$ [20], where the specific capacities were 5813 mA g^{-1}_{carbon} and 11 mAh cm^{-2} at 0.1 mA cm^{-2}. Jung et al. [21] reported good cyclability for lithium–oxygen cells with a tetra(ethylene)glycol dimethyl–lithium triflate electrolyte and a high specific capacity of 5000 mA g^{-1}_{carbon}; however, the area specific capacity was as low as 5 mAh cm^{-2}. The high area specific

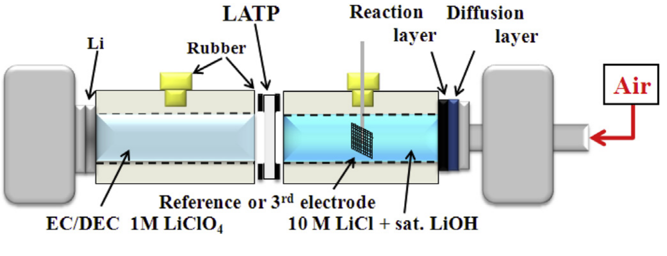

Fig. 1. Schematic diagram of the test cell.