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Silicon anode for rechargeable aqueous lithium–air batteries

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HIGHLIGHTS

- An aqueous lithium–air rechargeable cell with a silicon anode was proposed.
- The silicon anode with PI and VGCF showed a high reversible capacity.
- A Si/$LiClO_4$/LTAP/LiOH–LiCl aqueous/KB, air cell was charged to 4000 mA g^{-1}.
- The cyclic performance of the cell should be improved.

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ABSTRACT

A novel aqueous lithium–air rechargeable cell with the configuration of Si/1 M $LiClO_4$ in ethylene carbonate–diethylene carbonate/$Li_{1+x+y}Al_x(Ti,Ge)_{2-x}P_{3-y}Si_yO_{12}$/5 M LiCl–1 M LiOH aqueous solution/carbon black, air is proposed. A silicon anode composed of mechanically milled silicon power with an average particle size of *ca.* 0.5 μm, vapor grown carbon fiber and a polyimide binder was examined. The open-circuit voltage at the charged state was 2.9 V at 25 °C. The discharge capacity of 700 mAh g-silicon^{-1} was retained for 40 cycles at 0.3 mA cm^{-2} with cut-off voltages of 3.5 and 1.5 V. Significant capacity fade was observed at deep charge and discharge cycling at 2000 mAh g-silicon^{-1}.

1. Introduction

Lithium–air rechargeable batteries are attracting increased attention for application in electrical vehicles (EVs) because of their extremely high specific mass energy density compared to lithium-ion batteries [1–4]. The calculated specific mass and volume energy densities including oxygen (discharge state) are 3458 Wh kg^{-1} and 7990 Wh L^{-1}, and those excluding oxygen (charged state) are 11,429 Wh kg^{-1} and 6103 Wh L^{-1}, respectively, for a non-aqueous system. The aqueous system shows lower energy density of 1917 Wh kg^{-1} and 2895 Wh L^{-1} for the discharged state, and 2369 Wh kg^{-1} and 2010 Wh L^{-1} for the charged state. These energy densities are much higher than those of 387 Wh kg^{-1} and 1016 Wh L^{-1} for conventional lithium-ion batteries with a carbon anode and a $LiCoO_2$ cathode [2]. The energy density calculations for lithium–air batteries are based on the masses and volumes of lithium metal, the reaction product, oxygen, and water, assuming the following reactions and open-circuit voltages (OCV) of 2.96 V [5] for the non-aqueous system.

$$2Li + O_2 = Li_2O_2, \tag{1}$$

and of 3.0 V [6] for the aqueous system.

$$4Li + 6H_2O + O_2 = 4LiOH \cdot H_2O. \tag{2}$$

The cycling efficiency for lithium deposition and stripping is less than 100%; therefore, lithium should be in excess and charged threefold [7]. The calculated energy density is decreased by the excess lithium charge. The specific energy densities of the non-aqueous system with threefold excess lithium are 2154 kW kg^{-1} and 1769 kW L^{-1} for the discharged state, and 3810 Wh kg^{-1} and 2034 Wh L^{-1} for the charged state. For the aqueous system, the specific energy densities are 1440 Wh kg^{-1} and 1496 Wh L^{-1} for the discharged state, and 1680 Wh kg^{-1} and 1218 Wh L^{-1} for the charged state. The specific mass energy density of the cell with

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threefold excess lithium is still significantly higher than that for conventional lithium-ion batteries, but the specific volume energy density is not so attractive. The volumetric energy density is important for EVs; therefore, improvement of the lithium metal electrode cycling efficiency or replacement of the lithium electrode with an alternative is an important challenge to increase the volume specific energy density of lithium–air batteries. The non-aqueous system has higher energy density than the aqueous system, but the non-aqueous system has some severe problems that must still be addressed, such as lithium corrosion by water from the air, electrolyte decomposition and high overpotential. These problems with the non-aqueous system could be overcome for the aqueous system [1].

Silicon is an attractive anode material for lithium batteries because of its high theoretical capacity (4199 mAh g^{-1} as $Li_{4.4}Si$) and low lithium insertion potential as well as lithium dendrite formation free [8–10]. The specific energy densities for aqueous lithium air-batteries with a silicon anode are calculated from the following cell reaction with OCV of 2.9 V:

$$(4/4.4)Li_{4.4}Si + 6H_2O + O_2 = 4(LiOH \cdot H_2O) + (4/4.4)Si \quad (3)$$

The specific energy densities are 1608 Wh kg^{-1} and 2547 Wh L^{-1} for the discharged state, and 1927 Wh kg^{-1} and 2029 Wh L^{-1} for the charged state. The mass specific energy density is more than three times and the volume energy density two times higher than those of conventional lithium-ion batteries. However, the use of a commercial silicon anode for lithium-ion batteries has been hindered by the large volume change of over 300% during lithium-alloying and extraction, which results in the generation of an enormous amount of mechanical stress within the electrode [11]. Many approaches have been proposed to overcome these problems, such as using silicon nanostructural materials [12], silicon based composites [13–15], and a selection of binders [16]. Recently, Kim et al. reported the effect of a binder for the silicon anode and determined that a polyimide (PI) binder provided more stability and recuperative capacity against mechanical stress than the conventional polyvinylidine difluoride (PVdF) binder [17]. In this study, the possible of a silicon anode for aqueous lithium–air batteries is examined, where the silicon anode consists of a conventional mechanically milled silicon powder with a particle size of approximately 0.5 μm and the rigid PI binder.

2. Experimental

The silicon anode was prepared according to the following procedure. Silicon powder (average particle size of 0.5 μm, Kinsei Matec Ltd., Japan) was mixed with a conductive additive of vapor grown carbon fiber (VGCF; average 0.15 μm diameter and 20 μm long, CA-JP 200, Showa Denko Ltd. Japan) and a polyamic acid solution in *N*-methyl-2-pyrroliddone (NMP) (20 wt%) (Toray Ltd. Japan). The slurry was cast onto a copper foil. The cast silicon electrode was dried at 80 °C for 30 min, uniaxially pressed at 100 MPa, heated to 350 °C for 1 h and kept at 350 °C for 1 h, and then cooled to room temperature for 1 h under vacuum. The thickness of the silicon electrode was approximately 50 μm.

The performance of the silicon electrode with various weigh ratios of VGCF and PI binder was tested using a coin-type Si/non-aqueous electrolyte/Li half-cell to optimize the ratio of the components, where 1 M $LiClO_4$ in ethylene carbonate–diethyl carbonate (EC–DEC) (1:1 volume ratio) and 1 M $LiPF_6$ in fluoroethylene carbonate (FEC)-dimethyl carbonate (DMC) (4:6 volume ratio) were used as the non-aqueous electrolyte. A silicon–air full cell was constructed using the silicon electrode, a water-stable lithium ion conducting solid electrolyte of $Li_{1+x+y}Al_x(Ti, Ge)_{2-x}P_{3-y}Si_yO_{12}$ (LTAP; 150 μm thick and 19 mm diameter, Ohara Ltd. Japan), and a carbon black air electrode. A schematic diagram of the cell is shown in Fig. 1. The electrical conductivity of the LTAP plate was 1×10^{-4} S cm^{-1} at room temperature. The air electrode consisted of a reaction layer and an air diffusion layer. The reaction layer was prepared by mixing Ketjen black (KB, EC600JD, specific surface area of 1400 m^2 g^{-1}, Akzo Noble, Netherlands) and polytetrafluoroethylene (PTFE, Daikin Kogyo Ltd, Japan). The weight ratio of KB:PTFE was 95:5 and the weight of KB was approximately 60 mg. The mixture was dried at 80 °C and pressed onto a Ti mesh (100 mesh) with a carbon paper gas diffusion layer (Sigracet, SGL Co. Germany) under pressure at 64 MPa. The electrolyte at the silicon electrode side was 1 M $LiClO_4$ in EC–DEC and that at the air electrode side was an aqueous solution of 5 M LiCl/1 M LiOH. The contact area of the silicon electrode with the electrolyte was 1.1 cm^2 and the current densities were calculated using the contact area. The contact area of the air electrode with the electrolyte was 0.50 cm^2. The silicon electrode with the electrolyte was assembled in an argon-filled glove box. The cells were galvanostatically charged and discharged at 25 °C using a battery cycler (BTS 2004 H, Nagano Ltd, Japan). The electrode was examined using scanning electron microscopy (SEM S-4000, Hitachi Ltd, Japan) and the particle size distribution was determined using a laser diffraction particle analyzer (Micrometer MT 3300 EXII, Nikkiso Ltd, Japan).

3. Results and discussion

Nanostructural silicon has been reported to exhibit good cycling performance; however, a less expensive and conventional mechanically-milled silicon powder with average particle size of 0.5 μm was used in this study, because cost performance is an important requirement for EV applications. Fig. 2 shows an SEM image and the particle size distribution of the silicon powder. The SEM image shows that small sized silicon particles (*ca.* 0.5 μm) are aggregated. The particle size distribution profile shows that the size of the aggregated particles is approximately 40 μm, where the cumulative percentage was counted with respect to the volume of particles. The hard PI binder was selected to mitigate the physical volume change during the insertion and extraction of lithium ions into and from the silicon electrode [17]. The charge and discharge performance of the silicon anode was examined using coin-type cells of Si/1 M $LiPF_6$ in FEC–DMC/Li and Si/1 M $LiClO_4$ in EC–DEC/Li. Various ratios of silicon powder (Si), binder (PI) and the conductive additive were examined. As the conductive additive, VGCF, acetylene black (Denki Kagaku, Japan) and a mixture of both were tested. VGCF showed better first charge and discharge coulombic efficiency than acetylene black and the mixture of acetylene black and VGCF (1:1 wt ratio). An optimum weight ratio of Si/PI/VGCF for cyclic performance was determined to be 55/25/20. Choi et al. [18] reported that the addition of FEC into $LiPF_6$ in EC–DEC improved the discharge capacity retention and coulombic

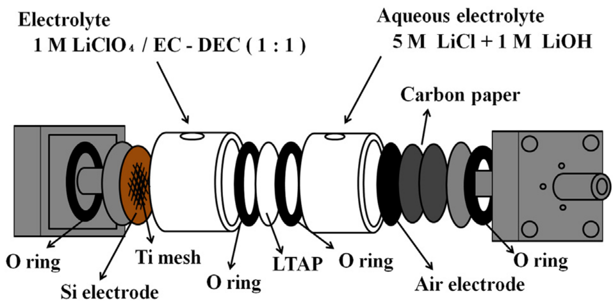

Fig. 1. Schematic diagram of the test cell.