



Study and development of non-aqueous silicon-air battery

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ABSTRACT

Silicon-air battery utilizing a single-crystal heavily doped n-type silicon wafer anode and an air cathode is reported in this paper. The battery employs hydrophilic 1-ethyl-3-methylimidazolium oligofluorohydrogenate [EMI:(HF)_{2.3}F] room temperature ionic liquid electrolyte. Electrochemical studies, including polarization and galvanostatic experiments, performed on various silicon types reveal the predominance performance of heavily doped n-type. Cell discharging at constant current densities of 10, 50, 100 and 300 $\mu\text{A cm}^{-2}$ in ambient atmosphere, shows working voltages of 1.1–0.8 V. The study shows that as discharge advances, the moist interface of the air electrode is covered by discharge products, which prevent a continuous diffusion of oxygen to the electrode–electrolyte interface. The oxygen suffocation, governed by the settlement of the cell reaction products, is the main factor for an early failure of the cells. Based on the results obtained from scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy studies, we propose a series of reactions governing the discharge process in silicon-air batteries, as well as a detailed mechanism for silicon oxide deposition on the air electrode porous carbon.

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1. Introduction

Metal-air batteries have been attracting the electrochemistry research and development community for the last 50 years. Their attractiveness lies in the principle that the cathodic reaction is a catalyzed reduction of oxygen consumed from the environment, rather than stored in the system. This aspect results in high energy densities (Wh l^{-1}) and high specific energies (Wh kg^{-1}) for the metal-air batteries.

Most metal-air batteries, including Zn-air [1–3], Al-air [4,5] and Fe-air [6] utilize aqueous alkaline solutions, mainly potassium hydroxide (KOH), due to the high conductivity of such electrolyte and the superb ability to regulate the reduced oxygen ion into hydroxide anions [7]. Zn-air batteries has received broad attention in the 1960s and 1970s, with the development of commercialized primary cells, in coin type structure, for hearing aids operation, although in the last 10 years there has been an enormous effort to construct large scale Zn-air batteries for electric vehicles (EVs) [8]. The Al-air couple has higher theoretical densities compared to its competitors (Zn-air, Fe-air) and was under investigation as a suitable power source for vehicles and some stationary application [9]. However, high open circuit corrosion rates lead to the consumption of the Al metal anode without any usable power output. The lithium-air battery presents the

highest theoretical specific energy value ($11,246 \text{ Wh kg}^{-1}$). However, Li suffers from severe corrosion in alkaline electrolytes [10] and safety concerns are still unresolved with aqueous systems. In 1996, Abraham and Jiang first reported [11] on a conducting polymer electrolyte based secondary lithium-air battery. This battery showed open circuit potential (OCP) of about 3 V and working voltage in the range of 2–2.8 V. Good coulombic efficiency was kept for only a few cycles. Ever since the lithium-air couple has been introduced it has been a subject for rapidly growing research.

In a recent communication, we have briefly discussed the construction of new, silicon based, metal-air battery [12]. From thermodynamic point of view, silicon exhibits attractive characterizations as an anode in metal-air batteries [12]. Unlike lithium, the world is ample with silicon (the second most plentiful element on earth crust) and it does not exhibit any safety issues. Silicon is non-toxic, and the reaction product with oxygen, SiO_2 , can be handled and disposed without any special measurements.

Room temperature ionic liquids (RTILs) are a relatively new group of materials that are being introduced as batteries electrolytes. These electrolytes exhibit wide electrochemical window, high chemical and thermal stability, high ionic conductivity, low vapor pressure and low toxicity. Their non-flammability, high thermal stability and low heat of reaction make them desirable especially in lithium batteries [13,14]. The EMI (1-ethyl-3-methylimidazolium, Fig. 1a) cation based RTILs group show as well low viscosity, thus high conductivity. Hagiwara et al. [15] reported the synthesis of EMI:(HF)_{2.3}F RTIL (Fig. 1) by a reaction of EMICl and

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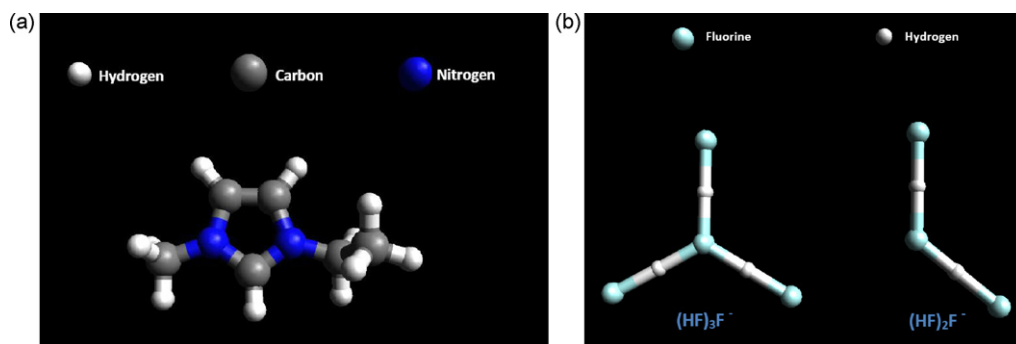


Fig. 1. Schematic diagram of the EMI·(HF)_{2.3}F RTIL electrolyte chemical structure: (a) EMI cation, (b) H₃F₄ (30%) and H₂F₃ (70%) anions.

hydrogen fluoride. This RTIL possesses some interesting properties, such as high conductivity (100 mS cm⁻¹, the highest among RTILs of its kind), low viscosity and chemical stability in air. Furthermore, Raz et al. reported [16,30] on the anodic dissolution reaction of EMI·(HF)_{2.3}F RTIL with n-type silicon and the formation of macroporous over the silicon surface, without illumination.

In the present work, we describe the study and development of a silicon-air battery with the unique structure of [Si wafer|EMI·(HF)_{2.3}F|air]. Detailed cell discharge mechanism and in-depth study of Si-air battery electrochemical behavior and characteristics are described, as well.

2. Experimental

2.1. Materials

Silicon single-crystal wafer anode electrodes were varied in their doping level, dopant type and orientation. Heavily doped n-type wafers, including (1 0 0) As-doped (0.001–0.005 Ω cm), (1 1 1) As-doped (0.001–0.007 Ω cm), (1 1 1) Sb-doped (<0.02 Ω cm) and (1 0 0) medium As-doped (0.1–0.6 Ω cm) were supplied by University Wafer (USA). Heavily doped p-type wafers, including (1 0 0) (0.001–0.005 Ω cm), (1 1 1) (0.005–0.01 Ω cm) and medium doped (1 0 0) (1–3 Ω cm) were supplied by Si-Mat (Germany). For cathode purpose, commercial air electrode (designed and formulated for alkaline Zn-air) was used, as supplied by Electric Fuel Inc. This air electrode comprised a polytetrafluoroethylene (PTFE) powder and carbon black (0.45–0.5 g cm⁻² loaded) structure catalyzed by manganese dioxide pressed onto a nickel 200 mesh. Teflon microporous layer was attached to the air side of the electrode. RTIL EMI·(HF)_{2.3}F served as the electrolyte. The IL was provided by R. Hagiwara from Kyoto University, Japan, and was synthesized according to methods described elsewhere [15].

2.2. Three electrodes cell preparation

Three electrodes cell configuration was used, with a single-crystal silicon wafer or air electrode serving as the working electrode, and platinum wires serving both as counter and quasi-reference electrodes. Experiments were carried out in an electrochemical cell containing a polypropylene holder of the silicon specimen, supported with a screwed back contact stainless steel plate. The exposed surface was 0.6 cm² (Fig. 2). Previous to any experiment the silicon sample was immersed in HF solution (1HF:5H₂O) for ten seconds in order to remove surface native oxide layer. The silicon was then rinsed with de-ionized (DI) water and dried using a nitrogen stream. After the cell was assembled, 0.5 ml of the ionic liquid was added.

2.3. Battery cell preparation

For silicon-air systems studies, a silicon single-crystal, air electrode (important note: as mentioned above, the air cathode was formulated to alkaline Zn-air) and ionic liquid were used. Schematic view of cell assembly is shown in Fig. 3. The cell was comprised of three plastic plates. Silicon wafers were cut to 1 cm × 1 cm pieces and were pressed into a viton O-ring, achieving 0.5 cm² exposed surface area. Air electrodes were cut into circular sheets, with 0.5 cm² exposed area, and outer circle periphery for electrical contact. Terminal contacts were established with Cu wires. Si wafer anodes were pretreated before cell construction as described in Section 2.2. Cells were held at OCP (open circuit potential) for duration of 4 h prior to initiation of the discharge process. This was performed in order to allow a proper wetting of the porous carbon (at the air cathode) with the RTIL electrolyte.

2.4. Electrochemical measurements and characterization

Silicon cyclic voltammetry, potentiodynamic and linear polarization studies were performed with EG&G Princeton Applied Research potentiostat/galvanostat 2273. Discharge experiments were carried out using Arbin BT2000 battery test equipment (Arbin Inc.). All experiments were conducted under ambient conditions. Surface morphologies of silicon electrode were studied using high resolution scanning electron microscope (HRSEM, Hitachi S 4700). SEM (FEI Quanta 200), equipped with energy-dispersive X-ray spectroscopy system (EDX, Oxford Inst.) was utilized in surface morphology studies and chemical analysis of the air electrodes. XPS analysis was performed using a Thermo VG Scientific, Sigma probe, X-ray photoelectron spectrometer with a base pressure in the 10⁻⁹ Torr, fitted with a monochromatized Al Kα (1486.6 eV) X-ray source.

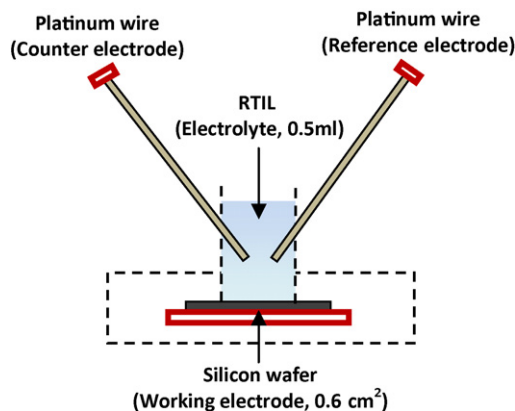


Fig. 2. Schematic diagram of the three electrodes electrochemical configuration.

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