Silicon–air batteries
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Abstract
A new “metal”–air battery based on silicon–oxygen couple is described. Silicon–air battery employing EMI 2.3HF room temperature ionic liquid (RTIL) as an electrolyte and highly-doped silicon wafers as anodes (fuels) has an undetectable self-discharge rate and high tolerance to the environment (extreme moisture/dry conditions). Such a battery yields an effectively infinite shelf life with an average working voltage of 1–1.2 V. Silicon–air battery can support relatively high current densities (up to 0.3 mA/cm²) drawn from flat polished silicon wafers anodes. Such batteries may find immediate applications, as they can provide an internal, built-in autonomous and self sustained energy source.

1. Introduction
A most important challenge in today’s materials and electrochemical sciences is the development of new materials and technologies for portable power sources. The prime objective is reducing the size of the power source and at the same time increasing its energy or power density. In recent years, a leap in metal–air battery technology has been accomplished with the introduction of a nonaqueous lithium–air cell [1–4]. Thermodynamically, silicon is an attractive fuel for battery (fuel cell) purposes. Silicon–oxygen couple has a specific energy of 8470 W h/kg and an energy density of 21,090 W h/l [5]. It is outperformed theoretically by only the H2/O2 system, and is comparable to Al/O2 couple, having a specific energy of 8146 W h/kg and an energy density of 21,994 W h/l [5]. Furthermore, silicon is plentiful (eighth most plentiful element in the universe and the second most plentiful in the earth’s crust [6]), is non-toxic, and the reaction product SiO2 is readily reduced back or can be disposed of safely or used in a multitude of applications (e.g., building materials).

The work described here resulted from our efforts to devise a silicon–air battery, which could find an immediate application by providing a built-in autonomous power driven silicon-based devices.

2. Experimental
Silicon cyclic voltammetry, potentiodynamic and linear polarization studies (performed with EG&G Princeton Applied Research potentiostat/galvanostat 2273) were conducted in an electrochemical cell comprised of Pt quasi-reference and Pt counter electrode, while silicon wafer anode or air cathode served as the working electrode. Silicon 1 0 0 single-crystal wafer electrodes (University Wafers, USA), As doped n (medium-doped) and n++ (heavily doped) type and heavily B doped p++ (Si-Mat (GmbH)), were supported with a screwed back contact plate made of gold plated stainless steel.

The air electrode comprised a PTFE powder and activated carbon black (0.45–0.5 g/cm² loaded) structure catalyzed by manganese dioxide (as produced and supplied by Electric Fuel Inc.) [7], pressed onto a nickel 200 mesh. A Si–air cells (with a diameter of 0.8 cm and a surface area of 0.5 cm²) comprising of a heavily doped n++-type silicon wafer anode and an air cathode were discharged at different current loads with a battery cycler (Maccor 2000). Et-Melm(FH)2.3F IL was synthesized at Kyoto University by one of the co-authors (RH), as describe in Ref. [8]. Theoretical equilibrium calculations and electrochemical cell potentials were calculated by HSC Chemistry Outotec Oy [5]. Electrodes characterization subsequent to battery discharge was conducted with high resolution scanning electron microscope (HRSEM, LEO-982, Geminete) and energy-dispersive X-ray spectroscopy (EDAX, Oxford Inst.).

3. Results and discussion
The yet unsolved problem of silicon’s extremely high self-discharge rate (corrosion) in alkaline electrolytes [9,10] has driven us to search for alternative attractive electrolytes. EMI 2.3HF F is a room temperature ionic liquid (RTIL), synthesized by a reaction of 1-ethyl-3-methylimidazolium chloride and hydrogen fluoride...
Evaluation of EMI 2.3HF RTIL as a viable candidate for electrolyte in a silicon-air battery system was conducted by potentiodynamic polarization studies of the RTIL-silicon wafer couples (anodic half cell), and then on the IL-air (oxygen) electrode (cathodic half cell), as shown in Fig. 1a. The reduction of oxygen is postulated to occur in the nonaqueous RTIL media either as 4-electrons \( O_2 + 4e^- \rightarrow 2O_2^- \) and/or 2-electrons reaction, \( O_2 + 2e^- \rightarrow O_2^- \). It can be noticed that there is a potential difference between the anode and the cathode of about 1.25–1.5 V (while conducting the polarizations close to the OCP), compared with a theoretically standard cell potential of 2.16 V [8]. All heavily doped silicon wafers evaluated did not show passivation behavior in the relevant potential range. The only silicon anode that exhibited passivity is the n medium-doped 1 0 0-Si (green line, \( \triangleright \) symbol), in accordance with an earlier study [14].

The results shown in Fig. 1a resolved a dilemma that we had faced since the inception of this work; whether to continue our investigation with n-type Si, which yields a higher cell voltage, or to proceed with p-type Si, which has much lower corrosion current values (indicative of a longer shelf life), as can be seen in Table 1. Stability and low corrosion rates obtained from highly-doped silicon wafers in the RTIL are comparable and even slightly lower than corrosion rates obtained from highly corrosive resistive metals, such as titanium (covered with a protective titania film) immersed in different mild oxidizing and reducing media [16]. On the other hand, etching rate of silicon immersed in alkaline electrolytes is found to be extremely high, in the order of a few 10th of \( \mu m/\)min [9,10]. The decision was made to continue the study primarily with n-type silicon-based system, which produces higher working potentials at current loads lower than 1 mA/cm². It should be noted that at high current densities the use of heavily doped p-type silicon anode (Fig. 1a, blue curve, \( \bigcirc \)) in the battery is favored, as both the expected working potential and shelf life would be substantially higher. For example, at a current load of 1 mA/cm² a Si–air battery utilizing heavily doped \( p^{+} \)-type Si is expected to provide a working potential of 1.05 V, vs. a potential of slightly lower than 0.9 V, being expected at these conditions from a battery utilizing heavily doped \( n^{+} \)-type silicon as an anode.

A typical discharge plot for a Si–air battery measured under constant current mode of operation (galvanostatic polarization) is shown in Fig. 1b. These data were collected from full cells utilizing a commercial air electrode, as the counter (cathode) electrode and heavily doped \( n^- \)-silicon as the fuel (anode), while the output voltage presented corresponds to a single cell potential. Si–air cells, having an open circuit potential of 1.45–1.55 V, were discharged initially (first 10 h) at a current density of 100 \( \mu A/cm² \); then the discharge was conducted via 10-h excursions in current densities ranging from 50 to 300 \( \mu A/cm² \) and then stepped-back to 50 \( \mu A/cm² \). Completion of these steps was achieved within a discharge time of 120 h, harvesting a capacity of 9.5 mA h. The remaining discharge process (for an additional of 230 h) was performed in a constant current mode; a current density of 100 \( \mu A/cm² \) was applied until a cut-off potential of 0.7 V was achieved. Stable and long lasting Si–air battery discharge potential profile (with potential plateau values of 1.25–0.9 V) was recorded as a function of current densities. The general trend for the cells voltage is to decrease with time. Such behavior can be attributed to the build-up of reaction products in the electrolyte and most likely to a progressive deactivation of the air cathode. This is well demonstrated in the observed working voltage oscillations, shown in the discharge profile over 20 h intervals (marked with a dashed oval, Fig. 1b). Scanning electron microscopy (SEM) micrographs obtained from the air electrode (Fig. 2a and b) show that during battery discharge the air cathode active carbon is being covered with sedimentation. A silicon-rich deposit, as determined by energy-dispersive X-ray spectroscopy (EDAX) analysis (Fig. 2c), is being formed on the moist side of the air cathode; this, we assume to be \( SiO_2 \) produced as the battery discharge product: \( Si^{4+} + 2O_2^- \rightarrow SiO_2 \).

![Fig. 1](image-url)

**Fig. 1.** (a) Potentiodynamic curves obtained in EMI 2.3HF RTIL at a scan rate of 5 mV/s from air electrode (black, \( \square \)) and 1 0 0 single-crystal silicon wafer: a heavily doped \( n^- \) (red, \( \bigtriangleup \)); a heavily doped \( p^{+} \) (blue, \( \bigcirc \)) and a medium-doped n silicon (green, \( \triangleright \)). (b) Discharge plot (at different current regimes) of Si–air cell using EMI 2.3HF F RTIL as an electrolyte and heavily doped \( n^- \)-1 0 0-Si silicon wafer as anode material. Inset table presents working potential values recorded from Si–air cells discharged at different current densities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

<table>
<thead>
<tr>
<th>Si wafer corrosion rates.</th>
<th>n-100</th>
<th>n⁻100</th>
<th>p⁺100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate (nm/min)</td>
<td>0.164</td>
<td>0.078</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*Corrosion currents and corrosion rates of different Si wafers immersed in EMI 2.3HF F ionic liquid; data was collected by applying a linear polarizations technique (±20 mV). Corrosion rates of Si wafers in concentrated KOH solutions are remarkably higher by 5–6 orders of magnitudes, in the order of few 10th of \( \mu m/\)min [9,10].
Overall, the cell presented in Fig. 1b delivered a total capacity of 21 mA h during the whole 350 h of the discharge process. Extremely high pseudo specific capacity of more than 10 Ah/g is envisaged if the mass of the air cathode’s carbon would be substantially reduced, as was reported by Beattie et al. [17]. Thus, silicon wafer anode can support high discharge rates, most probably due to the choice of heavily doped silicon wafer and highly conductive electrolyte. Further increase in Si–air battery power output can be envisioned by introducing silicon powder as the anode of choice.

4. Conclusions

We describe here a new “metal”–air battery based on silicon–oxygen couple in EMIm[BF4] RTIL electrolyte and highly-doped silicon wafers as fuels. The described battery benefits from very low self-discharge rate and high tolerance to the environment, with an effectively infinite shelf life and an average working voltage of 1–1.2 V. Such novel air battery can support relatively high current densities (up to 0.3 mA/cm²) drawn from flat polished silicon wafers anodes. It is anticipated that future studies will enhance the practical specific energy and power densities of the new Si–air battery system, as the need for materials and engineering optimization, both for the air electrode and the silicon anode, do exist. Si–air battery system seems highly promising, as it is capable of outperforming other existing metal–air battery technologies. Immediate applications of such novel battery system can be anticipated in applications such as MEMS, sensors and medical devices, as it can provide an autonomous and self sustained energy source for these silicon-based devices.

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References


Fig. 2. (a, b) Scanning electron microscopy (SEM) micrograph of air–cathode before (a) and subsequent to battery operation (b); (c) energy-dispersive X-ray spectroscopy (EDS) analysis of the deposit.