



# Long run discharge, performance and efficiency of primary Silicon–air cells with alkaline electrolyte



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## ABSTRACT

Si–air batteries, unlike other resource efficient metal–air batteries that were subject of investigations for quite a long time, came to the focus of research only recently. When operated with alkaline electrolyte, severe limitations of the discharge capacities were reported, which were attributed to a passivation layer on the anode. As a consequence, only small fractions of the surface from Si–anodes could be used for discharge. The objective of the present work is to reconsider the discharge behavior of Si–air cells with KOH electrolyte and to point out how a discharge process can be put forward until the complete anode is exhausted. Operating Si–air cells with alkaline electrolyte causes substantial corrosion, which produces also hydrogen gas as a reaction product. Moreover, along with the dissolution of Si in KOH, condensation of silicate structures in the electrolyte has been observed. Both effects accelerate electrolyte loss in the cell. Therefore, appropriately balancing the electrolyte supply of the Si–air cell is a precondition for ongoing discharge. Specifically, cells with As-doped Si-wafer anodes with 0.6 mm and 3.0 mm thickness were discharged in 5 M KOH electrolyte at current densities up to 0.05 mA/cm<sup>2</sup> for 260 and 1100 hours, respectively. The drawback is that a minimum amount of electrolyte is required in order not to exceed 4 M Si content, which otherwise leads to a gelation of the electrolyte. Although a considerable fraction of the anode material is not transformed to electrical energy owing to corrosion, specific energies up to 140 Wh/kg (for 1100 h) related to the total anode mass loss were realized.

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## 1. Introduction

Metal–air cells (technically described as “metal–oxygen” cells) for storage of electrical energy have been subject to investigations for more than 100 years. Recently, many studies focusing on the development of materials for metal–air batteries were reported. Among the aqueous metal–air batteries Zn–air, Fe–air, and Al–air batteries showed the most promising electrochemical performances. With respect to secondary, electrically rechargeable batteries, Zn–air cells are most advanced, but still under research and development. Dendrite formation upon recharge, non-

uniform zinc dissolution, low solubility of zincates in electrolytes have to be overcome to increase the cycle numbers, which currently are limited to 1000 cycles approximately [1–3]. Based on ionic liquid electrolytes that have proven to be suitable for deposition of Zn [4,5], development of cells that provide complete charge-discharge cycles is ongoing. On the other hand, Fe–air batteries are electrically rechargeable and practically capable of long cyclic stabilities (>1000 cycles); however, with a low energy density [6,7]. Primary Al–air batteries with aqueous electrolytes have already been under development since the 1960s. However, high corrosion rate and formation of a passivation layer lead to reduced discharge performance [8,9]. In spite of technical solutions available even for mechanically rechargeable Al–air batteries [10], a widespread application has not been obtained so far. Moreover, primary Zn–air batteries showed successful advancements and already available commercially for telecommunication and medical applications [2,3]. For the primary batteries, resource

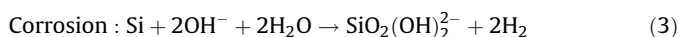
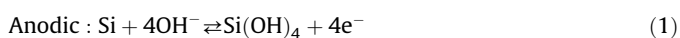
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availability and cost become an issue of major concern. In that respect, Silicon as being the 2nd most abundant element in the Earth's crust is an interesting option for this type of batteries.

Despite its high specific energy density of 8470 Wh/kg, Si as anode material has been less in the focus of research on energy storage compared to Li (11140 Wh/kg), Zn (1350 Wh/kg), Al (8100 Wh/kg), and Fe (1200 Wh/kg), probably due to the low intrinsic electronic conductivity of undoped silicon [11–14]. However, extensive work on electrochemistry and corrosion behavior has been reported on the etching of Si for semiconductor devices [15–18].

With large scale storage technologies for electrical energy becoming a major issue of scientific and technological concern, interest in the Si–air cells as a resource efficient type of battery has been emerging. While operation of Si–air batteries with ionic liquid electrolytes is one line of development [19–22], conventional alkaline electrolyte based systems are also subject to recent investigations [23,24]. A common feature of both types of systems in the current state of development is the limited discharge capacity, which means that electrochemical reactions stop before the complete anode is consumed [21]. Moreover in Si–air batteries with alkaline electrolyte substantial corrosion reactions during open cell potential (OCP) as well as under discharge lead to reduced anode conversion efficiency. The corrosion reaction and the half-cell electrochemical reactions for the discharge process can be described as follows [23,25,26]:



Si–air cells with aqueous electrolytes were subject to recent research by Zhong et al. and Park et al., who worked with As-doped [23] and B-doped [24] silicon wafers as the base material for the anodes. Common approach of both groups was to use surface modified silicon wafers while focusing on low molarity KOH as electrolyte. Discharge of flat Si-wafers resulted in rapid decrease of the potential within the time spans of a few minutes. The limited discharge capacity was attributed to surface passivation of the Si anode. In contrast to that, they reported extended discharge times when wafers with surfaces nanostructured by metal assisted chemical etching [23] or electrochemical etching [24] were employed as anodes. Zhong et al. showed data of discharge times up to 30 h, but asserted that even more prolonged discharge was possible. They also investigated the corrosion for 7 h discharge runs under current densities of 0.05 mA/cm<sup>2</sup> along with different KOH molarities of the electrolyte.

The main objectives of the present paper are (i) to point out crucial limiting factors to the discharge behavior of Si–air cells with KOH electrolyte, (ii) to characterize the discharge behavior under different operating conditions, and (iii) to reveal how a Si–air cell can be set up for discharge until the complete anode is consumed. The loss or drying out of KOH electrolyte plays the major role in limiting the discharge process in Si–air cells. The corrosion reaction also contributes to this by forming hydrogen gas and silicate structures in the electrolyte. Consequently, the provision of an appropriate electrolyte supply is the key issue for eliminating the discharge limitation. Complete discharge is demonstrated for selected operating conditions with different Si wafer thicknesses. The more compound characterization of the discharge behavior dependence on operating parameters–concentration and content of KOH–are elaborated from 24 h runs of the cells. Finally, an

assessment on conversion efficiency and specific energy of the Si–air battery with aqueous electrolyte in the present state of development is given.

## 2. Experimental

### 2.1. Materials

Anodes were prepared from n-type single crystalline silicon wafers with (100) orientation and arsenic-dopant (0.001–0.007 Ω cm) from University Wafer. The samples were cut into 12 mm × 12 mm size and treated with plasma (PICO, Diener) prior to experiments. In order to volatilize organic contaminations on the silicon surface, argon/oxygen plasma was employed as an initial surface treatment, which was followed by argon/sulfur hexafluoride plasma to remove oxides at the surface. The porous carbon-based air electrode with manganese dioxide catalysts (E4 type) was provided by Electric Fuel Ltd. Alkaline electrolytes were prepared by dissolving 0.75–5 M KOH (≥85% KOH basis, Fluka) in deionized water (conductivity of less than 10 μS/cm<sup>2</sup>). The electrolyte solution was purged with argon gas for several minutes to remove dissolved oxygen from the solution.

### 2.2. Cell Configuration

The refill-type Si–air cell (Fig. 1) was comprised of a single crystalline silicon wafer as anode, porous carbon-based air electrode as cathode, and KOH (dissolved in water) as electrolyte. The cell consists of three plastic discs (made of Poly(methyl methacrylate)) and the electrolyte volume of the cell is 0.6 ml. The active areas of silicon wafer and air cathode were 0.44 cm<sup>2</sup>. A peristaltic pump (Reglo Analog MS-4/12, Ismatec) was employed in order to keep the electrolyte level constant in the cell. The pump was connected to cell and reservoir via capillary tubing (inner diameter is 0.75 mm, PEEK, BOLA) which provides a flow rate of 0.1 ml/min. Electrolyte was supplied through the bottom hole and was discarded through the top hole. Both fresh and used electrolytes were kept in the same reservoir. The pump was operated under intermittent refilling mode during discharge every 4 hours for 5 minutes via a TTL pulse from Biologic VMP3 potentiostat.

### 2.3. Electrochemical Measurements and Microscopy

Electrochemical tests were performed by using a Biologic VMP3 potentiostat. Discharge behavior of the Si–air cells was investigated with variations of concentrations of alkaline electrolyte (0.75–5 M). Cells were initially kept at OCP for 4 hours, which was followed by 20 hours of discharge with 0.05 mA/cm<sup>2</sup> unless otherwise specified. All the discharge experiments were conducted in a climate chamber (Binder KMF115) to control the ambient conditions. Cyclic voltammetry (CV) experiments were conducted in a three-electrode half-cell setup with a mercury/mercury oxide (Hg/HgO) reference electrode. Si was used as a working electrode and a Pt wire was used as counter electrode. The active area was set to be the same as in the full-cell experiments (0.44 cm<sup>2</sup>). The surface morphology of silicon wafers after discharge was investigated by using a scanning electron microscope (FEI Quanta FEG 650). For the acquisition of the images the SEM was operated with 5 kV at working distances of approximately 10 mm.

### 2.4. NMR Experiments on Corrosion Products

The samples were prepared by dissolving plasma cleaned Si wafers in 1 M, 2 M and 5 M KOH. Si wafers were fully dissolved, with final Si concentrations of 0.5 M and 1 M. Ex-situ NMR measurements were recorded on a Bruker AVANCE III HD 400

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