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Investigation of the corrosion behavior of highly As-doped crystalline Si in alkaline Si–air batteries

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A B S T R A C T

High corrosion rate is one of the major obstacles that have to be overcome in order to establish practical application of primary alkaline Si–air batteries. At the current state of development the theoretical specific capacity of 3820 mAh/g is reduced to 120 mAh/g in long term operable alkaline Si–air batteries, with most of the capacity losses being due to corrosion reactions. In the present work the corrosion behavior of highly As-doped <100> oriented silicon wafers, that have proved stable performance as anode materials is summarized for a scope of conditions that may arise in battery operation. More specific, corrosion rates are presented and discussed with respect to (i) time dependence, (ii) influence of KOH electrolyte concentration, (iii) chemical vs. electrochemical corrosion, and (iv) corrosion under anodic potentials as present during the discharge of batteries. Corrosion rates were found to exhibit stable time profiles for immersion times longer than 8 h. With respect to concentration dependence, three ranges of KOH concentrations were identified. Within each range, the corrosion behavior is governed by similar mechanisms, but different limiting factors. Potentiodynamic measurements show that large part of the corrosion is chemical in nature. Under discharge conditions corrosion increases whereby the discharge potential, corrosion rates, and mass conversion efficiencies depend on KOH concentrations and discharge current densities.

1. Introduction

Increased demand on resource efficient energy storage devices has urged an interest on new battery technologies. Recently, metal–air batteries became prominent in this regard due to possessing high theoretical specific energies as well as using low cost, safe and abundant electrode materials. A new concept, Si–air, has received considerable attention lately as a promising candidate for primary metal–air battery research [1–10]. Besides being the 2nd most abundant element in the Earth's crust, Si provides very high theoretical specific energy (8470 Wh/kg) when related only to anode mass in Si–air batteries. Additionally, Si and its discharge products are easy to handle and non-toxic from the environmental point of view.

Despite the fact that Si has been one of the most investigated material in the field of semiconductor industry for many years [11–19], the first attempt to use it in a metal–air battery concept was reported only in the last decade. The first approach to utilize Si in a battery was conducted by employing a room temperature ionic liquid, 1-ethyl-3-methylimidazolium oligofluorohydrogenate (EMIm$(HF)_{2.3}F$), as an electrolyte [1]. Up to 27 mAh discharge capacities with cell voltages above 0.8 V were demonstrated in the presence of negligible corrosion rates (<0.2 nm/min) [2]. Another approach was the replacement of the ionic liquid with conventional alkaline electrolyte. The first studies by Zhong et al. and Park et al. showed a requirement of high Si surface area for an extended discharge time, otherwise the cell voltage rapidly dropped to zero due to passivation of the surface within seconds [6,7]. A more recent study, in contrast to that, illustrated discharge profiles with

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flat Si surfaces for more than 1100 h while providing cell voltages above 1.1 V [9]. However, as a result of substantial corrosion reaction, Si–air batteries suffer from low anode mass conversion efficiencies (~3%) in alkaline electrolytes.

Quantification of corrosion rates and mechanisms of the Si corrosion reaction have already been subject to many studies [14–26]. Generally, Si substantially undergoes (electro-)chemical dissolution at open-circuit potential (OCP) and at slightly anodic potentials as soon as it is in contact with alkaline electrolyte ($pH > 13$), while generating hydrogen gas and silicates simultaneously. Both reaction products could be detrimental to the battery performance; on the one hand silicates in high concentrations can saturate the electrolyte forming gel-like solutions, on the other hand, the electrolyte can leak due to increased cell pressure as a result of hydrogen gas production. Most important, however, the corrosion reaction consumes the active material in the battery without delivering electrical energy. It is therefore of high importance to investigate the corrosion mechanism of Si in such electrolytes to understand the possible influences on the battery shelf-life as well as on the discharge performance and efficiency.

The aim of this paper is to investigate the corrosion behavior of crystalline Si wafers in alkaline Si–air batteries. We refer to “etch rate” or “dissolution rate” as the “corrosion rate” throughout this paper. Four different aspects of the corrosion behavior are considered, with all the experiments related to Si-wafers with the same specifications (highly As-doped <100> Si) which have proved high performance when operated as anode materials in batteries [2,6,9]. (i) The OCP corrosion rates of Si are studied according to the influence of the immersion time together with the surface morphology development within 72 h; (ii) the impact of KOH concentration and resulting surface characteristics are investigated during 24 h OCP corrosion experiments; (iii) the contribution of the chemical and electrochemical mechanisms on the corrosion rates are pointed out by the comparison of the weight-loss experiments and potentiodynamic polarization experiments; (iv) the corrosion rates are analyzed under anodic potentials as present during discharge of a Si–air battery for cells with 1 M and 5 M KOH electrolyte under discharge current densities from 10 to 70 $\mu A/cm^2$.

2. Experimental

2.1. Materials and Chemicals

As-doped <100> oriented (0.001–0.007 Ωcm) single crystalline silicon wafers (University Wafer) were used in the experiments. The Si surfaces were treated with plasma (PICO, Diener) in two steps prior to experiments. Initially, organic contaminations were volatilized from the surfaces with argon/oxygen plasma, and then silicon oxides were removed by argon/sulfur hexafluoride plasma. After the plasma treatments the surfaces of the Si wafers are smooth [10]. Alkaline electrolytes 0.5–12 M KOH were prepared by dissolving KOH pellets (≥86.7% KOH basis, Fluka) in deionized water (conductivity<0.1 μS/cm, PURELAB Elga). The solutions were degassed with argon for several minutes to remove dissolved oxygen. The conductivity of the KOH solutions was measured by a conductivity meter (S230, Mettler Toledo).

2.2. Cell Setup and Characterization Methods

For the OCP corrosion experiments a half-cell setup designed as modified version of the full-cell made from Poly(methyl methacrylate) was used [9]. Surface areas of the Si wafers and electrolyte volumes of the cell in the experiments were 0.44 cm^2 and 0.6 ml, respectively. All the experiments were carried out in a climate chamber (Binder KMF115) to ensure controlled ambient conditions. The surface morphologies of silicon wafers after corrosion experiments were analyzed by using a confocal laser scanning microscope (OLS4100, Olympus Corp., Japan).

Biologic VMP3 potentiostat was employed to perform the electrochemical experiments. Cyclic voltammetry (CV) and potentiodynamic polarization experiments of Si wafers were conducted in a three-electrode half-cell setup with a Pt wire as counter electrode and mercury/mercury oxide (Hg/HgO) as reference electrode. Galvanostatic discharge experiments of Si–air cells were carried out with a cell consisting of a Si wafer as anode, KOH solutions as electrolyte, and a carbon-based air electrode (Electric Fuel Ltd.) as cathode [9]. Cell dimensions and ambient conditions were the same as for OCP corrosion experiments. Si–air cells were discharged for 20 h at different current densities with 1 M and 5 M KOH electrolyte. In order to provide proper wetting of the air electrode, cells were initially kept at OCV for 4 h.

2.3. Corrosion Analysis

The weight losses of silicon anodes before and after the experiments were measured by using an analytical balance with an accuracy of 0.01 mg (XA205, Mettler Toledo). For the Si–air cell discharge experiments, the anode mass conversion efficiencies were calculated according to:

$$\eta(\%) = \left(\frac{(j \cdot A \cdot t_d)}{m_{loss,tot}}\right) \cdot \left(\frac{(n \cdot F)}{M_{Si}}\right)^{-1} \times 100 \tag{1}$$

$$m_{loss,\ tot} = m_{loss,corr} + m_{loss,dis} \tag{2}$$

where j is current density, A is geometrical surface area, t_d is discharge time, n is number of electrons (assumed to be a four electron process), and F is the Faraday constant. The total mass loss $m_{loss,tot}$ is defined as the sum of the corrosion mass loss $m_{loss,corr}$ and the electrochemically discharged anode mass consumption $m_{loss,dis}$.

3. Results and Discussion

3.1. Time and Temperature Dependence of Corrosion Rates

Time Dependence of Corrosion Rates: The influence of immersion time on the As-doped <100> Si corrosion rates in 5 M KOH at 25 °C is depicted in Fig. 1. The concentrations of dissolved Si (in form of silicates) in the solutions at the end of each experiment are also illustrated. Fig. 1 shows remarkably different corrosion rates within 12 h. After some minutes of immersion into the electrolyte, the Si exhibited corrosion rates around 3 μm/h which were gradually decreased to 1.1 μm/h after 4 h. Exposing Si to electrolyte for longer times enhanced the corrosion rates slightly up to 1.5 μm/h (at 8 h) and stabilized them until 72 h. Concurrently, the concentration of the silicate species in the solutions were increased up to 0.8 M. Thus, there was no direct correlation observed between the corrosion rates and the silicate concentrations within 72 h.

The data represented in Fig. 1 emphasize explicitly the importance of immersion times on the Si corrosion rates. Si corrodes initially at higher rates when in contact with KOH solutions within the first hour. Steady-state conditions are only maintained after 8 h of immersion at room temperature. In order to investigate if the change on the Si corrosion rates over time originates from the Si surface conditions, the corroded Si surfaces in 5 M KOH (from Fig. 1) were studied by laser scanning microscope (LSM) and the micrographs are illustrated in Fig. 2.

An anisotropically etched <100> Si surface was already