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The Rechargeability of Silicon-Air Batteries

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14. ABSTRACT This project aimed to investigate silicon-air batteries as a rechargeable power source of high energy density. Si-air batteries are an attractive possibility due to high charge capacity (approximately 4 times higher than conventional Zn-air, and nearly that of Li-air) with less safety and environmental concerns. Studies of Si-air electrochemical cells using both liquid room-temperature ionic liquid as electrolyte and a gel polymer electrolyte (formed by incorporating an ionic liquid electrolyte into polymeric matrix) were undertaken. Research challenges included overcoming the SiO ₂ reaction product from clogging the porous carbon-air electrode, reducing the SiO ₂ byproduct during recharging and redepositing the Si ions in a manner to permit continued operation without loss of energy density, and avoiding the build-up of water byproduct in the electrolyte during reduction during recharge phase. This last issue was seen as a critical roadblock for the continued development at this time, although production of H ₂ O during operation could make an Si-air electrochemical cell a source of water for other applications.				
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The Rechargeability of Silicon - Air Battery:

2011-2012 Report

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A report covering the period of 6-16-2011 – 6-15-2012

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Executive Summary

Water play a major role in any process of chemical dissolution of crystal SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid. It is demonstrated that water can be produced by dissolving SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid. It is recommended to focus future research of extraction of water from the system. Thus, a cycle of water production from silica can be visualized, if a method for water extraction would be developed specifically for this system. In-depth NMR studies were conducted in order to better understand the role of water on the IL structure.

Free standing, mechanically stable, composite polymer gel electrolyte, based on $\text{EMI}(\text{HF})_{2.3}\text{F}$ IL and HEMA polymer, were produced. Different compositions, from 40 mol% to 70 mol% of RTIL, were investigated and characterized. The results show a relatively long battery discharge times, up to 850 hours. However, the operating voltage is lower with respect to a cell discharge utilizing the ionic liquid alone, due to higher ionic conductivity of the pure IL.

1. Introduction and Scientific Background

Although recent achievements in lithium-ion battery technology has witnessed tremendous progress in the past decade as energy storage device for small portable electric devices to large power systems, the energy density of current lithium-ion batteries is still insufficient to meet the demands for future applications such as electric vehicles. Therefore, electrochemical concepts with enhanced energy density are in the focus of intense research. In that respect, metal-air batteries which are considered as a promising candidate [1,2]. The most intensely studied metal-air concept is the Li-air battery that is characterized by a theoretically high specific energy value of 11246 Whkg^{-1} . However, a number of non-trivial challenges have to be overcome, such as low operating current densities ($< 100 \text{ mAcm}^{-2}$, blocking of air electrode by Li_2O_2 reaction products, as well as safety concerns regarding the use of lithium metal anode.

Recently, the alternative concept of a silicon-air battery has been introduced [3–5]. From a thermodynamic point of view, the corresponding silicon-oxygen couple is very attractive because four moles of electrons are generated per reaction of 28 grams of the silicon active anode material. Furthermore, the charge capacity of 3.816 Ahkg^{-1} is four times higher than in conventional Zn-air batteries and almost reaches that of Li-air batteries (3.86 Ahkg^{-1}). Finally, by the use of silicon as the anode material, there are no safety issues and both silicon and its reaction products with oxygen are safe and environmentally friendly.

In our last year report we have shown our studies towards the goal of achieving high electrochemical reversibility at each of the electrode, i.e. turn the Si - air battery to a secondary one. The first step was to enhance the electrochemical properties of the electrolyte and transform it to "supporting electrolyte", which can support silicon reduction. This was done by incorporating silicon salt, SiO_2 powder, into the electrolyte, and to examining its electrochemical reduction performance / ability. A solution of 0.1M SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid was examined, and a cyclic-voltammetry reduction peak was observed. Moreover, we have shown the feasibility of charging a silicon - air battery. A charging process for a period of 72 hours (21.6 mAh/cm^2 charge capacity) lead to a 25% increase in the total discharge capacity of the cell. Therefore, during the he charge period, a certain amount of the discharge

product layer, covering the air electrode, is being removed. The removal of this layer contributes to extended oxygen reduction ability, and, as a result, longer discharges time (capacity).

2. Scientific and Practical Goals for 2011/2012

The question of charging ability of Si - air battery should be answered first with the help of basic science question and research. First, the solubility of SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid should be studied in details. A vital instrument for such studies must be a stable and reliable reference electrode. Therefore, our study involves the development of such a reference electrode, based on a gel-phase ionic liquid.

An NMR (Nuclear Magnetic Resonance) measurement is a standard tool for organic chemistry research. Some work had been previously done in other IL's, and even in $\text{EMI}(\text{HF})_{2.3}\text{F}$ [6]. The possibility of gathering data regarding the nature of the species of Si in this specific IL, and the possible changes in the liquid as a function of applied electrochemical means, make the NMR an excellent way for a better understanding of the chemistry of SiO_2 dissolution.

Another issue that was treated this year was the development of solid-state Si - air battery. Such a battery consists solid electrolyte, gel polymer electrolytes (GPE), rather than a liquid one. The GPE's, formed by incorporating a liquid electrolyte into a polymeric matrix, are highly safe, shape flexible, mechanically stable, and display only a modest loss in ionic conductivity upon operation. Even though there is no need to improve the performance of the Si - air cell in contact with ambient atmosphere, by incorporating a GPE as a moisture barrier, the use of a gel electrolyte may eliminate the need to handle liquid electrolyte and will simplify technical issues in cell architecture.

3. Experimental Section

In this study two different SiO_2 samples were in use. Quartz (crystalline alpha, purum <230mesh, Fluka) and silicon(IV)oxide (amorphous, elec. grade, 99.999%, Puratrem). As parts of the experiments both of those powders were dissolved in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid (IL). Two different batches of the IL were in use, the first was received in

February 2009 and second in April 2011, both supplied by Professor Rika Hagiwara from Kyoto University, Japan. For the second batch of IL, Karl Fischer titrations were made using 831 KF Coulometer (Metrohm). All the electrochemical measurements were made in three electrode cell using EG&G Princeton Applied Research potentiostat/galvanostat 273/273A. In all studies Pt counter and quasi reference wire electrode were applied. Two types of working electrodes were utilized in present study; glassy carbon plate (GC, ALS Co. Ltd.) and Pt foil. All the Pt electrodes were washed in concentrated HNO₃, and then rinsed with water. The GC electrode prior to usage was cleaned in Acetone and hot Isopropanol. All the electrochemical experiments were conducted using 0.5ml of the IL.

NMR experiments were conducted with 5mm Teflon[®] tubes, (Wilmad-LabGlass) using 3mm internal Teflon[®] capillary (Wilmad-LabGlass) filled with Methanol-d₄ (Sigma – Aldrich). For proper placement in the NMR instrument an external 5mm glass tube was used (Economy 7, Wilmad-LabGlass). The experiments were conducted on Bruker Avance III 400 and Bruker Avance III 600. All the NMR data are presented in ppm. ¹H NMR data were referenced to TMS – tetramethylsilane (CH₃)₄Si, ¹⁹F was referenced to CFCI₃. The NMR measurements were conducted only to the second batch of the IL.

Gel-polymer electrolyte was prepared by mixing EMI(HF)_{2.3}F IL and HEMA (2-hydroxyethyl methacrylate, Alfa Aesar, 97%), in the proper molar ratios, together with 0.1 wt% benzoyl peroxide (Fluka, >97%) as a initiator. The mixture was polymerized at 80°C for 12 hours.

High resolution SEM (HRSEM, Hitachi S4700) was used to investigate the silicon electrode morphology.

4. Results

4.1. Water content

The dissolution experiments did not provided stable results. With the first batch of the IL, dissolution of up to 0.1M of quartz was obtained. With the same process (stirring, test tubes and other relevant details), a full dissolution was obtained only once with the second batch of the IL. Full dissolution considered to be dissolution of the powder

without a residue traces in the test tube, leaving behind a clear liquid. In both batches using Si(IV)oxide, full dissolution in the IL was not obtained. The product of incomplete dissolution was "polymer" like silicon oxide slurry. Further investigation of this slurry will be conducted.

The water level in the IL was measured on the second batch. The amount of water in the IL after 2 months of storage since its arriving was 1323ppm, and after 4 months the water measurements showed a level of 9912ppm. This significant change in the water quantity in the IL causes a difficulty in the experiment procedure. The fact that water amount is rapidly changed may provide some explanation for the instability of the dissolution results. But still, full dissolution was produced with the first batch of the IL, the one with longer "aging" time and probably the same or even higher amount of water in it. So as may be concluded, exposure to humid environment and water content have a major impact on the dissolution process of SiO_2 in the IL, an impact that is still not fully understood.

The next logical step was to try lower the water amount in the IL. The use of molecular sieves for this cause failed. The sieves reacted with the IL and were partially dissolved in it. Other possible paths for de-humidification were considered and rejected in this specific IL. Vacuum drying may cause HF evaporation and change the IL anion stoichiometry. Moreover the hydrophilic nature of the IL is also problematic concern in simple heat drying. Up to now, no effective method for IL drying has been found.

4.2. NMR measurements

Figures 1 and 2 show the ^1H NMR and ^{19}F NMR spectra of 3 different samples. Figures 1a and 2a show the NMR of neat IL. Figure 1b and 2b show NMR of IL with some amount of Methanol- d_4 in it. Figures 1c and 2c present spectra of not fully dissolved 1M of quartz in the IL. This sample contained SiO_2 slurry as was previously described. The ^{19}F NMR experiments were conducted in such procedure that only F – H conjugated bonds are shown as positive peaks.

It may be seen from the spectra in figures 1 and 2 that there is a shift in the peak position between the neat IL and the IL with dissolved methanol- d_4 . This shift is expected, as was already observed in other works on different IL's and deuterated solvents [7]. The cation peaks are as expected for EMI^+ cation, nevertheless the

location of the supposed anion peak (in $(\text{HF})_{2.3}\text{F}^-$) is shifted by more than 3.5ppm (from around 12ppm to 8.5ppm in the dissolved sample). This shift is different than expected [6]. One of the reasons may be different concentration of the IL in the deuterated solvent.

Different approach for understanding the stoichiometry of the anion in the IL may be seen in other NMR based researches [8]. In this specific research the experimental ^1H peak of same stoichiometry as the $(\text{HF})_{2.3}\text{F}^-$ is expected at 12.5ppm. Therefore, there is a difference of 0.5ppm between the above mentioned result and the data in Fig. 1a. However, the different temperatures in which the measurements were taken (present work around 298K compared to 120K at reference 8) and the strong temperature dependence of peak shift serve may both suggest that the stoichiometry of the IL is indeed $n=2.3$ as expected.

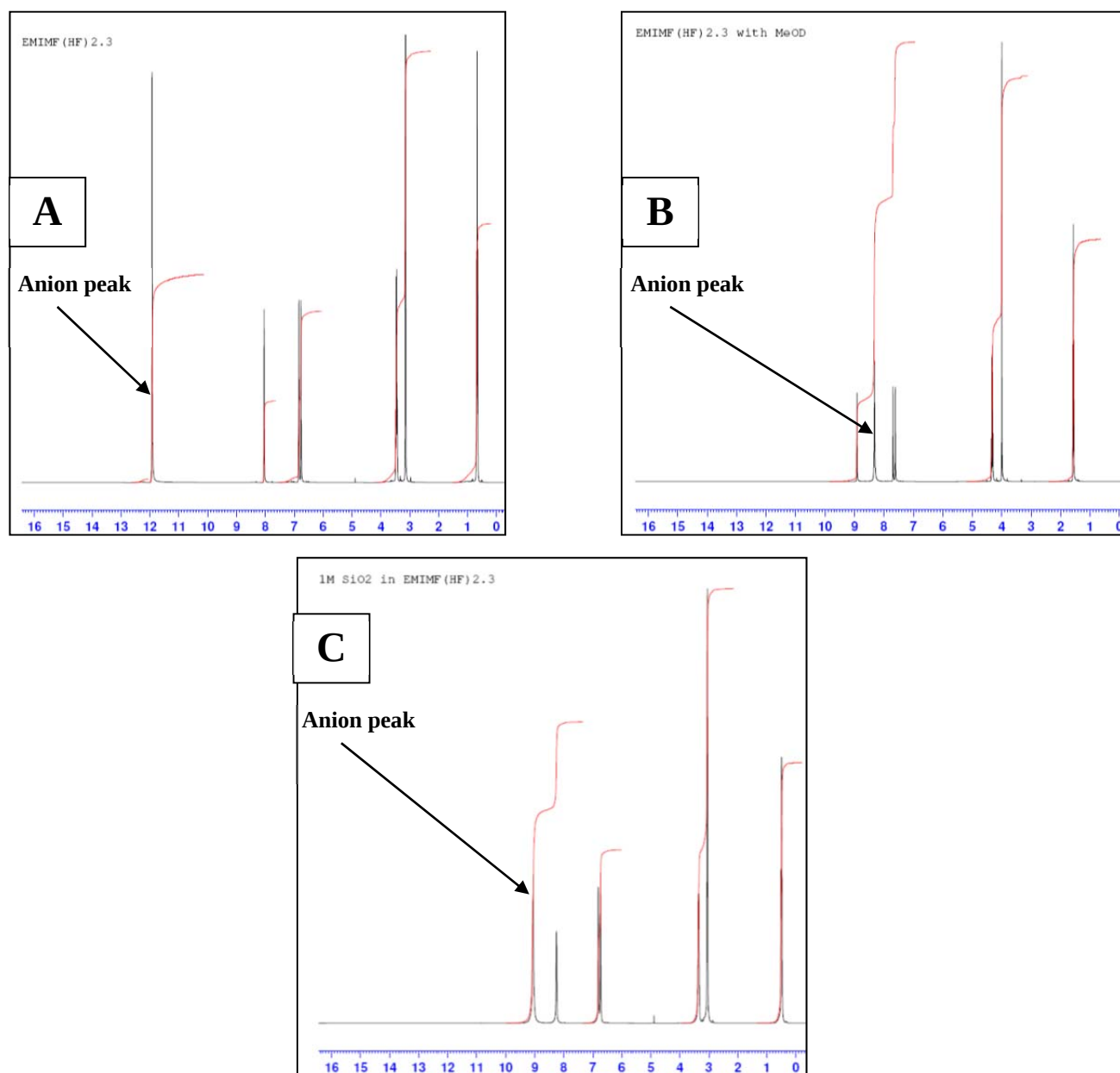


Figure 1. (^1H NMR) spectra of **a.** neat IL, **b.** IL with some amount of Methanol- d_4 , and **c.** not fully dissolved 1M quartz in the IL.

Moreover, due to high dependence of the anion peak shift of the IL on the its concentration in the deuterated solution, the proper approach for any future NMR measurements should be only with neat liquid.

From a comparison between figures 1a and 1c it may be seen that there is almost no shift between the cation peaks in both measurements. For the anion peak there is a shift of about 3ppm between the spectra. This shift may suggest on a possible reaction between the partially dissolved quartz and the IL.

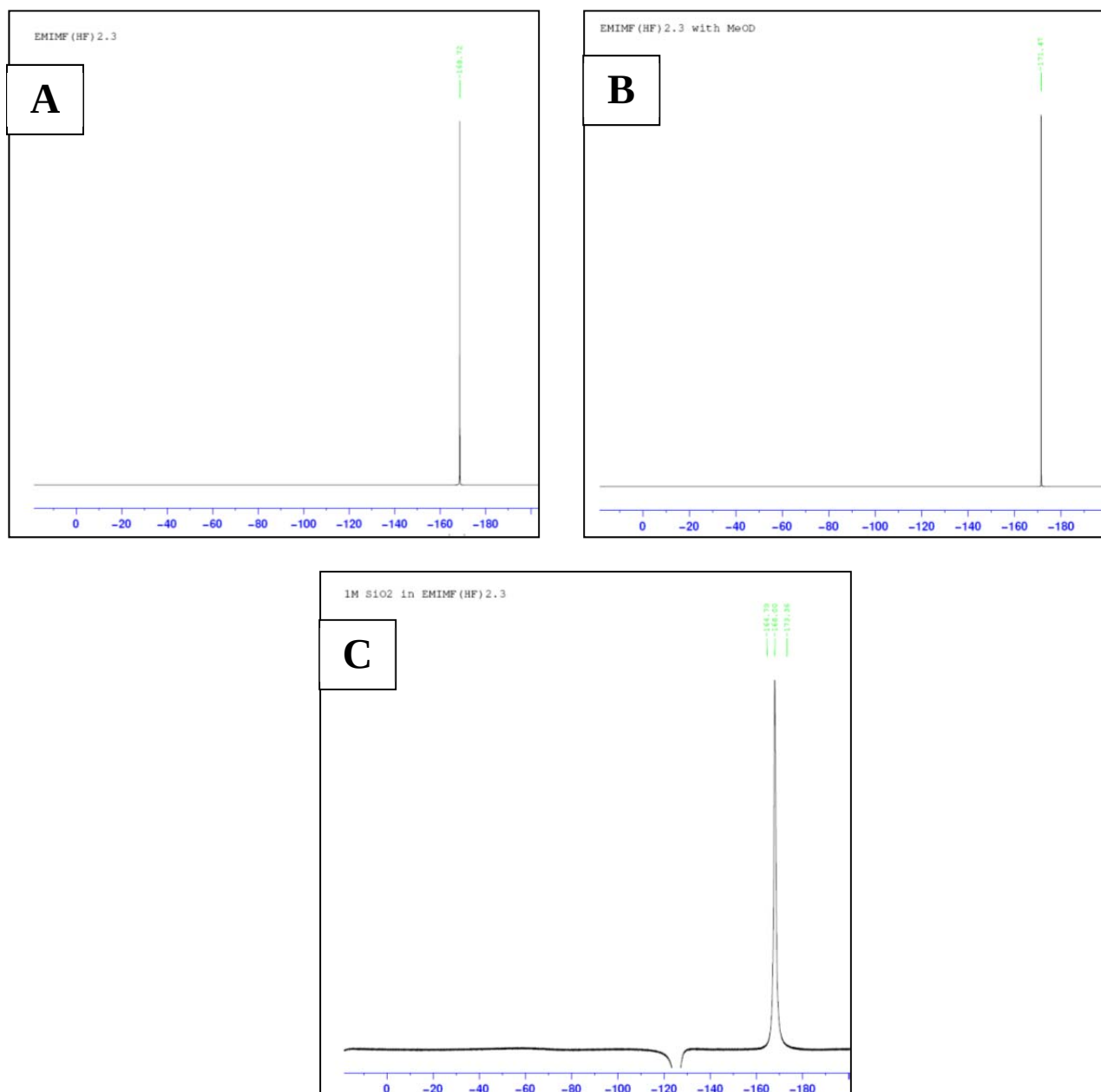


Figure 2. ^{19}F NMR - H conjugated spectra of **a.** neat IL, **b.** IL with some amount of Methanol- d_4 , and **c.** not fully dissolved 1M of quartz in the IL.

The ^{19}F NMR results provide additional data. The shift between the peaks of the neat IL and SiO_2 -dissolved (figures 2a and 2b, respectively) are of the same magnitude, 3.5ppm, as in the ^1H NMR measurements. From the comparison to other NMR publications it may be concluded that the NMR shift of -168ppm is suitable for the stoichiometry of $n=2.3$. The ^{19}F NMR average peak calculation, from previous work [8], brings to a value of -171ppm, which is a good match to the present data. The shift in the ppm measurements may also be the result, as previously explained, of temperature dependence.

In figure 2c two different peaks may be observed. The -168ppm peak is as in neat IL and another peak with negative intensity, due to F-H conjugation conducted experiment. This peak around -127ppm may suggest on the presence of other F bonded chemical specie in the solution. The shift is with good agreement to SiF_6^{-2} . But other silicon based species may be also possible, e.g. Si_2F_6 with typical shift of -126ppm. The broadening of the peaks in the spectrum is probably due to the previously explained not fully dissolved SiO_2 slurry.

Unfortunately, due to some technical problems, the ^{29}Si NMR measurements are still under investigation.

4.3. Electrochemical measurements

The electrochemical measurements with the first batch of IL were conducted on Pt working electrode. The gathered data showed problematic stability of the results. The smaller possible electrochemical window and the difference of initial open circuit potential (OCP) of the working electrode, even after the same cleaning process, made it almost impossible to reproduce an experiment. The use of Pt as a quasi reference made it difficult to compare different between experiments.

In order to provide more appropriate working electrode, a GC was utilized. The work on GC was conducted only with the second batch of the IL. Figures 3a and 3b show the results of these measurements. In figure 3a a CV in different scan rates of the IL on GC is presented. In figure 3b the CV in different scan rates of the 0.1M quartz in IL is shown. This scan was conducted on the single fully dissolved solution as was previously described.

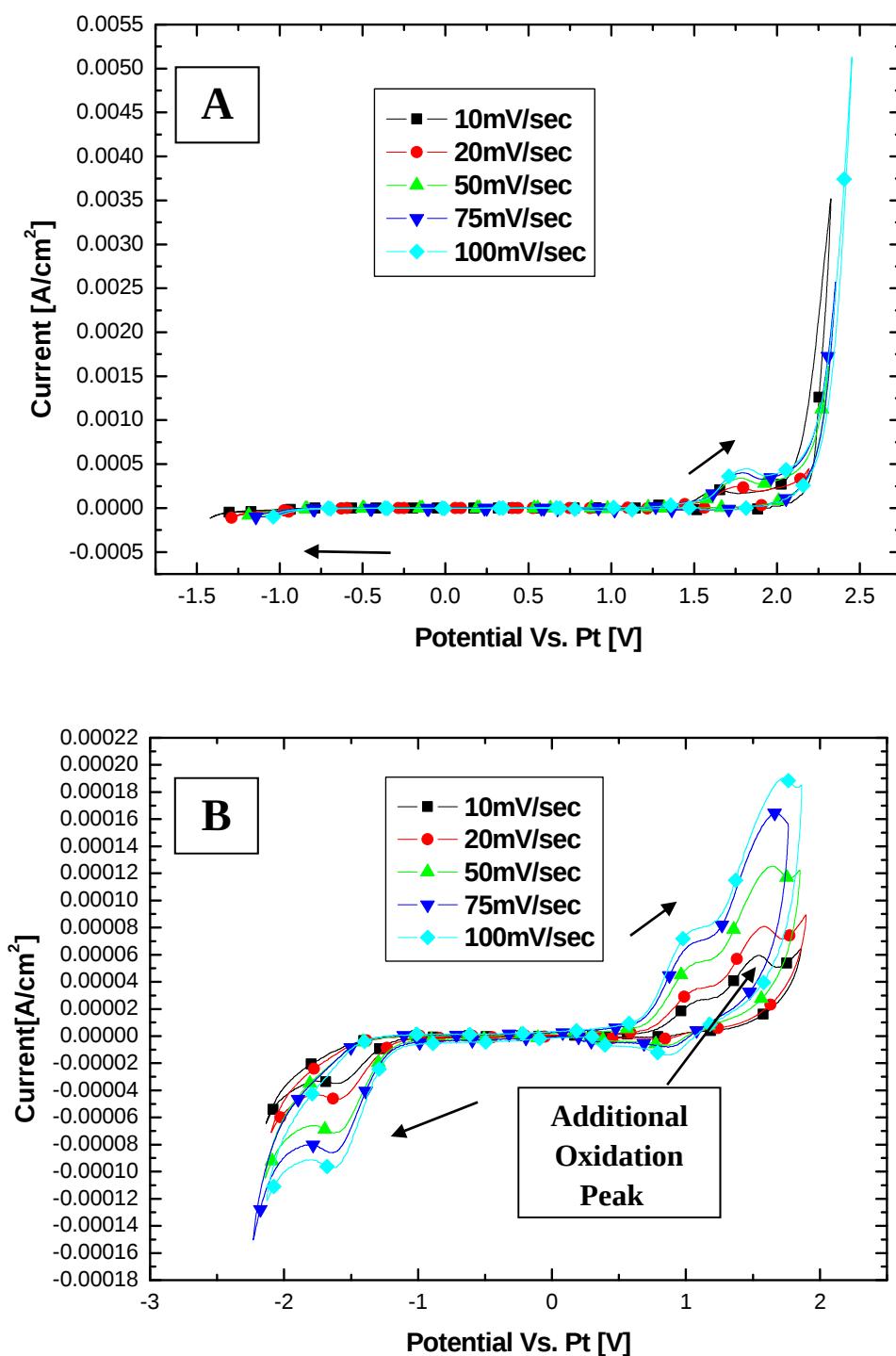


Figure 3. Electrochemical window of **a.** neat IL, and **b.** 0.1M fully dissolved quartz in IL. Both on GC working electrode.

From comparison between figures 3a and 3b it may be seen that the obtained currents from the 0.1M quartz solution are significantly smaller than with the neat IL. Moreover, additional oxidation peak is obtained, as may be seen in figure 3b, at 1.5V Vs. Pt. On the cathodic branch the peak at -1.75V Vs. Pt, shown clearly in figure 3b,

is also presented at -1.1V in figure 3a. This shift between the peaks may be partially due to the change of the reduction limit of the IL in the presence of quartz. To present day no possible explanation to the additional anodic peak is given.

Our understanding is that any further comparisons of different peaks in the voltammograms and future electrochemical measurements with IL's as electrolytes demand the use of a more stable and accurate reference electrode. The method for constructing such an electrode was chosen to be based on the ferrocene/ferrocenium (Fc/Fc^+) Red/Ox couple, a system known as a possible internal reference in ionic liquids [10-11]. Our approach was based on the addition of a gelling agent (for this specific IL, prop-2-enoic acid - Carbopol[®] 941) to the solution of $\text{EMI}(\text{HF})_{2.3}\text{F}$ and 10mM of Fc/Fc^+ , to produce a more robust and less leaky external reference electrode. The advantage of such an approach is the ability to measure exact potentials regardless of the applied working electrode, in contrast to the disadvantages seen with the internal reference experiments [11].

The electrode was constructed in a plastic capillary with a paper membrane (Whatman 2 paper) at the bottom. In this construction, 10mM of Fc/Fc^+ in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid with the addition of 5 %wt of Carbopol was stabilized as a gel and poured into the capillary. A Pt wire was immersed in the gel to provide electrical contact (figure 4).

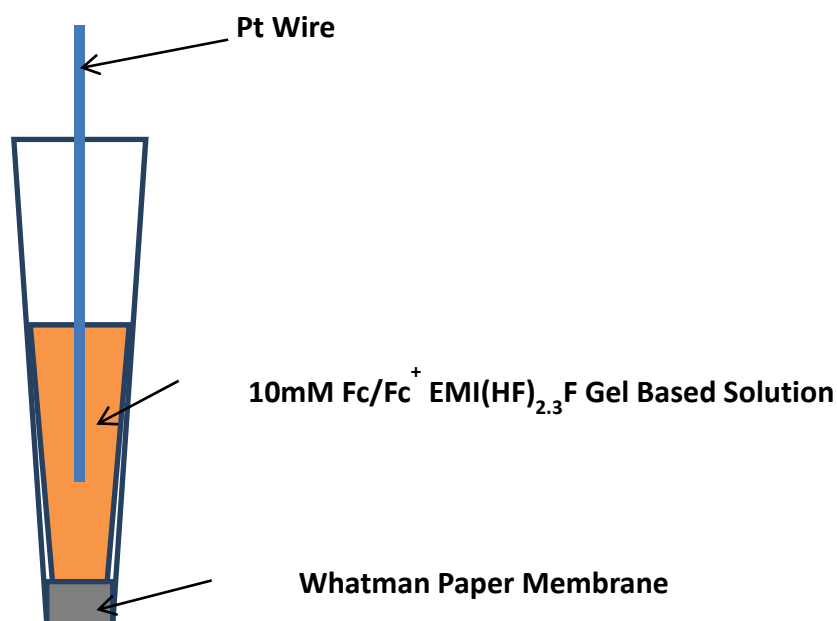


Figure 4. Schematic illustration of the produced 10mM Fc/Fc^+ in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid gel reference.

The initial experiments with the constructed electrode were performed by utilizing it as a working electrode. This was done in order to understand the stability and limitations of the construction.

Figure 5a presents the results of the cyclic voltammogram at different scan rates. The OCP of the electrode was recorded at around $-290 \pm 25 \text{ mV}$. This indicates a stable configuration of the produced electrode. The same stability in the potential was also recorded after three weeks (figure 5b). The measured OCP is around $100 \pm 25 \text{ mV}$. This shift in the OCP as a function of the "life time" of the electrode ($\sim 200 \text{ mV}$) may be attributed to the unstable Pt wire used as a reference electrode in the measurements. Additionally, it may be noticed that there is a certain degree of current decrease in the measurements of the three weeks-old electrode, as presented in figure 5b.

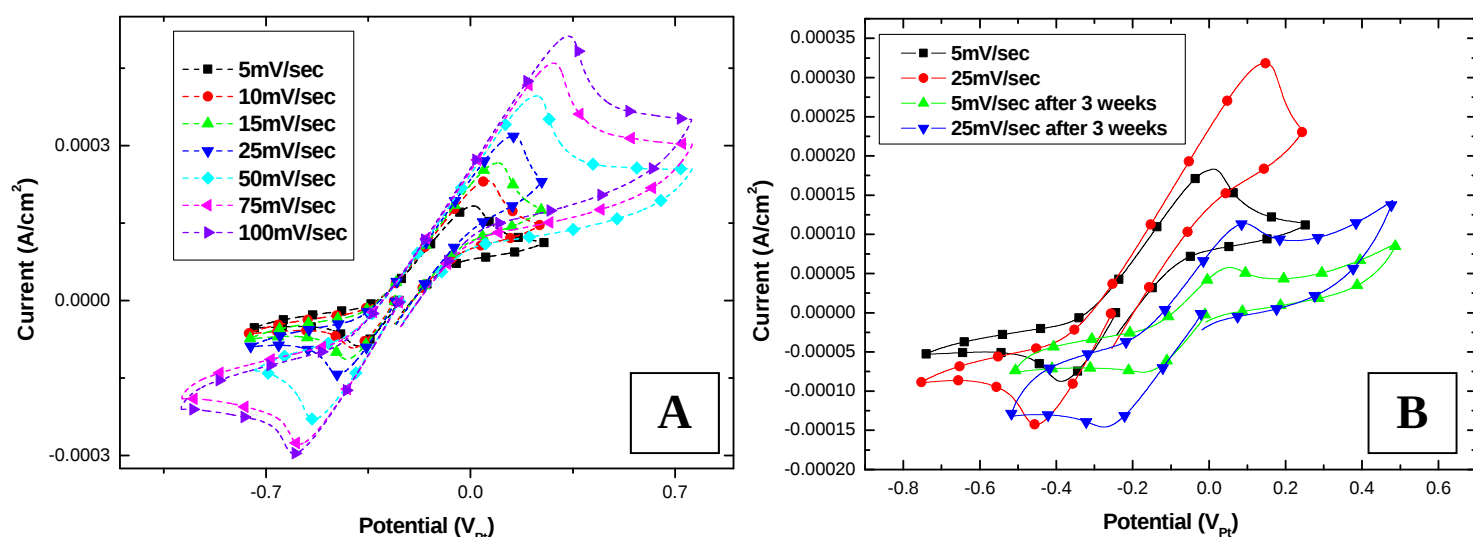


Figure 5. Cyclic voltammograms of 10mM Fc/Fc+ in EMI(HF)_{2.3}F ionic liquid with the addition of 5 %wt of Carbopol. Pt wire was immersed in the IL gel. Electrode was served as a working electrode, with Pt wire as a reference electrode. **a.** Different scan rates, **b.** comparison between fresh and three weeks old electrode.

These findings may be ascribed to some deterioration processes of ferrocene with oxygen and water [12]. This explanation is somewhat problematic and is not favored. Nevertheless, the stability of the potential for such a long period of time is reassuring. With better electrodes engineering their "life time" will increase rapidly.

Further utilization of the newly produced reference electrode was by applying it in dissolution measurements of 100nm thermally grown SiO₂ on (100) n-type highly doped silicon. The measurements of the OCP changes of SiO₂ on Si, knowing the Si potential in the same electrolyte, may provide information regarding the exact moment of complete silica dissolution. By taking the measured time and the initial

oxide thickness, an etch rate may be calculated. Moreover, by taking into account the reaction surface area and the oxide density, a prediction of the total SiO₂ concentration at the end of the dissolution process may be conducted. In figure 6 such an OCP measurements are demonstrated.

The initial potential of $-0.68V_{Fc/Fc^+}$ may be compared to the SiO₂ potentials in the acidic region of the Pourbaix diagram. The final plateau potential of $-1.29V_{Fc/Fc^+}$ indicates the end of the dissolution process of the silica layer. By knowing the exact oxide thickness an average dissolution rate may be calculated to be 1Å/sec. The nature of the measurement, i.e. potential recording without applying any current, suggests a possible chemical etching process of silicon oxide.

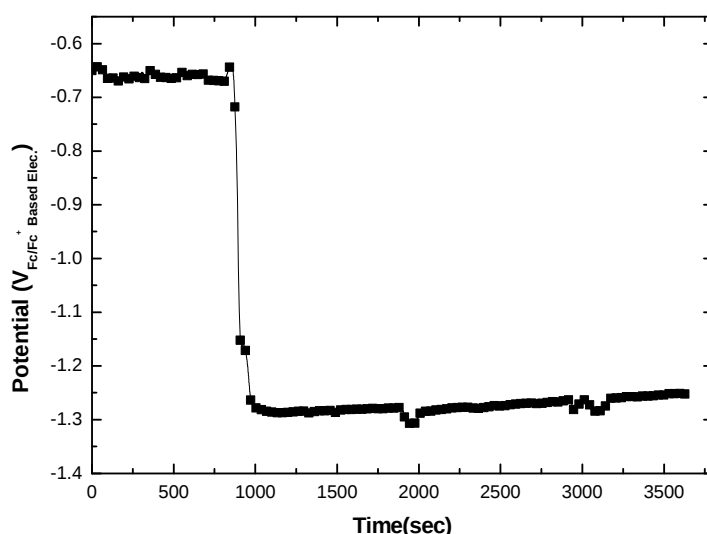


Figure 6. Open circuit potential measurement of 100nm SiO₂ on (100) n-type highly doped silicon immersed in 0.6ml of EMI(HF)_{2.3}F. 10mM Fc/Fc⁺ in EMI(HF)_{2.3}F ionic liquid gel based electrode was used as reference electrode.

4.4. Solid-state battery

Free standing polymer gel electrolyte films were obtained, using the process described in the experimental section, as shown in figure 7.

Figure 8 shows the discharge curves obtained from discharging Si - air batteries, utilizing GPE of 50-70 mol% ionic liquid, at a current density of 0.1 mA/cm², in an ambient atmosphere. It is shown that, with increasing RTIL concentration in the electrolyte (50 mol%, 60 mol%, 70 mol%), the operating potentials are 0.4, 0.5 and 0.6 V, at a discharge current of 0.1 mA/cm², respectively. These discharge potentials are significantly lower, by roughly 0.5 V than the discharge voltage of a cell



Figure 7. Photograph of a EMI·(HF)_{2.3}F RTIL / HEMA polymer gel electrolyte.

employing neat IL as electrolyte. This can be attributed to the difference in ionic conductivity of the GPE's, and hence the IR potential drop across the cell, compared with the ionic conductivity of pure ionic liquid. As reported by Tsuda et al. [13], the conducting gel polymer electrolyte, EMI·(HF)_{2.3}F RTIL and HEMA system, shows a typical conductivity of the order of 10^{-2} S/cm at room temperature, which is one order of magnitude lower than the neat RTIL conductivity. It is important to mention that due to the GPE preparation procedure and cell assembly, the contact between the Si anode and the GPE is inhomogeneous over the Si surface. Figure 9a shows HRSEM image of a silicon wafer, in low magnification, after discharging in a current density of 0.1 mA/cm^2 , utilizing 70 mol% IL in the GPE. One can see that the reaction area is non-uniform, but rather is confined only to selected (framed) areas, where contact between the Si anode and the GPE, presumably, was established. Figure 9b shows a higher magnification micrograph, taken from the same silicon anode shown in Figure 9a. As can be seen, the surface morphology of the silicon electrode is porous, with pores in the 100 nm size. This morphology is in agreement with the surface morphology obtained with pure IL [4]. As shown in figure 9a, the actual area available for electrochemical reaction and ion transport is lower than the nominal cell area of 0.5 cm^2 , determined by cell engineering. As a result of smaller contact area between the gel and the electrodes, the real current density is higher than 0.1 mA/cm^2 . Accordingly, the discharge voltages, recorded during cell discharge utilizing gel electrolyte, are an outcome of an actually higher discharge polarization and IR potential drop than expected. Consequently, we expect higher discharge voltage for GPE cell with enhanced contacts between the GPE and the silicon anode as well as with the air electrode.

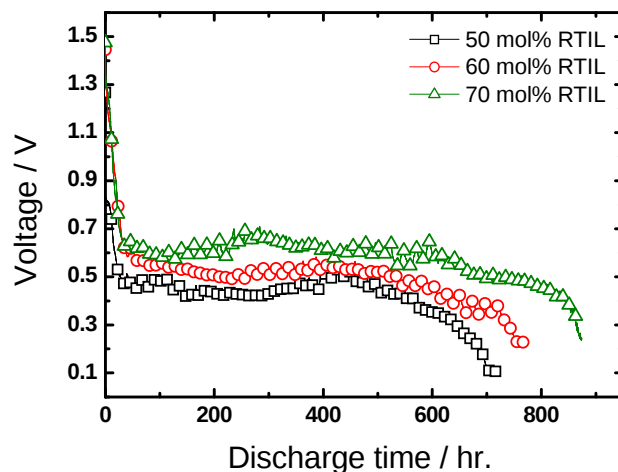


Figure 8. Galvanostatic discharge curves of Si - air cell, comprised of silicon wafer anode, air cathode and EMI·(HF)_{2.3}F IL - HEMA (70 mol%) gel polymer electrolyte.

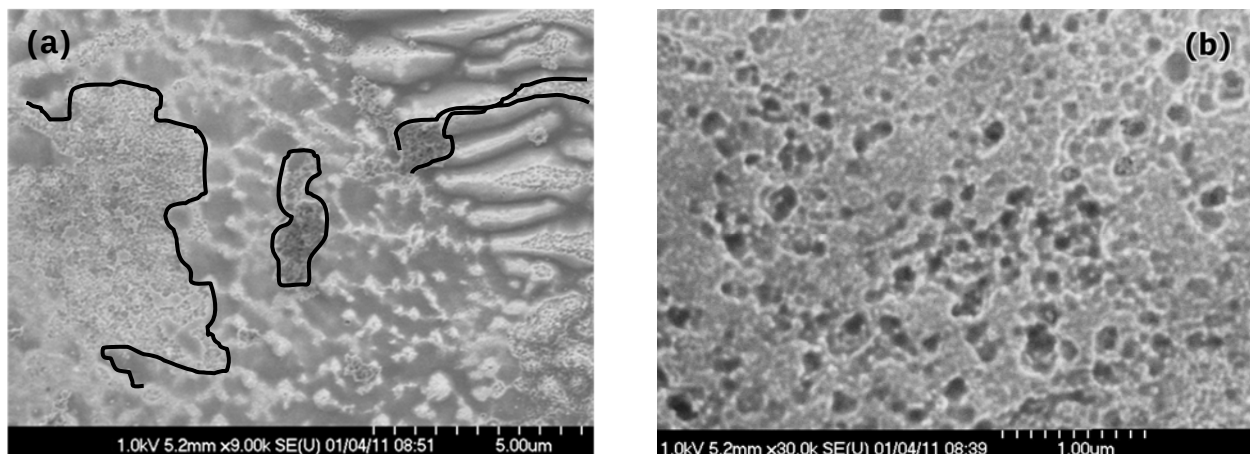


Figure 9. Top view HRSEM images of the silicon wafer anode after discharge curve (Δ symbol) in figure 8.

5. Conclusions and Future Work

- Water play a major role in any process of chemical dissolution of crystal SiO₂ in EMI(HF)_{2.3}F ionic liquid. As shown, the change in water amount in the IL, as measured by the KF, produced unstable dissolution results from full dissolution in as received IL to partially insolubility in more "aged" liquid. Nevertheless the full dissolution achieved with first long "aged" batch of the IL is puzzling. No real explanation to this phenomenon may be given. Any further research will certainly require a way to de humidify the IL.

- The NMR measurements provide a useful tool for chemical understanding of the IL. With the NMR tool, specific stoichiometry may be measured using neat IL. To properly achieve such progress, a temperature dependence of the anion ^1H and ^{19}F peaks are need to be understood. The ability to recognize the specific Si and F based species in the solution may provide addition information on the chemical and the electrochemical behavior of the IL.
- The use of Pt as reference electrode is problematic. The possible potential drift of the electrode generates a difficulty in comparison between different electrochemical experiments.
- The addition anodic peak is needed to be explained. Understanding the electrochemical process relevant to this peak may provide an explanation for mechanism for the chemical dissolution of SiO_2 in the IL.
- The temperature dependence of the anion NMR peak both ^1H and ^{19}F need to be evaluated. Those measurements must be done in temperatures as low as 200K and that to use the already established data on the anion NMR behavior in other $(\text{HF})_n\text{F}^-$ based systems. Any further work with this IL on NMR has to be of neat liquid.
- The NMR provides an ability to compare the stoichiometry of the anion in the IL to previous works. Other stoichiometry different then $n=2.3$ may be measured in such a way.
- The products of the IL reduction and oxidation on different working surfaces may be studied using NMR. Although it is clear that the reduction potential of the IL on Pt is smaller than on GC, no real chemical understanding of process is yet to be obtained. The NMR may certainly answer some of those questions.
- The change of water amount in the IL is problematic. Some methods for de-humidification need to be applied. Any future work on SiO_2 dissolution must be based on constant amount of water in the IL.
- The electrochemistry has to be based on more robust reference electrode. Some use of ferrocence Red/Ox couple as reference will be applied in any future work.
- Free standing, mechanically stable, composite polymer gel electrolyte, based on $\text{EMI}(\text{HF})_{2.3}\text{F}$ IL and HEMA polymer, were produced. Different compositions, from 40 mol% to 70 mol% of RTIL, were investigated and

characterized. The results show a relatively long discharge times, up to 850 hours. However, the operating voltage is lower with respect to a cell discharge utilizing the ionic liquid alone, due to higher ionic conductivity of the pure IL. Nonetheless, the contact between the silicon anode and the air cathode was not intimate; thereby the surface area for reacted silicon (oxidation) is lower than expected.

6. References

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On the Rechargeability of Silicon - Air Battery

Final Report

2010-2011

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On the Rechargeability of Silicon - Air Battery

2010-2011 Report

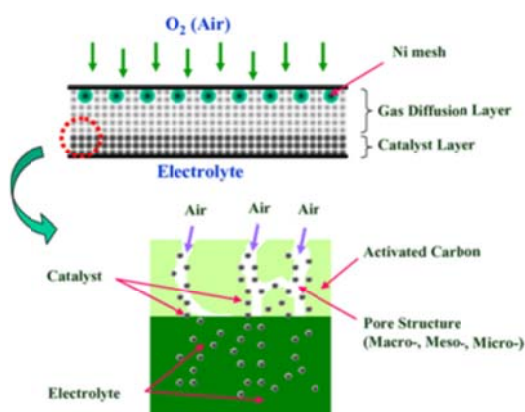
Prof. Yair Ein-Eli

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1. Introduction and Scientific Background

Global concern about energy consumption currently relies on fossil fuels and suffers economic and ecological problems. This call for increased use of renewable energy sources and replacement of combustion engine vehicles, and in turn requires suitable systems to store the power and to generate it. Electrochemical systems such as batteries are ideal for this purpose. Metal-air batteries (Figure 1) are highly attractive power systems, due to their high energy densities. This feature results from the fact that a metal-air battery does not contain stored cathodic active material, as do other conventional batteries. The only cathodic component is a thin membrane, acting as the cathode electrode, on which the reduction of oxygen occurs. In recent years, a leap in metal-air battery technology has been achieved with the introduction of the non-aqueous lithium-air cell.^[1-3] Although characterized by a theoretically high specific energy value ($11,246 \text{ Whkg}^{-1}$) from this system, lithium-air still suffers from nontrivial challenges, such as low operating current densities ($<100 \mu\text{Acm}^{-2}$), air electrode blocking by reaction oxides products (Li_2O and Li_2O_2), and safety concerns regarding the use of a Li metal as a fuel.



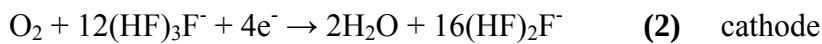
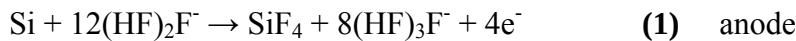
ration.

The unique properties of room temperature ionic liquids (RTIL) make them perfectly suitable to serve as electrolytes in many electrochemical systems, especially in batteries. Due to their non-flammability and non-volatility they are considered as replacements to the flammable and volatile organic solutions. Ionic liquids has become one of the most active areas in green chemistry, since they are considered as green solvents, which are superior to the conventional molecular solvents in the

context of greenness. The reasons are, again, their non-detectable vapour pressure and that they do not emit volatile organic compounds to pollute air.^[4,5]

In our recent work we have shown that silicon can be employed as the anodic active material in a metal-air battery.^[6,7] From a thermodynamic point of view, the silicon-oxygen couple is very promising and attractive, due to the release of 4 moles of electrons per reaction of 28 grams of the active anode material. The charge capacity is 4 times greater than conventional Zn-air batteries and is very close to that of Li-air (3.816 Ahkg⁻¹ for Si-air vs. 3.86 Ahkg⁻¹ for Li-air). Moreover, the use of silicon as the anode active material overcomes the availability problem of lithium metal, which is found in only a few locations world-wide. Safety issues are avoided as well by using silicon, since both silicon and its products with oxygen are safe and environmentally friendly.

A silicon-air battery comprises a heavily doped silicon single crystal wafer anode, together with a commercial air cathode and hydrophilic room temperature ionic liquid, 1-ethyl-3-methylimidazolium fluorohydrogenate (EMI·(HF)_{2.3}F) as the electrolyte of choice (Figure 2). This cell exhibits high discharge capacities, up to 53 mAhcm⁻² at a current density of 0.3 mAcm⁻² and the cell voltage lies within the range of 0.8 to 1.1 V, for current loads of 0.3 to 0.01 mAcm⁻², respectively (Figure 3). The discharge of the cell results in Si oxidation at the silicon wafer anode electrode and in reduction of atmospheric oxygen at the air membrane (cathode electrode). RTIL anions participate in both electrode reactions, as illustrated below:



Reaction (1) is the oxidation of silicon at the anode, while Reaction (2) is oxygen reduction at the air electrode. Reaction (3) involves the formation of a SiO₂ product, which takes place at the electrolyte – air electrode interface. The overall cell reaction, as can be deduced from Reactions (1)-(3), is



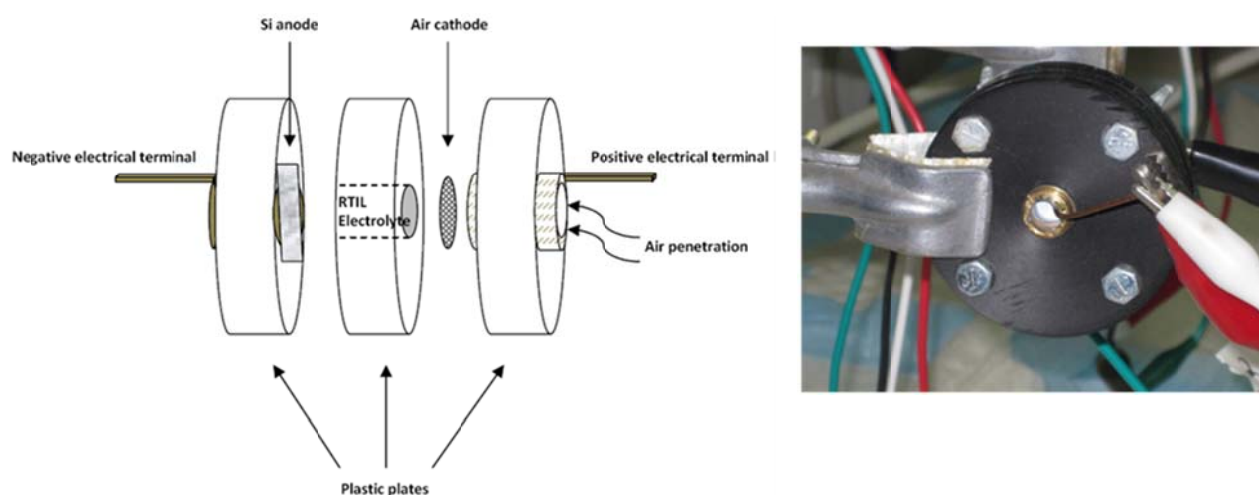


Figure 2. Schematic diagram of the silicon - air cell and its components, and a photo of the air electrode side of the silicon-air cell.

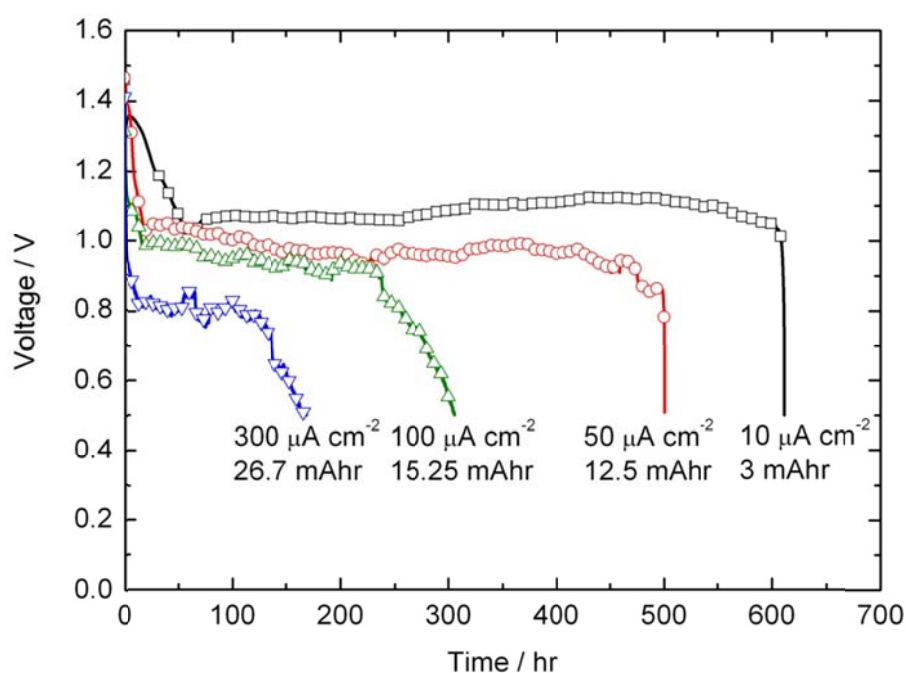


Figure 3. Discharge plots of silicon - air cells using $\text{EMI} \cdot (\text{HF})_{2.3}\text{F}$ RTIL electrolyte at different constant current densities.

2. Scientific and Practical Goals for 2010/2011

In principle, the silicon - air (oxygen) couple should provide the combination of both high specific energy and energy density yet investigated for advanced battery systems (Table 1). However, the problem to this time is identifying the routes for achieving high electrochemical reversibility at each of the electrode, i.e. turn the Si - air battery to a secondary one. The electrochemical reversibility should be accompanied with

long materials life-time and lowering materials cost. The first step toward achieving these goals was addressed in our recent work via the studies of Si salts solubility in the RTIL. The second measure was studying the electrochemical cathodic behavior of silicon in such an Si-salt containing electrolyte. At the same time, full cell discharging - charging experiment were evaluated, and the electrodes surface morphology and chemistry were examined.

Fuel	Fuel cell reaction	ΔH_R° (kJ/mol)	ΔG_R° (kJ/mol)	Specific energy (W·hr/kg)	Energy density (W·hr/l)
Al	$2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$	-1582.4	-1675.6	8146	21994
Be	$\text{Be} + 1/2\text{O}_2 \rightarrow \text{BeO}$	-578.1	-607.3	17823	33151
H ₂	$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$	-237.2	-258.5	32686	2693 (@ 1000atm)
Li	$2\text{Li} + 1/2\text{O}_2 \rightarrow \text{Li}_2\text{O}$	-561.9	-598.5	11246	5960
Mg	$\text{Mg} + 1/2\text{O}_2 \rightarrow \text{MgO}$	-569.4	-601.7	3942	6859
Zn	$\text{Zn} + 1/2\text{O}_2 \rightarrow \text{ZnO}$	-320.8	-350.7	1363	9677
Si	$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$	-856.5	-910.9	8470	21090

3. Experimental Section

3.1. Materials

The silicon-air battery configuration used in this work employed a Si wafer anode and a commercial air cathode (Electric Fuel Ltd). Silicon single-crystal wafer anode electrodes were cut from As-doped n-type wafers, <100>, 0.001-0.005 $\Omega\cdot\text{cm}$ (University Wafer USA). 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 gr 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 $\text{EMI} \cdot (\text{HF})_{2.3}\text{F}$ served as the electrolyte. The IL was provided by R. Hagiwara from Kyoto University Japan, and was synthesized according to methods described elsewhere [8].

3.2. Three-electrodes cell preparation

Three-electrode cell configuration was used, with a single-crystal silicon wafer or an 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 cm^2 (Figure 4). Previous to any experiment the silicon sample was immersed in HF solution ($1\text{HF}:5\text{H}_2\text{O}$) 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.

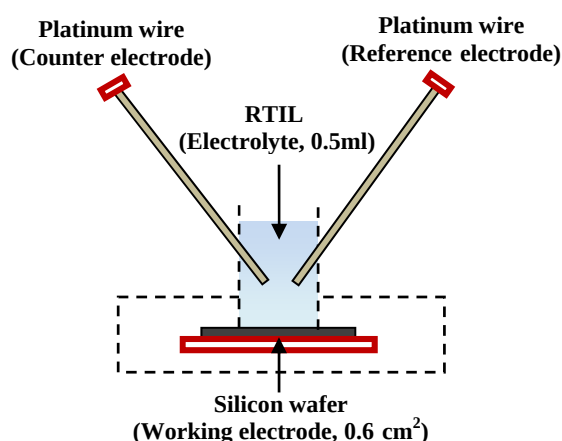


Figure 4. Three-electrode cell configuration, for half cell electrochemical investigation.

3.3. Battery cell preparation

For silicon - air systems studies, a silicon single-crystal, air electrode and ionic liquid were used. The cell was comprised of three plastic plates. Silicon wafers were cut to 1 cm x 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 3.2. Cells were held at OCP (open circuit potential) for duration of 4 hours 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.

3.4. Electrochemical measurements and characterization

Silicon cyclic voltammetry, 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, Zeiss Ultra Plus). 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.

4. Results

As mentioned earlier, the first step towards turning the Si – air battery to a secondary one is to incorporate silicon salt into the electrolyte, and to examine its electrochemical reduction performance / ability. The most simple and intuitive choice

is SiO_2 , as we already know it is slightly soluble in the RTIL, and it is the reaction product of the cell, therefore it is the specie which should be reduced back to silicon.

Dissolution of SiO_2 was performed by adding Quartz (Fluka, purum p.a. <230 mesh) to the IL producing 0.1M solution.

After achieving a SiO_2 containing electrolyte, the electrochemical characteristics of the electrolyte was investigated. Figure 5 shows the cathodic part of a cyclic voltammogram (25 & 50 mV/sec), performed with 0.1M SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ electrolyte, where Ni served as working electrode and Pt as counter and reference electrode. As can be seen from this figure there are some evidence of reduction process. The measured reaction is around -1.75V Vs. Pt in both rates. The highly noise cyclic indicates, probably, on high rates of IL decomposition. To prevent such those decomposition process other more suitable surfaces may be use (GC and such). No evidence of Si was found on the surface of Ni after 1 hour of potentiostatic measurement at -1.8V Vs. Pt.

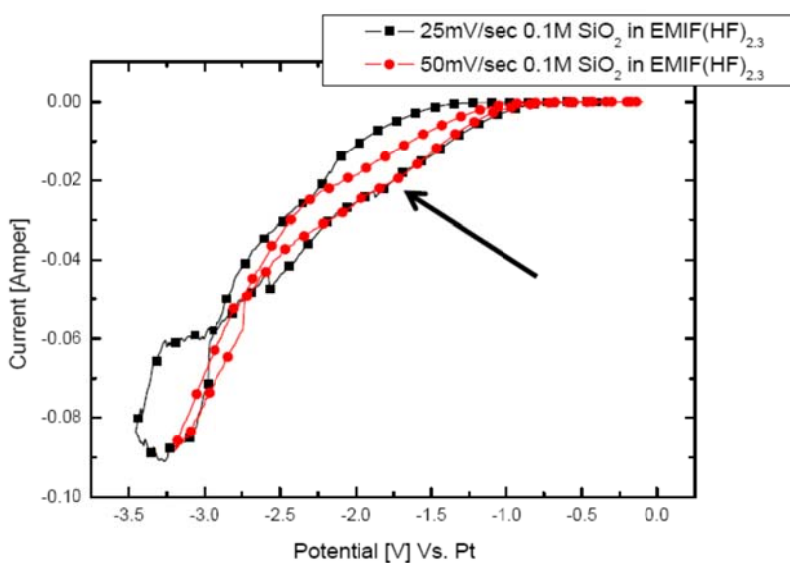


Figure 5. Cyclic voltammetry on Ni working electrode, 0.1M SiO_2 in $\text{EMI}(\text{HF})_{2.3}\text{F}$ ionic liquid.

Charging - Discharging

In order to obtain some preliminary understanding about the ability to charge - discharge the Si -air cell, charging experiments were conducted, after discharging the cell in different current densities, as can be seen in Figure 6. It is clear from Figure 6 that both rest period and charging period after a discharge procedure result in increased total discharge capacity, compared to a continuous, singular, discharge process. With a discharge period of 72 hours (21.6 mAh/cm² charge capacity) the discharge capacity is increased by 25%, while with an equivalent rest period the discharge capacity is increased by 43%. Therefore, we can say that during the rest period and the charge period, a certain amount of the discharge product layer, covering the air electrode, is being removed from it. The removal of this layer contributes to extended oxygen reduction ability, and, as a result, longer discharges time (capacity). However, the question to be asked is why with a rest period the discharge capacity extension is higher than with the charging step? The reason for this is probably related to the stability of the ionic liquid. What can be assumed is that during the charging process the electrochemical properties of the ionic liquid become poorer than a non-charged ionic liquid. However, charging with lower current densities or to shorter time periods might solve this issue of instability and lead to increased discharge capacity.

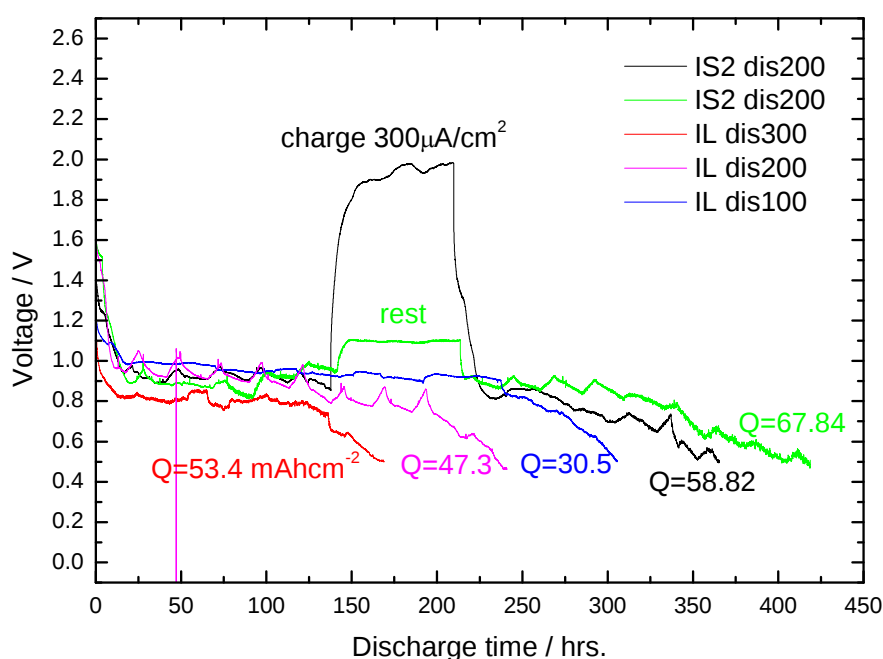


Figure 6. Discharging - charging profiles in various current densities and electrolytes:
 Black - 0.1M SiO₂ in EMI·(HF)_{2.3}F, discharge at 0.2 mA/cm², charging at 0.2 mA/cm².
 Green - 0.1M SiO₂ in EMI·(HF)_{2.3}F, discharge at 0.2 mA/cm².
 Red - EMI·(HF)_{2.3}F, discharge at 0.3 mA/cm².
 Magenta - EMI·(HF)_{2.3}F, discharge at 0.2 mA/cm².
 Blue - EMI·(HF)_{2.3}F, discharge at 0.1 mA/cm².

Figure 7 shows a comparison between short discharge - charge or discharge - rest cycles, with different cycle periods. Again, the same phenomenon is observed as in Figure 6, where rest period and charge period provide the same results. The capacity in both cases, discharging for 16 hours and afterwards charging for 8 hours or rest for 8 hours, is the same. However, when applying charging current for a short time periods of 8 hours, the resulting discharge voltage is higher by ~ 100 mV, than the one with rest periods. This happens not at the beginning of discharge but rather at later stages of the cycling. Therefore, more delicate charging procedure, more delicate than in Figure 7 should provide us with better discharge capacity results.

The Si - air cell was cycled at equivalent charging - discharging capacities as well, for periods of 12 hours. The discharge and charge profiles are shown in Figure 7. As can be seen, the discharge capacity is increased to 52.8 mAh/cm^2 , a 16.3% increase compared to the 16 - 8 cycling. Moreover, the discharge - charge reversibility is much better in this case. Discharge voltage remains stable for a long period of ~ 400 hours, and the discharge profile is very much similar along most of the cycles. At the last two cycles, both charge and discharge overpotentials are dramatically increase. Due to this rapid change, the ionic liquid is somehow destroyed, and therefore no longer ready for further electrochemical operation.

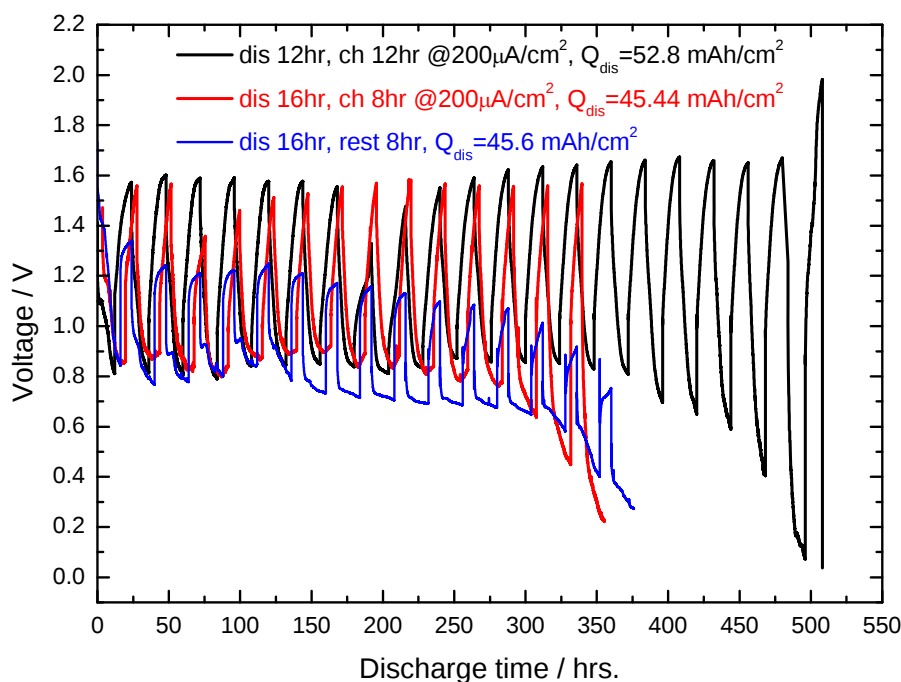


Figure 7. Discharging - charging cycling with $\text{EMI} \cdot (\text{HF})_{2.3}\text{F}$ ionic liquid:
 Black - 12 hours discharge followed by 12 hours charge, current density 0.2 mA/cm^2 .
 Red - 16 hours discharge followed by 8 hours charge, current density 0.2 mA/cm^2 .
 Blue - 16 hours discharge followed by 8 hours rest, current density 0.2 mA/cm^2 .

It is assumed that during charge SiO_2 is reduced at the air electrode, and silicon is plated onto the "metallic" silicon anode surface. This reaction is the one in question, since electrochemical reduction of SiO_2 is yet not clear, definitely not in ionic liquid medium. However, SEM examination of the silicon anode during several points along the cycling process should give us better understanding on how the surface of the anode is modified during the cycling. SEM micrographs (Figure 8) show that after discharge - charge cycle, the anode surface is covered with a deposition layer. The nature of this layer is yet to be investigated, however, the massive presence of Si in this layer is confirmed by EDX examination. Moreover, as can be seen at magnified part in Figure 8, underneath this deposition layer, a porous layer exist, which resembles the porous morphology of the silicon anode after discharge process.^[6-7] During the charging process a deposition layer covers the porous structure of the silicon anode, however due to incomplete covering or mechanical peeling, some of the porous surface is still uncovered, and the difference between those two surfaces can be easily distinguished. This distinction can be observed in Figure 9 as well, where a charge area lies next to an un-charged area. During discharging and charging the level of electrolyte in the cell decreased, due to absorption at the air electrode and due to expansion of the air electrode. Therefore, a portion of the discharge area is not charged at the charging period. This boundary between charge and un-charged areas can be identified with the SEM, and a part of it is shown in Figure 9. Again, the porous morphology, the result of discharge, is observed, together with a charged area, covered with a deposition layer.

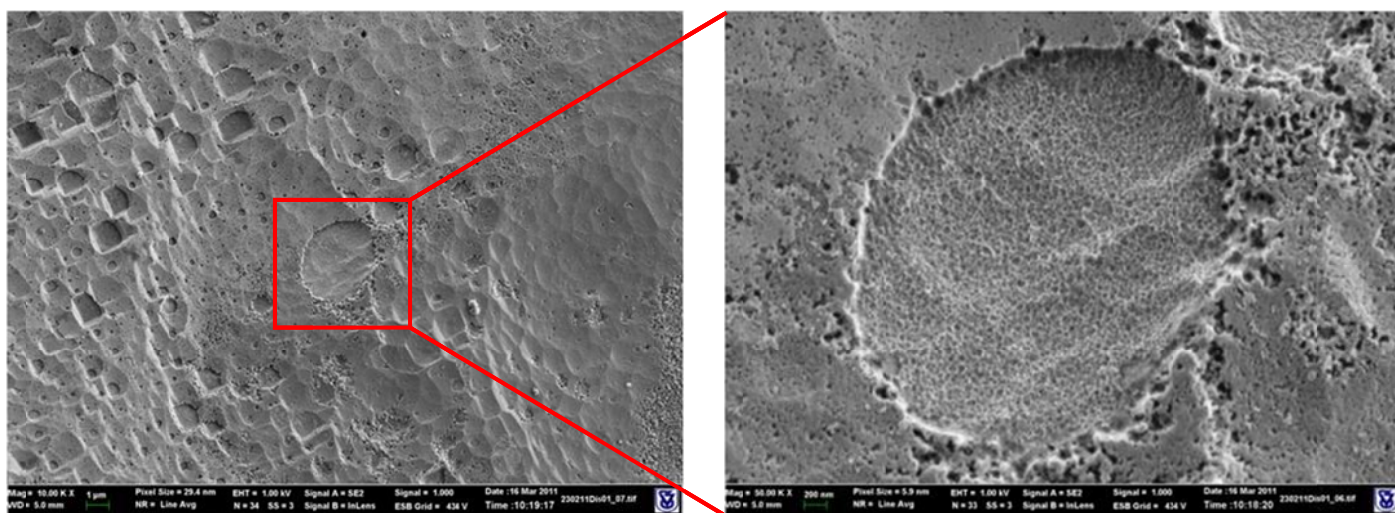


Figure 8. HRSEM micrographs of silicon wafer anode obtained after discharge-charge cycling with current density of 0.2 mA/cm^2 .

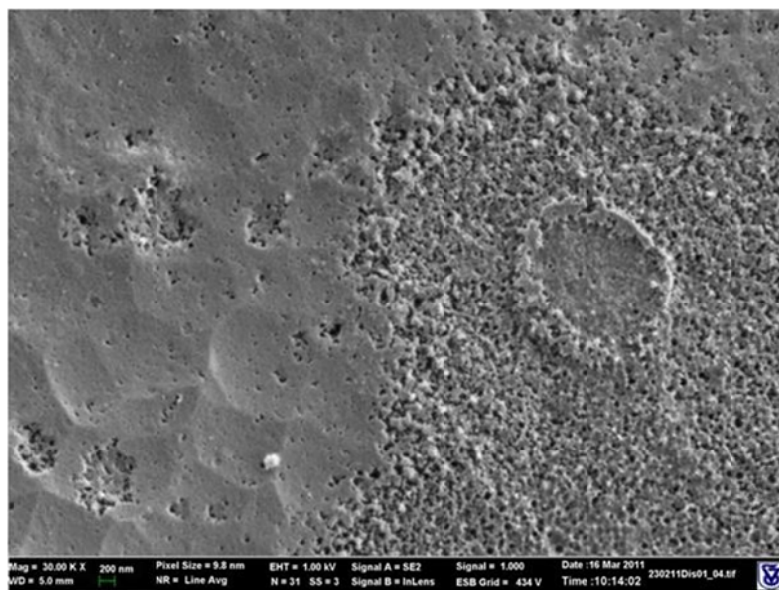


Figure 9. HRSEM micrographs of silicon wafer anode obtained after discharge-charge cycling with current density of 0.2 mA/cm^2 .

5. Conclusions and future work

The first year results justify the continuation of the program for at least another year, as it might be possible to extend the life time of a silicon-air battery by charge-discharge cycles. It should be stressed that the identification of the reduction and oxidation products at both the silicon anode and the air cathode should be carefully analyzed, as presence of water as by-product may alter the results and their understanding. Thus, it is extremely important to understand the electrochemical and chemistry behavior of silicon di-oxide in this particular IL. In the second year we plan to go to “basic” and this would mean an in-depth understanding of the processes the SiO_2 is experiencing in the IL.

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