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Publication Date
2012-12-31

The mechanism of HF formation in LiPF6-based organic carbonate electrolytes

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ABSTRACT

Spectroscopic ellipsometry was used to study the time-dependent formation of HF upon the thermal degradation of $LiPF_6$ at 50°C in a lithium ion battery electrolyte containing ethylene carbonate and diethyl carbonate. The generated HF was monitored by following the etching rate of a 300 nm thick SiO_2 layer, grown on both sides of a silicon wafer substrate, as a function of the immersion time in the electrolyte at 50°C. It was found that the formation of HF starts after 70 hours of exposure time and occurs following several different phases. The amount of generated HF was calculated using an empirical formula correlating the etching rate to the temperature. Combining the results of the HF formation with literature data, a simplified mechanism for the formation of the HF involving $LiPF_6$ degradation, and a simplified catalytical reaction pathway of the formed HF and silicon dioxide is proposed to describe the kinetics of HF formation.

KEYWORDS

Lithium ion batteries, hydrofluoric acid, spectroscopic ellipsometry, $LiPF_6$ degradation

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Introduction

Lithium hexafluorophosphate is one of the most common used conductive salts for organic carbonate based electrolytes in lithium ion batteries and is considered to be a baseline chemistry for electromobility in the U.S. BATT program in the USA.[1-5] However, despite the relatively high thermal stability in dry inert atmosphere up to 107°C where only solid lithium fluoride and PF_5 are formed[6], this salt suffers from degradation upon exposure to traces of water, moisture or alcohols[7]. In literature it is proposed that the reaction starts with the decomposition of $LiPF_6$[7-10]:

$$LiPF_6 \rightarrow LiF + PF_5 \quad (1)$$

to form phosphorous pentafluoride which can react with water to form HF and POF_3.

$$PF_5 + H_2O \rightarrow POF_3 + 2\,HF \quad (2)$$

Reaction (1) is almost negligible at room temperature; however in battery electrolytes, interaction of PF_5 with solvent molecules ethylene carbonate (EC) and diethyl carbonate (DEC) can shift the equilibrium of the reaction to the right and therefore increase the formation of HF.[8, 11] Furthermore, quantum chemical calculations demonstrate the influence of the highly positive lithium ion on the solvent coordination sphere of the complex anion.[7] As a consequence, a lowered stability of $LiPF_6$ in organic carbonate electrolyte is observed, when compared with other alkali metals hexafluorophosphates. The decomposition is not only catalyzed by the elevated temperature nor by the presence of moisture , it is also activated by the release of protons upon formation of LiF either within the Solid electrolyte interphase (SEI) at the negative electrode or within the passivation layer at the positive electrode.[8]

$$Li^+ + HF \leftrightarrow LiF(s) + H^+ \quad (3)$$

The precipitation of LiF(s) and therefore the removal of the lithium ion out of the solvated system has not a direct influence on the formation of HF. However, the protons released can react further with $LiPF_6$ molecules to produce additional HF.[8]

$$H^+ + PF_6^- \leftrightarrow H\text{-}F\text{-}PF_5 \quad (4)$$

$$H\text{-}F\text{-}PF_5 \rightarrow HF + PF_5 \quad (5)$$

HF formed by this different possible reactions, can significantly influence the calendar and cycle life time of the cell.[10, 12]

A special case of this degradation problem occurs when a $LiPF_6$ based electrolyte is combined with an electrochemical system containing SiO_2 or SiOH. This occurs e.g. when high capacity silicon or silicon graphite composite electrodes with possible native SiO_2 surface layer or surface silanol groups, are used with hexafluorophosphate based electrolytes[13, 14] or when soggy sand based electrochemical cells are combined with $LiPF_6$ containing electrolytes[15].

Especially and more importantly, when applying $LiPF_6$ based electrolytes in high-energy batteries based on silicon anodes, the etching can have a significant influence because the favorable interactions between the cellulose-based binder[14] and the active material surface groups (Si-OH) cannot take place anymore. Here, the formed HF can react with the oxygen-containing silicon electrode material [16, 17] to etch its surface or the complete material and led to a rapid break-down of the cell.[10, 12]

In this manuscript, we made an attempt to clarify the time dependency of the HF formation upon mild temperature exposure and try to explain the catalytic pathway of $LiPF_6$ degradation in the presence of Si-OX [X=H, O or OH] groups.

Experimental

Silicon wafers with a diameter of 4” and covered by a polished thermal oxide layer were obtained commercially (Silicon Quest International, Santa Clara, CA, USA). The wafer thickness was 500±25 µm while the thermal oxide grown on both sides, was 3,000 Å (± 5%). The wafer was diced into square samples (15 x 15 mm) using a high speed wafer cutting device. The samples were thoroughly cleaned with isopropyl alcohol (IPA), deionized water using ultrasonic procedures. Before and after the exposure to the electrolyte (EC:DEC 1:2, 1M $LiPF_6$, Ferro®, USA, water content 20 ppm) the surface roughness was investigated using a AFM instrumentation described elsewhere.[18] The Si/SiO_2 samples and controlled volume of electrolyte were placed together in gas-tight polypropylene (PP) vials in a glovebox, sealed and then transferred in a climatic chamber set at 50°C. After defined exposure time of the sample with the electrolyte, the vials were transferred into the glovebox and opened. The samples were taken out of electrolyte, cleaned thoroughly with IPA, deionized water using ultrasonic procedures and investigated using a Spectroscopic ellipsometry setup described elsewhere.[19] Each data point in Figure 2 corresponds to an independent single sample/cell that has been in contact with electrolyte. Ellipsometry measurements were implemented at least twice on each sample on a different surface area on both sides. All sample/electrolyte cells were prepared the same day and introduced simultaneously in the climatic chamber, to guaranty similar temperature aging conditions for all samples. The SiO_2 layer thickness on each sample was investigated prior to and after the electrolyte exposure using a multi-wavelength ellipsometer (Woolam®, Lincoln, NE, USA: M-44). A WVASE32® software using a Marquardt-Levenberg algorithm was used to interpret the ellipsometry results. The thickness of SiO_2 layers was determined using a simple two layer Si/SiO_2 model and optical constants for SiO_2 and Si found in the literature.

Results and Discussion

Figure 1 is a representative image of a SiO_2/Si wafer after contacting the electrolyte where almost a third of the SiO_2 layer has been etched by HF generated upon the degradation of the $LiPF_6$. The topography indicates that the etching process occurs homogenously over the whole surface area and therefore guaranties the accuracy of the ellipsometry results. This technique indeed requires a smooth and clean surface topography in order to deliver reliable results in the nanometer range. A rough surface would affect strongly the determination of the SiO_2 layer thickness. The decrease of the SiO_2 layer thickness with the exposure time to battery electrolyte at 50°C is plotted in Figure 2.

The HF concentration in the electrolyte has been calculated using following empirical formula [20] (with γ_d = etching rate [Å/min], [HF] = concentration of HF [mol/L] and T = absolute temperature [K]).

$$\gamma_d = 4.5 * 10^9 * [HF] e^{-\frac{4980}{T}} \quad (6)$$

These values plotted as right y-axis in Figure 2 have to be considered with care. The environment in which the empirical study has been carried out (aqueous systems, relatively high concentrations of HF ranging from 0.9 up to 4.0 mol/L) is not comparable with the one used in this experiment (organic carbonates, sub mmol/L content of HF). However, this calculation can provide an indication of the HF concentration, that we estimate below 0.5 mmol/L upon thermal aging of $LiPF_6$ at 50°C.

It is observed that the HF formation in the electrolyte does not start immediately but after slightly more than 70 hours. The plot can be divided into three different regions corresponding to different phases that we interpret as follows. An “activation phase”, (Phase 1) in which the activation energy is accumulated to break the first Si-O-Si bond, i.e. the HF concentration is initially too low to etch the thermal oxide layer. Here, the $LiPF_6$

decomposition starts, the salt is further dissociated and the PF_5 is reacting with the solvent and water traces to initialize polymerization of the organic carbonates[8] and further decompose to HF. Later, a second phase, namely the “formation phase” begins, in which the first Si-O-Si bond is broken, is observable. HF is formed and the etching of silicon dioxide starts leading to the release of more water, which further degrades $LiPF_6$. The PF_5 is also reacting with the water forming extra decomposition products. LiF may precipitate and therefore promotes the reactivity of the protons in the electrolyte systems as mentioned in literature.[8] Therefore more HF is formed in this phase. After 160 hours, the curve in Figure 2 displays a discontinuity, due to a power failure of the climatic chamber in the lab. As a result, the temperature of the chamber containing the remaining samples decreased almost to room temperature for several hours. The incidence on the experimental results emphasizes the strong dependence between the etching rate and the temperature of the system. However, as a matter of fact, it is not possible to determine the exact boundary between the Phase 2 and 3. At the end of the formation phase, the HF content and therefore the etching rate of the silicon dioxide becomes constant, leading to the third phase, the “steady state phase”, in which the formation and consumption of HF, i.e. the etching of SiO_2, are in equilibrium. Therein, the consumption of protons from HF to form water is equal to the amount of HF formed by the decomposition of $LiPF_6$ with water.

In the experiment, phase 3 is the last one visible, after the SiO_2 layer becomes too thin to obtain reliable results using spectroscopic ellipsometry. However, we can assume a fourth phase in which a “breakdown phase” must exist, the reaction has to stop somehow. Either the electrolyte is running out of fluoride ions, the induced polymerization of the electrolyte hinders the transport of the reactants or the protons or the Si-OX groups have reacted completely. The induced polymerization was also observed during these investigations; a color change of the electrolyte and some small colorless needles in the solvent in increasing amount with the exposure time of the sample to the electrolyte were visible in all sample cells.

Combining the profile of the SiO_2 loss curve and literature data for some degradation reactions,[8, 21] it is possible to propose a catalytic cycle pathway for the reaction of $LiPF_6$ to HF and the ongoing etching reaction in the system $LiPF_6/H_2O/HF/SiF_4$, displayed in Figure 3 . In this proposed mechanism, the blue lines represent the major pathways for the reaction of the formed HF with the silicon dioxide. $LiPF_6$ decomposes to form LiF and PF_5, which further reacts with water traces to yield OPF_3 and HF (Phase 1). The HF forms the intermediate HF_2^- with free fluoride and starts to etch the SiO_2 layer to form tetrafluorosilane.[21] In addition water is formed, and can further react (Phase 2). The side reaction associated to OPF_3 consumes another water molecule, forming $OPF_2(OH)$. This compound can now react either with water molecules to form $OPF(OH)_2$ or with solvent molecules to form an ester bond with the solvent or parts of it (methyl, ethyl groups….). Later, all the reactions of the major cycle (blue lines) are in equilibrium and the etching rate of SiO_2 becomes steady (Phase 3).

Conclusion

Using spectroscopic ellipsometry, crucial information on the spontaneous formation of HF in $LiPF_6$ containing organic carbonate-based lithium ion battery electrolytes upon thermal aging were gathered. The time-dependent formation of HF at 50°C was recorded by following the silicon dioxide etching. Different phases in the process have been identified by observing the slope change of the SiO_2 loss curve. Furthermore, using an empirical formula, the HF content has been evaluated. Although the use of silicon dioxide substrates allows to trace easily the generation of HF, we do not exclude that the presence of the SiO_2 promotes its formation. Different experiments have to be carried out to investigate this possibility.

The interpretation of the three phase process with reactions known from literature led to the proposition of a catalytic pathway for the reaction of HF with SiO_2 in battery electrolytes including $LiPF_6$, SiF_4, H_2O and several side products. This catalytic reaction has to be strongly considered regarding the future application of nano-silicon materials with possible silanol surfaces as anode material for lithium ion batteries or soggy sand electrolytes in combination with $LiPF_6$ based electrolytes.

Acknowledgements

The work was carried out under the joint sponsorship of the German Ministry of Education and Research (BMBF) in the project “LiVe” (03X4601A) within the “LIB2015” research alliance and by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, under contract no. DE-AC02-05CH11231.

FIGURES

Figure 1: Representative 3-dimensional images of the quadratic surface area 1.5 x 1.5 µm of a) a pristine SiO2/Si wafer, b) an etched SiO2/Si wafer (exposure time 182 hours @ 50°C, SiO2 layer thickness = 200.68 nm, SiO2 lost = 98.44 nm).

Figure 2: SiO_2 layer thickness loss on one side of the wafer (black points, left y-axis) and HF concentration in the electrolyte (right y-axis) upon thermal aging at 50°C under inert atmosphere (EC:DEC 1:2, 1M $LiPF_6$).

Figure 3: Proposed simplified mechanism for the reaction of $LiPF_6$ with water traces and reaction cycle of HF in the presence of SiO_2.

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