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Corset-like solid electrolyte interface for fast charging of silicon wire anodes

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HIGHLIGHTS

- Propylene Carbonate as old candidate leads to elastic SEI layer.
- Silicon microwire anodes do not need any graphite material.
- Silicon allows very fast charging with high capacity.

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ABSTRACT

The most challenging tasks in today's batteries are the need for fast charging and large energy densities for longer lifetimes. Micro-structured silicon microwire anodes show a nine-fold increase in gravimetric capacity over standard graphite batteries. The anodes exhibit an areal capacity of 4.25 mAhcm^{-2} with a specific capacity of 3150 mAhg^{-1} . The high specific capacity implies a 400% volume expansion of the Si wires. This paper demonstrates that by modifying and adapting the electrolyte composition a charging speed of 5 *C* (12 min charging time) can be reached completely maintaining the area and gravimetric capacity of the silicon anodes. Detailed analysis of the charge transfer processes across the solid electrolyte interface into the silicon wires reveals highly relevant mechanisms for this stable performance. A well-established solvent candidate, like propylene carbonate, which was rated not at all suitable for graphite electrolyte allows modifying the mechanical properties of the SEI layer in oder to support revery individual silicon wire to buffer the inevitable volume expansion.

1. Introduction

Electrolytes for graphite electrodes in Li-ion batteries have been under constant investigation for the last 30 years. All electrolytes for Liion batteries need to fulfill some general requirements [1–4]. First, they must have a high ionic conductivity. This guarantees lithium diffusion and ionic mobility for a long lifetime, otherwise diffusion limitation sets in. As a consequence, the internal resistance increases and the capacity decreases. Most common electrolytes using LiPF₆ in EC-DMC mixtures have an ionic conductivity of 11 mScm⁻¹. Different salts containing for example As, Br or Cl give strong ionic pairs or conglomerates, as their charge is not localized [1]. Second, electrolytes must be thermally and chemically stable in order to prevent unwanted side reactions at the electrode-electrolyte interface. Third, every electrolyte component has to be electrochemically stable in their specific voltage region during cycling without irreversible decomposition. This is essential for highpower applications of up to 5 V. Specific salts, for example LiNO₃, irreversibly decompose below 1.7 V and do not contribute to the battery performance anymore [5–7]. Anyhow, the key requirement of any type of electrolyte is the formation of a stable solid electrolyte interface (SEI) balancing the potential differences between the anode, cathode, and the electrolyte and minimizes any oxidation or reduction of the electrolyte [1,8].

A standard non-aqueous electrolyte for Li-ion batteries consists of a Li salt dissolved in a heterocyclic carbonate, like ethylene carbonate (EC) combined with a linear carbonate like dimethyl carbonate (DMC). Especially for graphite electrodes, the EC is an essential electrolyte component for stable cycling [9]. Graphite anodes have a low gravimetrical capacity of only 372 mAhg^{-1} , corresponding to LiC₆. The major drawback of graphite electrodes is the possible exfoliation of the

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basal planes. This oxidation of the edges leads to complete disintegration of the active material and naturally to a very poor cycling stability. Increasing the EC concentrations should help forming a stable SEI layer on graphite (> 44.1 wt %), suppressing the disintegration along the basal planes, and other kinds of degradation [9]. Propylene carbonate (PC), on the other hand, is chemically very similar to EC. For a long time, it was the solvent of choice because it exhibits very promising properties. Unfortunately, the decomposition products of PC severely degrade the graphite electrode by co-intercalating into the structure, especially at grain boundaries, opening the structure for further electrolyte flow [9–11]. This vicious circle repeats until the electrode is completely destroyed.

When considering lithium-rich silicides, e.g. $Li_{22}Si_5$ and $Li_{13}Si_4$, for electrode, the volume expansion increases significantly (i.e. up to ~400%) and completely different problems on the side of the electrolyte and SEI part are occurring [12–14]. Researchers were not aware of these problems before, because the silicon content in anodes is typically small (10–20 wt %) [15,16]. For the first time, this study focuses on pure silicon electrodes and their specific electrolyte and SEI development without any additional graphite. We show that it is possible to benefit from long-known solvents like PC and electrolytes developed for graphite electrodes, and establish them now for silicon anodes. Some groups discussed about the chemical nature of PC and its interaction with different solvents. But its influence and contribution on the cycling performance of pure silicon anodes have not been investigated before.

The here described silicon microstructure is a completely freestanding microwire array anode, produced with a tailored top-down approach involving standard MEMS- and silicon technology [17,18]. The benefit of pure silicon anodes is the complete elimination of heterogeneous particles, which can disturb the local SEI formation, and can even act as arbitrary nucleation sites for failure. These situations cannot be controlled easily and negatively influence the cycling performance [19]. Therefore, the here discussed architecture does not require any additional graphite enhancing the energy density due to the lack of any inactive material. Our anodes have a specially designed geometry with pre-defined space to cope with the volume expansion.

The formation of a closed and flexible SEI is more difficult due to the large volume expansion of this material. During silicon expansion, silicon and the SEI layer can easily be perforated and break. Consequently, the SEI layer needs a self-healing property acting during each lithiation and delithiation cycle again. On the other hand, the electrode compatibility is the most important criterion for designing a full cell with silicon anodes and the cathode material of choice, e.g. a novel sulfur cathode. When combining silicon and sulfur electrodes, different lithium salts like LiTFSI compared to the LiPF₆ or even additional solvents are favored to enhance the cycling stability and minimize the capacity retention [20-22]. This includes ether-based electrolytes as well as LiTFSI as salt to enhance the viscosity. For the here described silicon wires, LiTFSI in combination with DME and DOL has an optimal viscosity. The direct interaction between the electrode and the surrounding electrolyte is found to be very important, including the formation of the supportive solid electrolyte interface (SEI) around the electrode as well as possible aging mechanisms of the electrolyte [1]. For pure silicon anodes, it is important to minimize the SiO_x formation leading to lithium as well as silicon disintegration [13,23].

In this paper, the reduction mechanisms of various electrolytes during the SEI formation are analyzed and modelled with respect to the SEI layer mechanically supporting the Si wires. Thus by combining several Li salts and solvents, the C-rates allowing for stable cycling could be increased by a factor of ten (compared to standard charging and discharging processes [17,18,24]) up to 5 *C*. At the same time, the gravimetric capacity remains stable at 3150 mAhg⁻¹.

2. Experimental details



Fig. 1. Highly-symmetric silicon microwire array anodes for Li-ion batteries. The SEM images show individual process steps for the mechanically stable, freestanding array anode. a-b) Diameter variations along a wire implemented during electrochemical and chemical etching. c) A thin, chemically deposited copper layer enhances the contact between silicon and thick copper layers. d) The thick copper current collector allows a large mechanical integration and stability for the silicon wires, in order to remove the complete array from the silicon substrate. The parts covered with copper are highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

structuring and the macropore etching in p-doped silicon. This study focuses on the macropore etching in organic (water-free) electrolyte with HF at a low concentration (~10 wt %) and PEG (M~3360 g mol⁻¹). Pore modulation and etching in n-doped silicon is a standard process by adequate backside illumination and pure current density variation. The same parameters with p-doped silicon lead to deep and wide pores, without any (deliberate) diameter modification along the pore [25–27]. However, for the proposed application, the pore modulation in p-doped silicon could be achieved by increasing the electrolyte viscosity by adding PEG. Consequently, the pore walls are passivated and the local diffusional reaction is directed towards the pore tips. Locally the diffusion is reduced, to allow a controlled pore modulation. Fig. 1 shows an example of the highly-oriented silicon microwire arrays anodes with the integrated copper current collector.

The pores in this study were $70 \,\mu\text{m}$ long (deep in < 100 > direction) and have two design features: a) two diameter variations resulting in stabilizing planes along the pore (Fig. 1a–b), and b) a narrow pore tip. The pore modulation and diameter variation during the macropore etching affects the wire geometry. By deliberately adjusting the organic electrolyte and additionally, by adapting the current density profiles to the desired pore length, it is possible to obtain a defect free high quality pore array (with a diameter variation of less than 1%) [30]. Subsequent pore wall dissolution in a low concentrated KOH (~0.45 wt %) chemical etching solution leads to the desired wire

dimension and thickness [17,28,29]. Electrochemical analysis showed that a diameter of 1.2 μ m results in the most stable anode [17,19], with the highest volume for Li uptake and without Si fatigue during cycling. In order to have a symmetric array electrode, the current bursts during the macropore etching need to be directed that they all form and grow at pre-defined nucleation sites, by using a completely pre-structured silicon wafer (for further details on the pre-structuring consider [29,30]) [25,31,32]. In contrast to standard slurry paste electrodes, this architecture uses standard MEMS and Si technology instead.

Furthermore, as mentioned previously, the anode is partially integrated in a copper current collector to even enhance the mechanical stability for the silicon wires. During a two-step galvanic metallization step, a silicon-copper contact is formed. In order to enhance the adhesion between the copper and silicon, a thin Cu seed layer is chemically deposited along the individual wire walls in a low concentrated HF (2.1 wt %) solution with CuSO₄ (Fig. 1c) [33-35]. During the chemical deposition process, silicon is partially oxidized by the fluorine ions inside the solution, feeding free electrons into the redox reaction to form copper on the silicon surface. Anyhow, with this process only a thin copper layer can be formed which cannot carry any current. Therefore, in an additional galvanostatic step, a thick Cu layer $(\sim 45 \,\mu\text{m})$ is deposited in a 10 wt % sulfuric acid solution with additional CuSO₄, at current densities of 35 mAcm^{-2} . An optimal thickness for the current collector allows the removal of $70\,\mu m$ deep wires from the silicon substrate material. The current collector can carry the high current densities, necessary for fast charging [17,18].

In fact, this integrated current collector ensures high mechanical stability and defines the ohmic contact for the anode. During standard casting processes of paste electrodes, the active material is casted on a copper mesh current collector foil and tempered to ensure a good ohmic connection. This process, on the other hand, has a very defined ohmic contact due to the redox reaction at the silicon copper interface [35]. Anyhow, this mechanical stability is another benefit of the very controlled macropore modulation: An additional diameter variation (Fig. 1b and d) is already defined during the macropore etching as stabilization layer, which acts as diffusional barrier during the metallization process for further galvanic deposition.

The resulting anodes are investigated in half cells with metallic lithium as counter and reference electrodes. The tests are performed in purely inert electrode housings with standard glass fiber separators provided by Whatman company. Different electrolytes are tested during the charging and discharging of the silicon anodes. The base electrolyte is the two-blend solvent mixture with EC and DMC (Selectilyte LP 30, provided by BASF). Both cyclic and linear carbonates are used to dissolve the lithium salt LiPF₆ (11.8 wt %). In order to check how additional solvents like diethylcarbonates (DEC), 1,2-dimethoxyethan (DME), PC, triethylenglycoldimethylether (TEGDME) and others react with this electrolyte and influence the performance of the silicon wire anode, they are added to the base electrolyte (i.e. 10 wt%).

A combination of EC and DMC in an electrolyte, like Selectilyte LP 30, is beneficial especially for standard graphite electrodes. EC, in even higher concentrations than 44.1 wt %, tends to stabilize the SEI formation of graphite electrodes. Without this solvent, no sufficient, thick SEI layer forms resulting in poor cycling stability.

2.1. Methods

In order to analyze the electrolytic influence on the silicon wires, *in-situ* Fast-Fourier-Impedance Spectroscopy (FFT-IS) was performed. This linear response analysis superimposes 30 frequencies (10 Hz up to 20 kHz) on an applied DC operation point [19,36,37]. *In-situ* FFT-IS measurements are performed for all electrolyte compositions. This analysis is performed first on pure electrolytes, which eliminates additional interface reactions from the cell. Additional FFT-IS measurements allowed identifying the interaction mechanisms between the electrolyte and the silicon wires. Thus, the measured FFT impedance

data could be well fitted by just one RC circuit and one resistance in series. Gaberscek et al. discussed the necessity to analyze every interfacial reaction inside a battery, in order to model which physical parameters contribute to the cycling performance [38,39]. A previous study [18,19] distinguished three individual characteristics, which limit typical silicon paste electrodes. The purpose of the impedance analysis of a pure electrolyte is to deliberately separate the reactions happening due to the electrolytic decomposition reactions from those, which arise due to the electron transfer reactions around silicon. In combination with subsequent cycling experiments with silicon microwires and additional *in-situ* as well as *ex-situ* characterizations, it enables to define specific parameters and characteristics for solvents and salts. As a consequence, a special electrolyte for the free-standing silicon microwire arrays could be designed, which allows fast charging and high cycling stability.

Simultaneously to the FFT-IS analysis, cyclic voltammetry measurements have been performed to identify phase transformations and diffusional properties. In the anodic range (for anodes), the electrolyte as well as electrodes are cycled between 20 mV and 2 V, for at least five cycles in order to correlate the SEI formation to the first five cycles. In contrast, electrolytes for cathodes are analyzed in the opposite voltage window, between 3.5 V and 1.5 V but with the same voltage sweep rate of 0.1 mVs^{-1} .

For further chemical composition analysis of the electrolytes and anodes, Raman spectroscopy was performed (alpha300 RA, WITec), with a triple grating spectrometer with attached CCD detector. The exciting wavelength (λ_{ex}) of the laser source utilized for the measurements was 532.2 nm. The spot size of the laser on the sample was ~ 1.41 µm and its maximum power was 52 mW. In order to inhibit any oxidation of the Si wires during measurement, all measurements were performed via an Ar filled pouch cell. A spectral filter of 515–520 cm⁻¹ was applied to the Raman scan, which highlights Si having a peak in the mentioned range.

Microstructural and chemical investigations have been carried out by transmission electron microscopy (TEM). In order to have electron transparent, thin samples different preparation approaches were followed, but mechanical grinding was the most promising [23] inside an argon-filled glove box. TEM measurements were performed on a Tecnai F30 STwin (FEG, 300 kV, $C_s = 1.2$, EDAX EDX detector). Overview images were recorded in bright field mode. Investigations on crystallinity were performed by selected area electron diffraction (SAED) and high resolution (HR)TEM. Chemical compositions were determined by energy dispersive X-ray spectroscopy (EDX) in scanning (S)TEM mode.

3. Results and discussion

This section discusses the influence of different electrolyte compositions on the cycling performance and fast charging of pure (100%) silicon anodes. The built-in current collector provides high mechanical stability for the wires during cycling. The reactions of electrolytes are usually visible at the interfaces between the silicon surface and the surrounding electrolyte. The electrolyte requirements for silicon anodes are completely different compared to standard graphite electrodes. Therefore, it is necessary to investigate the contributions and influences on the cycling performance of silicon with varying electrolytes. Additionally, the SEI formation process for silicon strongly depends on the charging rate. Quiroga et al. previously showed that a combination of slow (0.1 C) and faster charging rates (0.5 C) is necessary to allow a stable, homogeneous SEI layer around each individual silicon wire, thus enabling a stable high capacity. The SEI formation is crucial, but its function and formation is not yet clear for this type of freestanding array structure.

Using the base electrolyte Selectilyte LP 30, as discussed in the experimental section, silicon wires showed already long-term stability over 400 cycles, as reported by Quiroga et al. [24]. The anode achieved a very high capacity of 3150 mAhg^{-1} throughout the long-term cycling



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Fig. 2. Discharge and charge rate characteristics depending on various electrolyte solvent additives. a) The base electrolyte is Selectilyte LP 30. The indicated solvents are always added to this electrolyte. With the addition of PC to the electrolyte, silicon anodes exhibit a constant capacity even at high C-rates. b) Typical charge and discharge curve demonstrating the potential of a higher viscous electrolyte with alternating C-rates.

test, without any irreversible losses. Higher C-rates than 1 C could not been realized in this type of electrolyte [24].

The influence of the electrolyte additives and their impact on cycling performance and SEI formation is summarized in Fig. 2.

Successive optimization of the electrolyte (see Fig. 2a) and b)) allowed the drastic increase of the charging rate of the silicon anodes.

Fig. 2a) emphasizes the silicon performance with varying electrolytes. Here, the main focus lies in the fast-charging capability. The added solvents to the base electrolyte Selectilyte LP 30 include PC, DME, DOL or DEC and are discussed in detail during this study. They are very common solvents for Li-S, Li-Air and Li-Ion batteries and can be categorized into carbonates, glymes, ethers and esters. As the silicon anodes proved to be a good candidate for a combination with sulfur cathodes [70], LiTFSI replaces even the standard lithium salt LiPF₆ commonly used in combination with sulfur cathodes. The electrolyte contains DOL and DME, instead of DMC and EC. These solvents are also discussed in combination with LiPF₆.

The C-rate variation during cycling already demonstrates the large influence of PC. Even at a charging rate of 5 C, the gravimetric capacity remains constant compared to all the other investigated electrolytes. For the other added solvents, 5 C is too fast and the capacity decreases. Cycling in the base electrolyte Selectilyte, which showed already good long-term cycling performance, proved to be not a good choice for fast charging silicon anodes. Adding DME to the electrolyte already improved the cycling stability by a factor of two.

The galvanostatic curves in Fig. 2b) indicate two alternating C-rates for the addition of PC to the electrolyte, as it is the only solvent capable of increasing the C-rate. The complete discharging process is realized in 60 min (1 *C*), while the charging could be successfully performed in only 12 min (5 *C*). The anodes still maintain their exceptionally high gravimetric charge capacity of 3150 mAhg^{-1} and an extremely high areal capacity of 4.25 mAhcm^{-2} , even at these high charging rates. 130 charging and discharging cycles could already be demonstrated with the alternating, high C-rates. The wires still maintained mechanically and electrically intact, as proven by the SEM images in Fig. 6. Charging and discharging pure silicon anodes with this velocity has not been realized before, which are the first steps towards new, high capacity battery storage systems. For many applications like e-mobility, the smaller discharging rate is no restriction; but discharging should occur significantly slower (*i.e.* 1 *C*). During this study, major factors, which allow for this drastic increase of C-rates will be discussed. In the end, PC was the solvent of choice, which significantly changed the properties of the SEI layer and thus stabilized the individual wires. Graphite electrodes have to be charged with 35 *C* in order to have a comparable current density. This illustrates the large stress each individual silicon wire can withstand.

3.1. Dependence on cyclic carbonate solvents

The cycling experiment indicated a drastic C-rate increase with an additional cyclic carbonate propylene [9–11,40,41]. Together with the Li ions, solvated PC co-intercalates between the graphite layers and there forming decomposition products, which are responsible for the structural degradation. Mostly, solvated PC reacts at the crystal boundaries. During a vicious circle, electrolyte flows inside the graphite layers and destroys the microstructure. These points are not covered by a passivation layer, which has to form every time again. At the same time, the solvated PC diffuses to these parts and destroys them again [9]. Consequently, active material is lost and the electrode fails. Exactly this established candidate is re-used for complete silicon anodes, changing completely the SEI layer morphology and the fast-charging capability.

Generally, silicon nano- or microstructures require an additional graphite or carbon layer surrounding the structures for enhancement of the electric conductivity, hence, PC is not commonly used in silicon anodes due to the well-known destructive mechanism [7,42-44]. However, PC is still an attractive solvent and investigated further within this study due to its lower melting, higher flash and boiling point than EC. Consequently, PC is attractive for a broader temperature range and leads to a safer electrolyte if spontaneous explosion and internal



Fig. 3. Systematic FFT-IS analysis of pure electrolytes. a) Example of series resistance curves of varying electrolytes with the base electrolyte Selectilyte as reference as well as the addition of PC and DEC to the base electrolyte. b) A change in the series resistance could be correlated to the electrolyte viscosity.



Fig. 4. Raman spectra of the solvent and salt mixture, pure PC and 50 wt % PC before and after cycling.

resistance are considered. Due to the chemical similarity of PC and EC, it is quite astonishing that both solvents have completely different influences and consequences on silicon. Therefore, we mainly concentrate on PC because the performance increase is enormous.

The interaction between PC and graphite or between PC and silicon electrodes is very different. Therefore, it is necessary to investigate the surface chemistry and the interaction between PC and silicon with the help of a detailed FFT-IS analysis.

Fig. 3a) shows the results of the impedance measurements for the standard electrolyte and for the electrolyte with PC (without the silicon wires). Details of such impedance analysis have been published [19]. Here, we will only focus on the results for a single resistance R_s extracted by fitting the impedance data. The resistance R_s represents the linear response at high frequencies of 20 kHz where most chemical reactions cannot respond (they are too slow), thus, mainly transport phenomena are reflected in R_s .

As depicted in Fig. 3a), the addition of PC leads to an increase in R_s . An offset between the curves is visible as well as an increase in the slope of a straight line fitted to the first cycles (with slower C-rates). At first glance, an increase in series resistance is attributed to the higher resistance losses inside the battery. The consequences on cycling of silicon wires still need to be evaluated.

By repeating this analysis of the individual slopes, a straight fitting for all electrolytes under investigation is possible and allows a clear correlation to the electrolyte viscosity (adapted from the literature), as shown in Fig. 3b) [2,20].

The plot in Fig. 3a) illustrates the time evolution of the series resistance, which can be divided into two different regions. The first region 1, as indicated in Fig. 3a), shows the mentioned linear increase. This increase is found to be characteristic for various electrolyte solvents. As seen for PC, the slope of this first region increases drastically when adding an additional component to the already existing EC-DMC electrolyte. The second region 2 is considered as the electrochemical dynamics of the electrolyte. After the first reduction of the solvents and the salt, this region indicates how the electrolytes behave on the longer term. Especially when cycling an anode or a cathode for Li ion batteries, the long-term stability of the electrode is one of the most important parameters.

The transition between region 1 and region 2 is always considered with an increase in series resistance. The series resistance of the standard electrolyte increases steadily with smaller amplitude. This is not practical because this means that the continuous salt-solvent or solventsolvent interaction would lead to a complete reduction and could no longer be used. The curves show a periodic increase and decrease with significant maxima and minima, which can be explained by the Li transport. Viscosity physically describes the force required to move a particle or an ion inside a medium. In contrast to the standard EC-DMC electrolyte, the behavior stabilizes with pronounced (large), stable amplitudes for PC. The maximum is directly correlated to the applied voltage of 1 V, whereas the minima are correlated to the zero crossing of the voltage curves. With the help of this background, it is possible to explain the extremes.

During lithiation (maximum, below 1 V), the Li ions diffuse from the counter electrode inside the anode through the viscous electrolyte, at least in the case of PC. The pristine SEI layer becomes thick and highly resistive [7,45]. The minima are formed during delithiation, when the ions are removed or consumed; liberating parts of the SEI layer (into solution) and transport it away from the interface, leading to a thin, low resistive SEI layer. The SEI layer appears to the outside always fresh and new, which is supported by Raman measurements. The importance of the amplitudes gets even more important during this study.

In order to understand the viscosity increase in the presence of PC, it is necessary to discuss its interactions with the co-solvents and the influence of the lithium salt LiPF_6 and PC. Fontanella et al. [46] and Kondo et al. [44] spent time and effort to fundamentally analyze the



Fig. 5. Raman spectra of the solvent and salt mixture, for DMC (LP 30) and DEC (LP 40) containing electrolytes before and after cycling.



Fig. 6. Silicon-Electrolyte interaction with respect to different carbonaceous electrolytes. The schematic shows the highly-oriented silicon microstructure with the embedded current collector. The enlarged inset on the right shows the cross-sectional image of the electrolyte-electrode interface. The color gradient indicates the subsequent lithiation and structural change of silicon. Postmortem SEM images show four characteristic silicon surfaces cycled in different electrolytes. The surface morphology and SEI layer changes drastically towards a more elastic layer with the addition of PC, enabling fast charging of the anode. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

interaction between the lithium salt and PC. Additionally, Nie et al. concentrated on the different coordination possibilities of PC for graphite electrodes. The fundamental background of PC and its chemical nature allowed explaining the viscosity change [1,11,40,43,44,46–48]. By using a similar approach as for graphite electrodes, the interpretation will be applied to silicon accordingly.

There exist several reaction pathways how the reaction might continue [40]. According to the reduction pathways, a one-electron reduction reaction is not probable [40], because the PC molecules tend to form complex coordination environments in the presence of salts or acids. The EDX analysis showed high amounts of fluorine around the silicon wires, which can be attributed to either the HF formation or the reaction products of the PF_6^- ions with the solvents.

 $LiPF_6$ dissolved in the organic solvents attains an equilibrium as shown in the following reaction $LiPF_6 \leftrightarrow PF_6^- + Li^+$.

For PC electrolytes, it is common that the equilibrium reaction shifts towards the products and thus the products reduces further to PF_5 . Raman spectroscopy was adopted to study the interactions between the salt and the organic solvents. One of the by-products of the electrolyte reduction in graphite electrodes is LiF, which is an unstable solid and agglomerates on the electrode surface [40].

These particles were not identified by the post-mortem analysis, this leads to further defined differences between the two electrode materials. Another possible product might be Li₂O₂. Several small peaks occur in a Raman spectrum between 603 and 612 cm^{-1} due to Li_2O_2 formation. Neither for the PC variation nor for the other solvents, these peaks appeared. Therefore, this reaction is not very likely to occur during the reduction process. In addition, Li₂O₂ is very unstable and is likely to decompose. The unstable Li₂O₂, which is very unlikely to form in the first place, could decompose back to its ionic state releasing Li + ions. It does not react back to its salt state (LiPF₆) as we can the peak appearing from PF_6^- in the Raman spectra. This remains even after cycling. Summarizing, the Raman measurements did not reveal any of the most common components of a typical SEI layer of graphite, like Li₂CO₃, Li₂O₂ etc. [2,49,50]. These components and bonds would have a very characteristic Raman peak, which did not appear for the silicon surface.

Depending on the solvent in these electrolytes like addition of DME, DMC or PC etc., the decomposition products changed. We detected different amounts of fluorine or oxygen concentrations with the EDX or even Raman when we changed the electrolyte composition. This means that apparently the coordination and interaction with the $LiPF_6$ changes. Especially when adding PC to the discussed base standard LP 30 electrolyte (EC, DMC, LiPF₆), the fluorine concentration drastically changes depending on the PC concentration. Different groups like Kondo et al. reported a tetra- or trivalent coordination of PC with the salt LiPF₆, thus changing the fluorine concentration on our silicon surface. On different tested solvents like DEC for example this was not at all observed and instead more oxygen-containing by-products are observed.

Using PC, it appears that the electrolyte as well as the SEI layer is fresh and not degrading very easily, allowing a long term stable cycling with these necessary components.

The long-term stability of the electrolytes containing PC relies on the coordination of PC with the lithium salt. Kondo et al. indicated that PC molecules tend to change their coordination with Li⁺, thus shifting the equilibrium towards the products [44]. If PC is added to the electrolyte mixture, the equilibrium that exists between $\text{LiPF}_6 \leftrightarrow \text{PF}_6^- + \text{Li}^+$ the energetically favorable co-ordination between PC and Li⁺ shifts the equilibrium towards the products. Once the equilibrium shifts, the viscosity could locally be increased. Inside the optimum viscous medium, the ionic conductivity is maintained. In comparison to the standard system, LiPF₆ is not degenerated or decomposed irreversibly. The type of coordination depends on the viscosity and the diffusion coefficient of PC electrolytes. Usually, higher molar concentrations of PC lead to a higher viscosity, in which the PC molecules tend to show tetra-covalent co-ordination around Li+ ions as supported by the Raman spectra in Fig. 4a). The peak at 721 cm^{-1} is attributed to bond bridging between Li⁺ and the oxygen atom present in the PC molecule [44]. In Fig. 4a) the peak at 712 cm^{-1} in the spectrum of pure PC occurs due to the ring breathing of PC. At 50 wt % PC added to the base electrolyte, a peak shift is observed after cycling (Fig. 4a). Such a shift could be assigned to EC molecules present in the mixture. EC molecules show a peak at \sim 714 cm⁻¹ resulting from out-of-plane ring bending.

However, at a PC concentration higher than the 5 wt % PC, uncoordinated PC molecules remain in the electrolyte, which can be seen in the Raman spectra in Fig. 4b) via a well separated peak at ~849 cm⁻¹ which is attributed to the ring breathing of a PC molecule. The effect of the homo-polymerization and the interrelated consequences on the anode characteristics could not be detected. The decomposition of LiPF₆ in an electrolyte mixture leads to the formation of a Lewis acid like HF, in the presence of which solvents like PC are known to polymerize (homo-polymeriszation) or at least forming oligomers. This increases the viscosity to a point that the freedom for the mobility of Li⁺ ions is lost [44,46,51,71,72]. The presence of excess PC might have helped in keeping the SEI layer from drying and cracking. The Raman spectrum of LP 40 shows a ring-breathing peak of EC at 900 cm^{-1} . A slight shift in this peak is observed after cycling such shift and peak broadening could indicate solvent-solvent and/or solvent-salt interaction.

The periodic maxima and minima show a strong correlation between the electrolyte stability with time and the interaction. It has a direct consequence on the SEI layer properties around the silicon wires, resulting from the interaction between the used lithium salt and the added solvents. Thus, this series resistance has a directly consequence on the battery performance, shown in Fig. 2.

3.2. Dependence on linear solvents (carbonates, ethers)

Fig. 3a) showed the basic difference when changing the electrolyte composition by adding a cyclic carbonate. Fig. 3b), on the other hand, summarizes the influence on the series resistance when adding different solvents (like linear carbonates or ether-based solvents). For the analysis of the linear solvents on the electrolyte, the same base electrolyte Selectilyte LP 30 is taken as reference. In this electrolyte, the linear carbonate is DMC.

The list of tested, additional linear carbonate solvents is quite long including i.e. DEC, DMC, TEGDME and DME and others. Usually, these carbonates are added to the electrolyte in order to reduce the melting point of EC and to form low viscous electrolytes. Therefore, it is clear that the initial viscosities of all the linear carbonates are very low, compared to the cyclic carbonates analyzed in Fig. 3a) [20,51]. Their influence on the series resistance is mainly seen in the second region, as a result of the low viscosity during the SEI formation. The slopes of all the linear carbonates range even below the standard system, which is not very surprising. They just dilute the Selectilyte and the viscosity reduces. This low viscosity has a direct influence on the electrochemical dynamic in the second region. The effect of the low viscosity of the used linear solvents can be directly exported to the dynamic because the stability changes (also supported by a change in the order of magnitude of the series resistance). Due to the correlation between viscosity and ionic conductivity, it is clear that the solution is more conductive. But nevertheless, the periodic minima and maxima are not very stable, especially for the different ethers. These instabilities can be correlated to decomposition reactions. Especially, DME and TEGDME are very instable in combination with fluorine ions. They will react and lead to electrolyte depletion. Ethers have typically the problem that they are very volatile and evaporate very fast, compared to the viscous PC electrolytes. Experiments supported this electrolyte depletion and indicated an increase in internal resistance and slow diffusion. The silicon wire anodes cycled in this electrolyte showed a very thin SEI layer. Already after several cycles, no electrolyte remains inside the half-cell [3].

Adding co-solvents to the electrolyte changes drastically the dynamic of the individual electrolytes. For DEC, DMC or DME solvents, for example, the series resistance does nearly increase periodically like in Fig. 3a), but increases steadily with very small amplitudes. This indicates a low and thin resistive SEI layer. To summarize these experiments, the pure electrolytic analysis revealed a) a viscosity change of the electrolyte during the SEI formation, and b) the electrochemical dynamic of the individual electrolytes.

3.3. Cycling Si microwire arrays with high performance electrolytes

The previous analysis indicated why the cycling performance shown in Fig. 2 differs significantly. In addition, it allowed decoupling possible interactions between the electrolyte components from transfer reactions into the silicon. During postmortem analysis of the silicon wires, the influence of the individual solvents on the morphology of the SEI layer became evident (Fig. 6).

Fig. 6 shows a schematic of the highly-oriented silicon wires during cycling. The color gradient in Fig. 6 illustrates the on-going lithiation

process and emphasizes how important it is to understand the effects at the microscopic level at the interface. Any change at this interface will propagate forward into the silicon (i.e. core of the wire), leading to a crystal change and to a performance loss. Postmortem SEM analysis shows an excerpt of four different modified electrolytes revealing drastic morphology changes around the wires after cycling. The viscosity decreases from PC to TEGDME (Fig. 6). The SEM image in DECcycled electrolytes is a good example for the oxygen-containing SEI layers. The small spikes are the result of the oxygen, liberated by the decomposition of DEC.

The SEI layer formed in PC electrolytes has meshes incorporated inside this layer. Additionally, the surface of this SEI layer is smooth, compared to the other layers in Fig. 6 [18]. The modified SEI layer has different mechanical and chemical properties, which now allow fast charging processes of the silicon, while maintaining the crystallinity. Due to the discussed decomposition and stabilization reactions of the PC, possible cationic polymerization leads to a more flexible SEI layer with a grid-like structure stabilizing the wires. The volume expansion of silicon of 400%, anyhow, puts new requirements and problems to this elastic layer. In the best case, it should also expand as much as silicon does, but without breaking. Since the electrolyte becomes more viscous during aging, it could be considered as a polymeric liquid. For a polymeric liquid, it is very difficult to expand and retract periodically without losing their mechanical properties, like tensile strength and elasticity.

Like this, as stated already in Fig. 3, the viscosity and elasticity of the SEI layer play a crucial role in the performance of the silicon wires. For example, DEC containing electrolytes or even LiNO₃ containing electrolytes produce commonly a very thin SEI layer. The SEM images of DEC cycled silicon show severe degradation of the silicon wires. The complex interaction of the DEC with LiPF₆ is known to produce an SEI layer with high amounts of oxygen [52,53]. As shown in Fig. 2, silicon cannot be cycled in DEC without severe capacity fading. Due to a high oxygen content at the surface, most probable SiO_x forms, which shows different cycling behavior compared to pure Si (Figs. 7 and 8). This formation leads to a change in crystal structure and amorphization, accompanied with the ablation of silicon and crack propagation [23] during lithiation. The lithiation front propagates, like indicated in the cross-section and a sharp front between amorphous and still crystalline silicon forms. The freestanding silicon wires are not mechanically stable anymore. Thus, the active material is lost and the capacity fades. The impedance spectroscopy supports the dynamics and instability of the electrolyte (Fig. 3). There are neither periodic minima and maxima, nor an offset in the beginning. Thus, the transport processes are different in this electrolyte.

For most types of electrode architecture, this could be beneficial in order to allow sufficient ionic diffusion. Only with the addition of PC to the electrolyte, the specific capacity stays constant at 3150 mAhg^{-1} and is almost independent of the C-rate. Even high C-rates like 5 *C* could be realized for silicon anodes. Thus, a battery could now be fully charged at high current densities in only 12 min, without losing the integrity and stability of the anode.

Anyhow, for the freestanding wire arrays discussed here, it turned out to be far more important to have an elastic, self-supporting SEI layer with PC. In this case, the passivation layer stabilizes the silicon wires like a second skin and enhances the mechanical stability of the individual wires.

In addition, the detailed electrolyte analysis revealed that PC has the ability to stabilize the surrounding electrolyte due to already discussed stereoisomerism. That means that the electrolyte is not aged and decomposed easily, but readily allows continuous ionic diffusion in and out of the silicon anode.

A mechanical stabilization of the silicon wires is found to have an effect on the crystallinity of the wires, also after several cycles. The mechanical stability is already partially given by the architecture of the structure, but now, it is even increased by an artificial, self-organizing



Fig. 7. Raman spectroscopic analyses of Si-microwires before and after lithiation. a) An optical microscope image of Si wires placed inside the pouch cell. b) 3D areal/image scan under Raman spectrometer (50*50 µm) of Si-microwires before lithiation. c) Single Raman spectra of the Si-microwire before and after cycling with LP 40. The change in the peak position and shape indicate the partial amorphization of the wires.



Fig. 8. Lithiated Si-microwire in BFTEM with corresponding SAED pattern from circled position in EC/DEC electrolyte (LP 40).

effect due to the enhanced cationic polymerization reaction.

As indicated previously in Fig. 2, the increase in series resistance (i.e. internal resistance of the battery) is usually not beneficial. In most cases, it leads to higher incorporation voltages with every new cycle and thus imposes capacity losses on the anode. For the silicon wire arrays, on the other hand, this increase in voltage is willingly accepted and readily compensated by the drastic increase in C-rate. Furthermore, the optimized interface reaction with the addition of PC might also be considered as local diffusion limitation for the first cycles. Thus allowing a slower, but more controlled SEI layer formation [27]. Electrochemical macropore etching uses a similar effect. By adjusting deliberately the electrolyte viscosity, the diffusion of fluorine ions (for macropore etching) and of lithium ions (for the battery) reduces and allows a very controlled etching and incorporation. These implications could be understood by taking into account the Einstein- Smoluchowski equation as well as the diffusion equation [22,45,54,55]. Higher viscosity would mean a lower diffusion through the medium. It is not necessary to have a viscous electrolyte from the beginning, but only that it becomes viscous during the SEI formation, thus creating a mechanically, supportive SEI layer. The stabilization, indicated in Figs. 2-5), allows maintaining the crystallinity of the wires.

The inset at the silicon-electron interface shows three driving forces for the lithiation. The difference in concentration between the non-lithiated silicon wire and the surrounding electrolyte forms the first driving force j_1 . The already lithiated phase starts to push forward in the direction to the bulk silicon wire, described by j_2 , where it comes to a hold due to high stress j_3 . The color gradient indicates how the lithiated front moves. Consequently, the enhanced stress during volume expansion (due to 5 *C*) can be buffered by the additional mechanical stabilization of the wires due to the modified SEI layer. As it is an additional mechanical support, the SEI layer homogeneously compresses the silicon wire and therefore allows a controlled ion incorporation along each silicon wire. Like this, the typical failure mechanism and pulverization of comparable silicon anodes is avoided. Common problems include the disruption or re-deposition of the SEI layer during volume expansion. Under these circumstances, the silicon surface is exposed to the electrolyte and new, repeated surface reactions occur until the SEI layer closes again [1,14,48]. The role of the SEI layer is still under ongoing discussion; nevertheless, this study gives first, strong hints to clarify its importance.

During lithiation and de-lithiation processes, naturally the entropy increases inside the anodes, leading to a volume expansion and crystal re-orientation. This re-orientation is always accompanied by mechanical movement of the anode material, like breathing of the wires followed by an (partial) amorphization process [14,56–60].

Different types of solvents like DEC, DME and TEGDME lead to a thin and low resistive SEI layer, which is in agreement with [20,51]. The SEM image in Fig. 6 showed small oxygen spikes around the silicon wires for DEC electrolytes. Due to the well-known decomposition products of DEC-containing (LP 40) electrolytes, these oxygen peaks can be understood. They are a result of the (repeated) step-wise reaction between PF_6^- and DEC. In order to avoid that this oxidation is the result of the sample transfer process, a specialized holder, transfer box or pouch cells are designed, to have reliable results. The high oxygen content of these samples and the corresponding thin SEI layer results in the drastic capacity fading of the anode (Fig. 2). By postmortem Raman as well as TEM images, the change in the macroscopic Si structure is confirmed (Figs. 7 and 8).

As previously discussed in the pure impedance spectroscopy, DEC electrolytes (LP 40) show comparable viscosity values as the standard DMC electrolyte (LP 30). Thus, the difference in battery performance could be traced back to the SEI components and the lack of mechanical support. Campian et al. proposed a possible reduction mechanism between DEC and LiPF₆ inside the electrolyte. Upon repeated reaction between the used salts and solvents, a complex is formed from PF₅ and the decomposition products of DEC. These products contain high proportions of additional OH and O-groups [52,53]. Filipovic et al. indicated that the decomposition rate is accelerated leading to an enhanced diffusion rate for further oxidization of silicon [53,61–63] inside this type of electrolyte. Raman spectroscopy supported the amorphization process with the wires being in an intermediate state from crystalline to completely amorphous.

Crystalline Si has a sharp Raman peak at ~ 520 cm⁻¹, which occurs due to the transverse optical phonon mode (TO). The optical image in Fig. 7a) shows the Si microwires before lithiation. The 3D image scan shows a similar morphology of the Si microwires as shown in the optical image. The spectra displayed in Fig. 7c) supports the theory of electrolyte-electrode interaction which causes diffusion of the oxygen through the SEI oxidizing the Si microwires. The corresponding Raman spectrum supports the crystallinity of these wires before lithiation, having the indicated peak at $\sim 520 \,\mathrm{cm}^{-1}$ with an full width have maximum (FWHM) of 11 cm⁻¹ in Fig. 7c).

The wires cycled in DEC, on the other hand, show a completely different behavior. These spectra shown in Fig. 7c) show different spots (I-V) on different wires, indicating systematic amorphization. They indicate a large shift in the TO mode from ~499 to 473 cm⁻¹. Additionally, it even shows a peak broadening (I = 33.4 cm⁻¹, II = 50.3 cm⁻¹, III = 24.9 cm⁻¹, IV = 32.19 cm⁻¹ and V = 39.6 cm⁻¹), suggesting strong amorphization. The SAED pattern supports this amorphization process by the absence of any Bragg intensities, cf. inset of Fig. 8.

It appears more transparent and homogeneous, as a part of the SEI (dark area, Fig. 8, center position) is visible at the backside of the wire. These results support the direct correlation between electrolytic reactions and structural changes inside the silicon.

After cycling, the wires still have their initial thickness (additionally covered with a thin SEI layer). This means that (almost) no surface ablation happened [23] and the wires are still intact. With ongoing cycling, the problem could be more pronounced, leading to a phase separation between the crystalline core and the amorphous part. The volume expansion induces anisotropic stress on the wires. In the beginning of the lithiation, a concentration gradient builds up, thus inducing a driving force for lithiation. Once the first lithiation took part, the lithiation (reaction) front propagates into the crystalline silicon core. With ongoing lithiation, the movement of the reaction front slows down due to an increased stress and eventually leads to a complete lithiation stop. The amorphous-crystalline interface, anyhow, is prone for plastic deformation if the stress is released during delithiation. In the case for DEC electrolytes, this amorphous layer is very large. If such stress and stress relaxation is inhomogeneously distributed inside the amorphous layers, cracks are induced and likely to propagate, leading to a phase separation of the amorphous and crystalline silicon and therefore to mechanical failure of the silicon wires [56,57,64-67]. Due to the high lithium diffusivity, the lithium ions preferentially propagate towards these cracks and locally break additional (still crystalline) silicon bonds, further propagating the induced cracks [68,69].

Summarizing these results, the choice of the electrolyte is directly correlated to the change of the mechanical stability. The same behavior is dominating the cycling behavior with nitrate electrolytes. Although DEC electrolytes are very common for porous architectures, for the array structures they are not suitable. A possible explanation might be the very small amount of SiO_2 around the silicon wires. This layer has a maximal thickness of 2 nms. Compared to porous structures, it is very limited and not the same bonding properties are available.

4. Conclusion

This study points out the importance of the mechanical and chemical stability of the SEI for the fast charging process of pure silicon anodes. Using a well-known, but forgotten electrolyte additive of graphite electrolytes for silicon anodes enabled an elastic, self-supporting layer around the individual wires. PC was not used anymore in Li-Ion batteries. But with the trend going towards higher silicon concentrations, special attention is given to the effect of PC. The SEI layer becomes elastic and viscous, creating a supportive layer around the individual wires. Now, the inevitable stress during charging and discharging could possibly be reduced to a minimum, which in turn means that the microstructure can withstand even higher current densities. Consequently, the anodes do not suffer from the common failure mechanisms, like crack formation or pulverization, as standard, commercially available electrodes do. This highlights the strength of the highly-oriented silicon microwire anodes even more, which are competitive to the commercially available batteries.

By successfully tuning the electrolyte properties of the anode, a completely charged battery could be realized in just 12 min. These high C-rates – 5C – could be achieved by optimizing the electrolyte components that contribute to the SEI layer. Consequently, the complex interaction between silicon microwires and a non-aqueous electrolyte is not just the result of the electrochemistry of the electrolytes, but more importantly of the mechanics.

This study demonstrated how an electrolyte could be designed whose main purpose is to mechanically stabilize the silicon wires. Furthermore, the Raman as well as impedance spectroscopic analyses indicated that PC stabilizes common carbonaceous electrolytes. Using PC leads to an increase in viscosity and in turn leads to a drastic decrease in cycling time. The silicon wires still maintained their high degree of crystallinity, as supported by TEM as well as Raman spectroscopy.

Contrary to this high performance electrolyte, different electrolytes with additions of DEC, on the other hand, showed strong amorphization of the silicon wires. Consequently, the cycling performance in this electrolyte is very poor.

Concluding, we cannot detect a technological or strategical disadvantage in using silicon anodes, except the complicated and advanced fabrication process of our silicon wire array. Another benefit of our structure is the high amount of Li incorporated into the silicon across a large surface area. This additionally stored energy in the system changes completely the morphology of the SEI layer and thus forms a novel self-stabilizing layer instead. The SEI layer seems to be fresh and new in every lithiation and delithiation cycle, showing a periodical behavior in impedance analysis, discussed in this study. Establishing the old acquaintance PC for the high-performance silicon anodes stabilizes the SEI formation making it possible to establish the necessary, fast charging processes for the e-mobility sector.

Author contributions

The manuscript was written through contributions of all authors.

Notes

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