

Alloying of electrodeposited silicon with lithium—a principal study of applicability as anode material for lithium ion batteries

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Abstract The possibility to electrodeposit silicon directly on a copper current collector out of organic electrolyte and ionic liquid was investigated with the aim to alloy the deposited silicon with lithium to prove the possible use as negative electrode in lithium ion batteries. Cyclovoltammetric analyses have shown in comparison to electrodes containing high crystalline silicon similar behaviour during the electrochemical alloying and dealloying process. SEM analyses have shown a particle size of the deposited silicon in submicron range.

Keywords Electrodeposition · Silicon · Ionic liquid · Lithium battery

Introduction

Lithium ion batteries (LIB) are today one of the most promising high energy power sources and extensive

research still continues to achieve further improvements in terms of higher rate capability, cycle life, safety and to enlarge the temperature operation field.

In general graphite or other carbonaceous materials are state-of-the-art in lithium ion batteries as active mass in negative electrodes. A theoretical capacity of 372 mAh g^{-1} can be achieved from the LiC_6 compound but this is poor compared to $4,200 \text{ mAh g}^{-1}$ from $\text{Li}_{22}\text{Si}_5$ [1].

To obtain suitable thin film silicon electrodes the method of electroplating can be convenient. Due to the redox potential of silicon it is necessary to perform the electroplating in organic [2, 3] or ionic liquid electrolyte [4, 5].

Ionic liquids (ILs) are room temperature molten salts and they typically show a very low vapour pressure, high thermal stability, wide electrochemical stability windows and good conductivity at room and sub-room temperature [6, 7]. In our investigations, we used propylene carbonate (PC) and *N*-butyl-*N*-methylpyrrolidinium bis (trifluoromethanesulfonyl)imide ($\text{Pyr}_{14}\text{TFSI}$) as electrolyte solvent.

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Experimental

The electrodeposition experiments were performed in a self-made three-electrode Swagelok® cell. A copper foil (Schlenk Metallfolien GmbH & Co. KG, Germany) was implemented as the working, lithium piston as the reference and lithium foil as the counter electrode. On the one hand, the electrolyte solution used in this study was composed of 1 M SiCl_4 (Aldrich) as the silicon source, PC (Honeywell Inc.) as solvent and 1 M LiTFSI (3M Company) as conducting salt. On the other hand, 1 M SiCl_4 and 1 M LiTFSI in $\text{Pyr}_{14}\text{TFSI}$ room temperature ionic liquid for the electroplating with ionic liquid was used. The preparation of the $\text{Pyr}_{14}\text{TFSI}$ is described by Appetecchi et al. in Ref.

[8]. All samples were deposited at room temperature at 1.0 V vs. Li/Li^+ for 3,600 s and characterized with SEM and CV. For further characterisation, the electrodes were cleaned in diethyl carbonate (DEC) and afterwards dried under vacuum at 80 °C for 24 h. The composite silicon electrodes were prepared by mixing 90 wt.% of nanosized silicon powder (Nanostructured & Amorphous Materials, USA), 6 wt.% of carbon black (Super-P, TIMCAL, Switzerland) and 4 wt.% Na-CMC (Merck) as binder in deionised water as solvent. The resulting slurry was coated by the doctor plating method on a copper foil and dried 24 h at 180 °C under vacuum before use. The cyclic voltammetric characterisation was performed in self-made Swagelok® cells with lithium as counter and reference electrode with ADESYS® potentiostat. The electrolyte used was 1 M LiTFSI/PC, 0.3 M LiTFSI/Pyr₁₄TFSI and 1 M LiPF₆/EC/DEC 3:7. The scan rate for these experiments was 50 $\mu\text{V s}^{-1}$ (Table 1). The SEM images were obtained with the microscope JWS-7515 from JEOL Ltd.

Results and discussion

Pyr₁₄TFSI exhibits an adequate electrochemical stability window with a cathodic stability of around 0.1 V vs. Li/Li^+ [9] and a sufficient solubility for the SiCl_4 precursor [4] to perform the electrodeposition at the required low potential. The potential windows of the electrolytes in Figs. 1 and 2 show that the reduction of the used SiCl_4 precursor occurs in PC and Pyr₁₄TFSI around 1.0 V vs. Li/Li^+ . Therefore this potential was chosen for the potentiostatic deposition.

The SEM images in Fig. 3 show that the deposited silicon particles have a size in the range of 100–500 nm. However, our experiments have displayed that the selection of a suitable copper substrate is important to the surface properties. Satisfying results were obtained by using a copper substrate with a dendritic roughened surface as shown in Fig. 3 sector 3 [10, 11]. It is expectable that the deposition process will start in regions on the substrate with the highest current densities, respectively, on the copper dendrites. Sector 1 shows a region in the right corner where the copper dendrites are just capped with a small film of silicon. In the left part of sector 1, larger particles were observed which lead to the conclusion that it is necessary to

Table 1 Abbreviations used for comparative CV studies

Type	Electrolyte for deposition	Electrolyte for cycling
A Deposited	Pyr ₁₄ TFSI	Pyr ₁₄ TFSI/0.3M LiTFSI
B Deposited	PC	PC/1M LiTFSI
C Composite	–	EC/DEC 3:7/1M LiPF ₆
D Composite	–	Pyr ₁₄ TFSI/0.3M LiTFSI

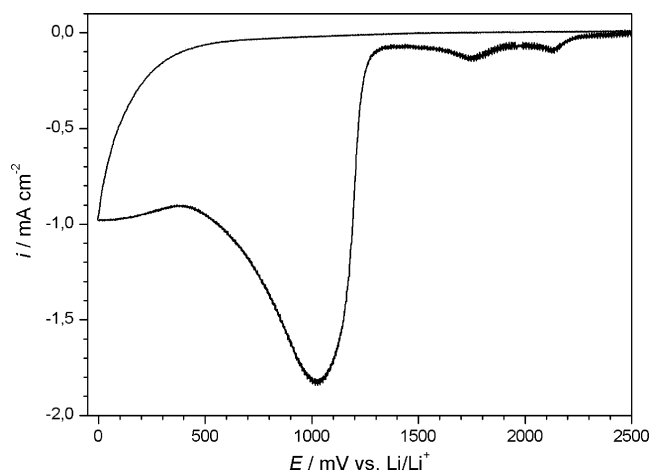


Fig. 1 Cyclic voltammogram for a Cu electrode in PC containing 1 M SiCl_4 and 1 M LiTFSI. Scan rate, 5 mV s^{-1}

provide locations on the substrate where the initial deposition can occur and constitutive on the primary deposit, market in sector 1 with cycles, the deposition can be continued. Sector 2 shows a region on the electrode where the silicon particles have reached a particle size up to 500 nm and the whole area is covered with a silicon film. In difference to substrates without structuring, a strong increase of adhesion for the deposited films was observed especially under the applied cleaning conditions. This means that the apparent deposit was not connected well enough to the surface of the substrate.

Figures 4 and 5 illustrates the typical behaviour of crystalline silicon during electrochemical alloying with lithium. In the first cathodic sweep, only one sharp peak can be observed, which maybe the result of the high over potential caused by the low conductivity of silicon. This peak can also be monitored in the cyclic voltammograms in the inset of Figs. 5 and 6 for the high crystalline silicone

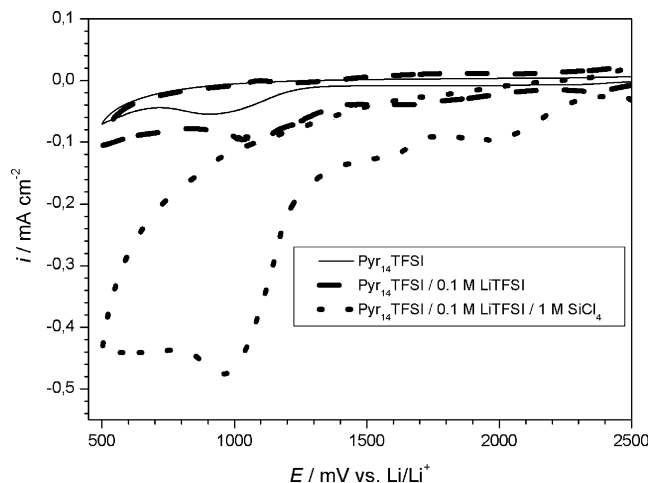
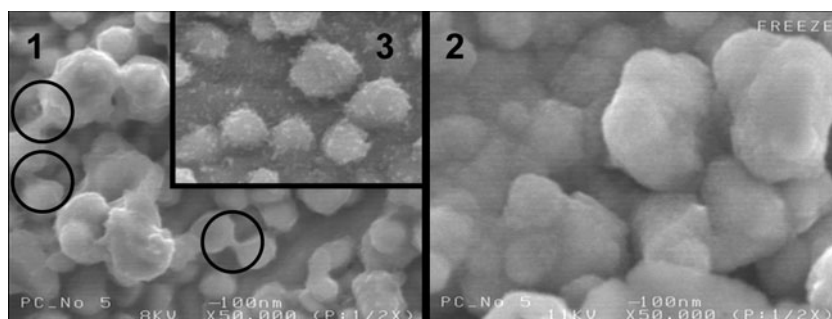


Fig. 2 Cyclic voltammograms for a Cu electrode in Pyr₁₄TFSI containing 1 M SiCl_4 and 0.1 M LiTFSI. Scan rate, 5 mV s^{-1}

Fig. 3 SEM images of electro-deposited silicon in PC (1), in ionic liquid (2) and (3) the copper foil



composite electrodes. The anodic sweep in the first cycle shows two peaks at a potential of ca. 330 mV and ca. 470 mV which indicate a phase change from crystalline to amorphous silicon. In the anodic peak of the second cycle, two peaks appear which belong to amorphous high and low voltage delithiation plateau of silicon [12, 13]. This presumably results from the conductivity enhancement and structure modification of the Li–Si matrix caused by a small amount of trapped lithium [14]. During the following cycles, the shape of the voltammograms changes marginally. Both the anodic and cathodic peaks in the cyclic voltammograms indicate a crystalline morphology of the deposited silicon, which is comparable to the high crystalline silicon used for the nano-scale silicon composite electrodes. For silicon electrodes, it is typical that a loss of capacity in the consecutive cycles is observable. Caused of the brittleness and due to the fact that during the alloying processes a large volume change of the alloy phases occurs, particles can break down and lose furthermore the contact within the electrode and a capacity fading results [1, 15].

In the following cycles in Figs. 4 and 5, a decrease of the cathodic current during the lithiation process is observable which is descending with the number of cycles. This effect can be explained by two causes. The first effect is that the connection of the deposited silicon particles among each

other is not uniform so that during the alloying process accompanied with large volume changes, some particles lose either the contact among themselves or to the copper substrate and are no longer electrochemically active. A second reason for such behaviour is to presume that the film forming parasitic reactions on the silicon surface are not completed. This means that during the alloying and dealloying process caused by structural changes, new reactive surfaces will be generated and therefore irreversible capacity will be consumed [16, 17].

Figure 6 represents the relative charge capacities comparative for silicon composite electrodes and deposited silicon electrodes during the first five cycles. A and B displays a strong decrease of charge capacity between the first and second cycle adverse C and D. A and B represent deposited silicon electrodes and the loss of capacity is presumable caused by lax connected silicon particles among themselves or to the current collector. Otherwise, in Fig. 8 the constant relative discharge capacities indicate incipient with the second cycle that parasitic reactions caused by in-situ-generated fresh silicon surfaces are dominant. In the further cycles the relative charge capacity trend to become constant. On the other hand, C and D for the composite electrodes indicate a slow decrease of the charge capacity for the first five cycles. Explanatory for this

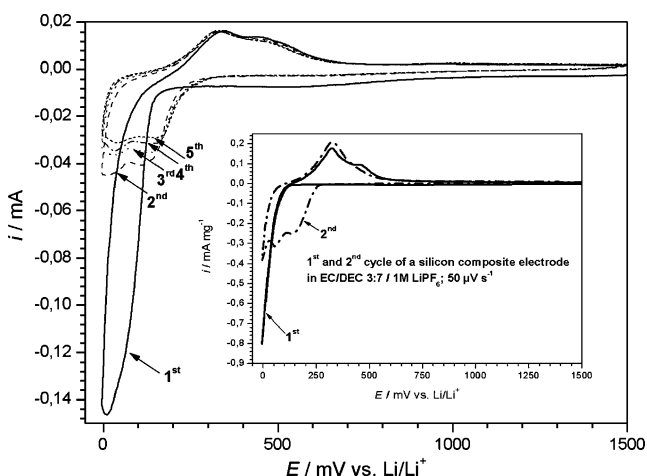


Fig. 4 Cyclic voltammogram for a, in PC-deposited, silicon electrode in PC containing 1 M LiTFSI. Scan rate, 50 $\mu\text{V s}^{-1}$

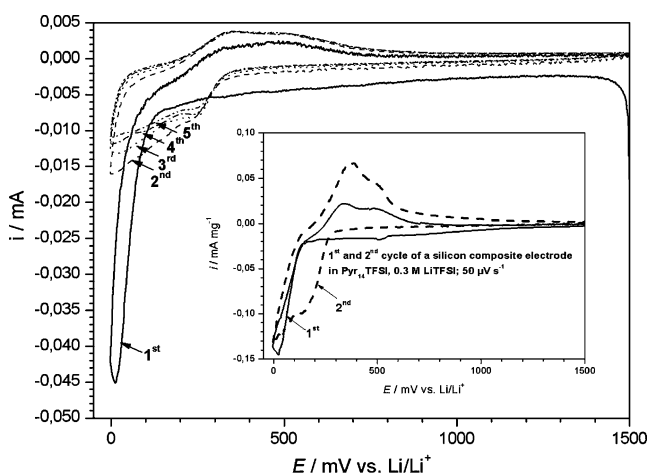


Fig. 5 Cyclic voltammogram for a, in ionic-liquid-deposited, silicon electrode in Pyr₁₄TFSI containing 1 M LiTFSI. Scan rate, 50 $\mu\text{V s}^{-1}$

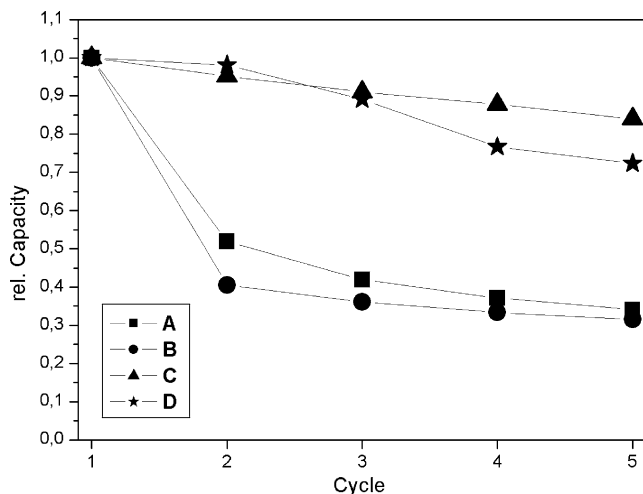


Fig. 6 Comparison of charge capacities

manner is the ability of the CMC binder to stabilise the silicon electrode matrix by covalent binding on the OH-functional silicon surface groups [18].

Fig. 7 illustrates the relative discharge capacities of the investigated electrodes. A and D both cycled in organic electrolyte exhibit a quite flat discharge behaviour during the first five cycles. B and C cycled in an ionic liquid based electrolyte show an increase of the discharge capacity after the first cycle which is allegeable in way that the entire active electrode material was not accessible in the first cycle. In the following cycles, the entire active electrode material is developed and a constant discharge capacity is given. This effect is presumably affected by the properties of the ionic liquid electrolyte in terms of conductivity, viscosity and wettability [19].

Charge–discharge efficiencies shown in Fig. 8 exhibit that the best performance was shown by the composite electrode C cycled in organic electrolyte, respectively, the first cycle and the consecutive ones too. A and D suffer in

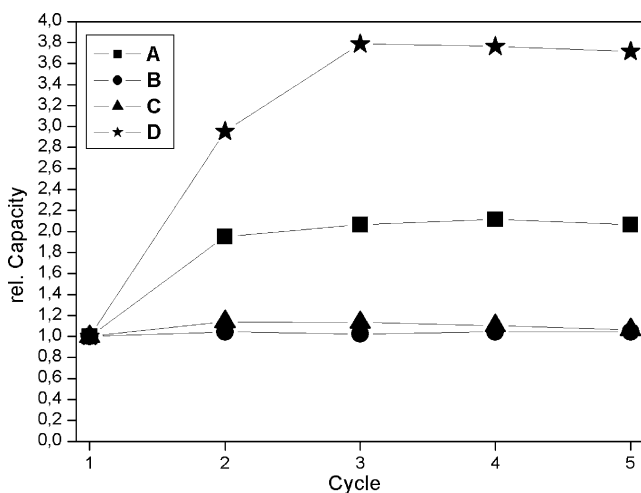


Fig. 7 Comparison of discharge capacities

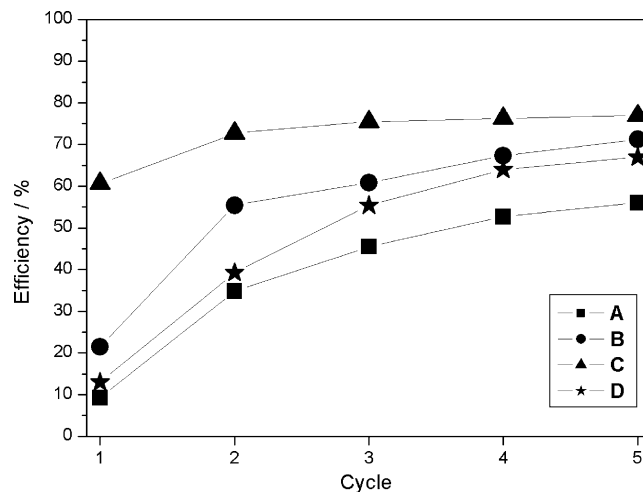


Fig. 8 Comparison of the charge–discharge efficiencies

the first cycle from a quite high irreversible capacity caused by a disadvantageous ratio of material development and parasitic reactions. Electrode B exhibits incipient from the second cycle, a related performance to C. In the first cycle, the efficiency is quite low caused by the limited film forming ability of the used electrolyte and particle loss. However, electrodeposited silicon shows electrochemical activity and a cycling behaviour which is promising for further development.

Conclusion and comments on the results

In this short paper, it was shown that it is possible to deposit silicon directly on a copper current collector out of organic and ionic liquid electrolytes using SiCl_4 as the silicon source. The reductive decomposition of the SiCl_4 precursor occurs around 1.0 V vs. Li/Li^+ in PC and $\text{Pyr}_{14}\text{TFSI}$. An alternative silicon sources would be preferable to avoid complex plating conditions regarding to corrosiveness and the disadvantageous physical properties of SiCl_4 . The SEM images illustrate that the deposited silicon particles have sizes ranging from 100 to 500 nm and the application of a structured copper substrate is suggested. Comparative studies on deposited silicon electrodes and nano-scale silicon composite electrodes have shown that the deposited silicon is electrochemically active in matters of electrochemical lithation and delithation. Cyclic voltammograms of electrodeposited silicon electrodes exhibit that they are consistent with the shape of crystalline nano-scale silicon composite electrodes. In comparison to silicon composite electrodes, the deposited ones show a limited performance in terms of efficiency and absolute capacity but the results in this preliminary study seems to be promising to establish this method as alternative for the silicon anode preparation. Especially for thin film silicon anodes, an electrochemical method provides an opportunity

for a cheap approach on these. In summary, for the possible use as anode material for LIB, further investigations are required to optimize the deposition conditions to improve the deposited silicon in terms of morphology, homogeneity, adhesion and the amount of the deposited silicon.

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