Electrochemical investigation of ion-beam sputter-deposited carbon thin films for Li-ion batteries

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Abstract
The C-rate capability of 230 nm- and 16 nm-thin ion-beam sputter-deposited amorphous carbon films, an interesting class of carbonaceous material for lithium-ion batteries, was investigated up to Li-platting. Stepwise ascending and descending constant Li⁺ currents after each fifth cycle, followed by hundreds of cycles with the highest current were applied. The carbon films show similar cycling with irreversible losses during the first five cycles, followed by reversible cycling with a capacity close to that of graphite. The capacity is significantly lower at high currents; however, it is restored for subsequent cycling again at low currents. Differential charge and differential capacity curves reveal three Li⁺ uptake and three Li⁺ release peaks located between 0 and 3 V. Irreversible as well as reversible Li bonding can be associated with all these peaks. Irreversibly bonded Li can be found at the surface (solid electrolyte interphase) and in the bulk of the carbon films (Li trapping). Reversible Li bonding might be possible inside the carbon films in graphite-like nano-domains and at defects. The thinner film reveals a more pseudo-capacitive cycling behavior, pointing to enhanced Li kinetics.

Graphical abstract

Keywords Lithium-ion batteries · Electrochemistry · Lithium · Amorphous carbon films · C-rate capability · Differential capacity curve · Differential charge curve

1 Introduction
Carbon is abundant, environment benign, and a long-standing basic material for industrial purposes. For example, graphite is by far still the most commonly used Li⁺ storage media (active electrode material) in commercial lithium-ion batteries (LIBs) [1–4]. The success story of graphite as a
negative electrode mostly relies on its good cycling capability, i.e., reversible Li\(^+\) insertion and extraction, with low potential hysteresis and low Li de-intercalation potential. Graphite possesses at least a 2000 cycle life and a reversible Li storage capacity of 372 mAh/g [2]. The proper cycling stability is thought to originate from the relative large distances between the densest packed (0001) carbon atomic layers [Fig.S1a in the supplemental information (SI) accompanying this work] and the resulting weak interlayer bonding. Moreover, the densely packed carbon sheets with its strong bonded atoms are actually not affected during Li insertion and release. This offers a suitable weak bonding of Li\(^+\) to the host carbon material and enough free space to accommodate Li\(^+\) for a smooth intercalation and de-intercalation process. Nevertheless, there are huge efforts to increase the Li\(^+\) storage capacity for the next generation of LIBs, but no strategy was successfully without a heavy incorporation of graphite in the composite LIB electrode [5]. There were also attempts to reduce the content of graphite using thin amorphous carbon films [5–13].

Although graphite is vastly used in LIBs and was studied thoroughly [1–22], investigations on amorphous sp\(^2\)-bonded, sputter-deposited thin carbon films as active material are relatively rare [17, 18, 21, 23–28]. It is stated that thin amorphous carbon films do not show reversible Li intercalation, not even at the lowest possible potential of 0 V vs Li reference material [21]. Moreover, graphite electrodes cannot be cycled in propylene carbonate (PC) electrolyte [15]. With PC, a massive solvent reduction occurs with a relatively low degree of electrode passivation [15] and without reversible Li intercalation. A massive solvent reduction which impedes Li\(^+\) insertion into electrodes was found not exclusively for carbon electrodes cycled in PC [15], but also for Si wafers [29]. On the other hand, other research groups [17, 20, 22–26] found disordered carbon to be of interest because of capacities higher than for graphite. Consequently, contradictory results were reported.

Briefly, hundreds of different carbon types were found useful as negative electrodes in LIBs [3, 4] such as natural and synthetic graphite, coals, and a wide variety of other materials prepared by pyrolysis of organic precursors [3, 4]. Pyrolysis produces the so-called soft and hard carbon when the precursor decomposition stacks planar carbon aromatic structures (graphene sheets) in a parallel fashion (Fig.S1a) or in a house-of-cards manner, respectively. Soft carbon graphitizes upon heating to very high temperatures, whereas hard carbon does not graphitize at all [3, 4]. The house-of-cards stack arrangement of hard carbon produces a lot of pores with the size of the graphene sheets [3, 4]. In soft carbon exist regions of unorganized carbons, called turbostratic disorder [3, 4], which continuously diminishes by heating [3, 4]. Heating hard carbon above 1000 °C diminishes the porosity, but the misalignment (disorder) does not disappear even not at 3000 °C [3, 4]. The carbon types can be classified in three categories on the basis of the dominant physical mechanism for reaction of lithium with the carbonaceous materials [3, 4]. These classes are graphite carbon, hydrogen-containing carbon, and hard carbon [3, 4].

Carbon atoms in a graphite structure are arranged in parallel dense packed hexagonal atomic layers (Fig.S1a). There is only a weak bonding between the hexagonal layers, and Li can be inserted and extracted rather easily between the layers, which results in a low potential hysteresis between Li intercalation (at ~0.1 V) and de-intercalation process (at ~0.15 V) [3, 4].

More Li can be reversibly inserted into the second class of carbon materials, i.e., in hydrogen-containing carbon. For example, petroleum pitch heated at 550 °C gives H\(_0.4\)C with a reversible capacity of ~900 mAh/g which is almost three times that of graphite [3, 4]. Lithium is thought to bond in the vicinity of the hydrogen atoms which unfortunately induces also disadvantages. A large potential hysteresis between Li insertion and extraction of up to 1 V is present with a high Li extraction potential of about 1 V. This resembles that the additional inserted Li may bond strongly in the vicinity of the H atoms and is difficult to extract. The inserted Li may transfer a part of the valence electron density to the H–C bond and in this way disturb the H–C bond, i.e., the atomic positions of the corresponding H and C atoms. This change leads to activated processes which produce the large potential hysteresis of 1 V [3, 4]. The H-containing carbon shows also irreversible Li insertion taking place continuously cycle by cycle [3, 4]. When Li is extracted, the original H–C bonds may not fully reform and the cycling capacity slowly decreases [3, 4]. The H-containing carbon cannot maintain the large capacity for more than a dozen cycles [3, 4].

The third class of carbon materials, i.e., hard carbons, possess a lower potential hysteresis for Li insertion and extractions, but also a lower reversible capacity than H-containing carbon, but still up to two times that of graphite [3, 4]. The higher amount of reversibly inserted Li is thought to stem from weak bonds of Li to disordered sides of hard carbon [3, 4]. On the other hand, disorder (high porosity and impurities) is responsible although for a high amount of irreversible bonds [3, 4, 24, 26].

Summarizing, hard carbon possesses nano-porosity, and a reversible capacity of around 550 mAh/g [26] but suffer from large irreversible capacity [3, 4, 26]. Hydrogen-containing carbon possesses capacities up to 900 mAh/g but suffer from high irreversible capacity, low-density, large charge–discharge potential hysteresis [3, 4, 26] and bad cycling. The advantage of good cycling, low potential hysteresis, and low irreversible Li insertion makes carbon in the graphitic structure to be the predominant carbon material in LIBs.
Recently [26], a fourth class of carbonaceous materials that reversibly reacts with lithium was proposed. This is sputter-deposited amorphous carbon [26], where the amount of porosity is thought to be low [23]. Magnetron-sputtered carbon films show metastable amorphous sp$_2$ (graphite-like) carbon domains interconnected by a random network of sp$_3$ (diamond like) bonded atomic sites, also known as diamond like thin films [23]. The sp$_3$ bonded random network can be visualized as regions showing a lot of carbon atoms with dangling bonds where Li may bond in a reversible or also irreversible way. A large fraction of sp$_3$ bonding was found to be not favorable for reversible Li insertion and release [23]. Further experiments done by annealing the carbon films up to 700 °C reduces the sp$_3$ content and increases the sp$_2$ content [25] which should favor reversible Li insertion and release. However, this expectation was not met [25]. The reason is thought to be the high level of compressive stress in annealed films [25]. After annealing, stress up to 30 GPa can be present as calculated from Raman measurements [25]. The stress may act against Li insertion (diffusion) reducing considerable the capacity [25]. Beyond the first cycle, non-annealed carbon films reveal large reversible capacities of about 800 mAh/g [26] due to Li bonding to dangling bonds of amorphous carbon [26]. Due to the amorphous structure, there are varying bonding positions [26] which spread the potentials of both Li insertion and release over a 2 V range [26]. Some of the defects may arise from H, O, and N impurities. The bonding of Li to oxygen is strong and, consequently, it should be more difficult to remove Li bonded in the vicinity of oxygen than from clean carbon [26]. This may also explain the large hysteresis found in magnetron-sputtered carbon films [26]. Unfortunately, magnetron-sputtered carbon films show also irreversible capacities exceeding 60% [25], presumable due to SEI layer formation.

It is generally assumed that during charging of a carbon electrode from the open-circuit voltage (OCV) down to 0 V vs Li reference electrode, the incoming Li$^+$ ions with their solvation molecules build up an SEI layer and are intercalated into the carbon structure. SEI formation takes place during the first few cycles [22], while the initial SEI layer is composed of Li$_2$O [18]. The potential for SEI formation is not a fixed value, but it is generally thought to range from 0.3 to 2 V [15, 19, 22]. Operando experiments on the investigation of SEI formation on a 70 nm-thin amorphous carbon film produced by magnetron sputtering was done by neutron reflectometry (NR) [27, 28]. NR is very sensitive on layer thickness changes and was applied for the first two cycles [28]. The analysis of the NR pattern allowed to gain results on the SEI layer growth and, separately, on changes of carbon film [27, 28]. SEI layer formation was measured to happen over the whole potential range down to an electrode potential of 0.05 V [27, 28]. The SEI layer thickness reached approximately 35 nm at 0.05 V [27, 28], and reduces to 31 nm for delithiation to 3.3 V [28]. The intercalation of Li ions inside the carbon film enhanced the carbon film thickness from about 70 nm to 84 nm at 0.05 V [27] which corresponds to a film thickness increase of 20% which is larger than that expected for graphite (12% for full lithiation) [28]. The Li concentration inside the carbon film at the lithiation cut-off potential of 0.05 V was found to correspond to Li$_{0.2}$C. The Li ions inserted into the carbon material could not be fully extracted [28]. A Li concentration corresponding to approximatively Li$_{0.3}$C remains trapped into the amorphous carbon material [28], which is more than half of the maximum inserted Li concentration. Adding to the Li trapped inside the carbon film also the Li consumption due to the SEI layer growth, a large irreversible Li capacity results with a Coulomb efficiency well below 50% for the first cycle of the carbon films deposited by magnetron sputtering. Although the trapped Li concentration of Li$_{0.3}$C is larger that than for full lithiation of graphite (Li$_{0.16}$C), the amorphous carbon films can be further cycled [28], but with a reversible capacity lower than that of graphite. However, the cycling proceeds to Li concentrations higher than that of graphite, pointing to different, and up to date unknown, Li insertion and extraction processes. Some updated and closely related reviews on a more complex picture about LIB electrodes can be found in [30–33].

For film electrodes composed of graphite particles, an extremely low potential change in cyclic voltammetry (CV) with a sweep rate of only 2 × 10$^{-6}$ Vs$^{-1}$ [16] found reversible Li$^+$ intercalation at potentials below 0.3 V [14, 16]. Higher scan rates shift continuously the Li insertion (extraction) to lower (higher) potentials [14, 15]. A reason for the potential shifts may be overpotentials. They may originate from resistance to the Li$^+$ flow, e.g., the potential decay at the electrolyte resistance and the charge transfer resistance at the electrode surface. Consequently, there is an overpotential increase when the Li$^+$ current increases. The overpotentials shift the intercalation (de-intercalation) potentials to lower (higher) potentials, reaching in that way sooner the lower (higher) end-potential (cut-off potentials) [35–37]. This has the consequence that the CV cut-off potential is reached even before Li intercalation into carbon has finished. In the present work, full lithiation up to the onset of Li-plating was realized by the use of negative cut-off potentials, partly avoiding the problem with overpotentials.

The long-term cycling stability and C-rate capability of sputtered carbon films were not studied until yet [23–26]. Here, we present such a study for ion-beam sputtered thin (16 nm) and thick (230 nm) carbon films. The investigations were performed with low and high Li$^+$ currents in PC-based electrolytes, where, as mentioned, literature commonly neglects reversible lithiation [15].
The article is organized as follows. The first part of the experimental procedure section describes the electrodes. The last part of the second section describes the electrochemical cell, the applied electrochemical measurement techniques, and the cycling procedure. The results and discussion section present the data obtained from the electrode without carbon film, and from an electrode coated with 230 nm and 16 nm carbon films. The first subsection presents the tests performed on electrodes without carbon films to enable a distinction of the cycling contribution from solely the carbon films. The next two subsections present first the potential-integrated results followed by the potential-resolved results of the electrodes coated with carbon films. The fourth subsection incorporates concluding remarks and an outlook. The last section summarizes the findings. The appendix shows how the results and the errors were calculated.

2 Experimental procedure

2.1 Electrodes

Figure S1b presents a photograph of the working electrode. It consists of a 1-inch polished quartz crystal disk of 3.2 mm thickness with a 15 nm-thin chromium film on top acting as an adhesion layer for a 200 nm-thick copper current collector film. Afterwards carbon thin films were deposited as active material. The layer deposition was performed by ion-beam sputtering as described in reference [38]. A graphite target disk was used for carbon film deposition. The radius of the circular lithiated surface, the carbon film thickness, and the mass density of the carbon film are crucial parameters for capacity determination (see appendix). The radius of the lithiated zone was determined visually on the electrode surface after cell disassembly and coincides with that of the Li counter electrode and the radius of the electrolyte chamber tube. Grazing incidence X-ray diffraction (GI-XRD) and X-ray reflectometry (XRR) were measured with the help of a Bruker D8 DISCOVER diffractometer using CuKα radiation. Raman scattering investigations were performed with a Bruker SENTERRA Raman microscope using a laser wavelength of 532 nm.

The thicknesses of the amorphous carbon films were chosen as 16 nm and 230 nm due to reasons based on LIB improvement. Carbon coatings are claimed to represent a mitigation strategy to solve the challenge of low conductivity and degradation in LIBs, i.e., the Li⁺ lost by side reactions and the contact loss of LIB active material from the current collector [2, 7, 33]. Nano-meter carbon coatings were found to improve cycling of (i) the cheap and environment friendly LiFePO4 and the high-voltage LiNiₓMnᵧCo₂O₄ (NMC, x + y + z = 1) positive electrodes, and of (ii) the cheap and environment friendly graphite and silicon negative electrodes [2, 7–14, 33]. Beyond carbon coatings, Si/C nanocomposite materials are anticipated to be the anode material for the next-generation LIBs [5–13]. Magnetron-sputtered Si/C multilayers with amorphous carbon layers with thicknesses ranging from some tenths of nm [7, 11–13] down to 2 nm [7–10] were found useful for silicon cycling. Consequently, we selected a very thin carbon film of only 16 nm thickness for investigation. Carbon films with 230 nm thickness were also investigated to analyze bulk properties of ion-beam sputter-deposited amorphous carbon. This enables to compare the results obtained from confined amorphous carbon (16 nm-thin carbon film) to that from more bulk like amorphous carbon (230 nm-thin carbon film).

The film deposition rate was determined using XRR and/or mechanical profilometer experiments. For that purpose, films are deposited for a given time interval, e.g., 19 min, on substrates with flat surfaces. For films thicker than about 100 nm, half of the samples surface was capped by aluminum foil and removed after film deposition. The height of the film step edge is then measured with a mechanical profilometer. The step profilometry measurements were confirmed by XRR measurements applied on the same samples. For films thinner than, e.g., 100 nm, only XRR was applied to determine the film thickness, as described in the following.

Figure 1a presents the measured XRR pattern from a silicon wafer coated with carbon for 19 min. The X-ray reflection from the carbon film interface to air and Si wafer produces oscillations (the so-called fringes). The fringe periodicity in the scattering vector space (Qz) is given by the film thickness. XRR simulations based on the Parratt formalism using the Parratt32 package were performed. The best fit to the measured XRR pattern is plotted in Fig. 1a with a continuous line. This XRR simulation corresponds to a flat carbon film with a roughness value below 1 nm, a thickness of (15.9 ± 0.3) nm, and a mass density of (2 ± 0.03) gcm⁻³. The error values correspond to a 10% deviation of χ². Correspondingly, the carbon film deposition rate amounts to (0.84 ± 0.02) nm per minute.

The film thickness can be determined from XRR measurements also without the need of XRR simulations using a simple method based on Kiessig fringes analysis (for details, see the supporting information of ref. [38]). There (Fig. 1c), the square of the fringe order added with 0.5 due to reflection reasons, is plotted against the square of the scattering vector position of the corresponding fringe. The slope b delivers the film thickness (d) according to the equation \(d = 2\pi b^{0.5}\) (for details, see the supporting information of ref. [38]). The Kiessig analysis of the 19 min carbon film deposition (Fig. 1c) delivers a carbon film thickness of (16.5 ± 0.05) nm which agrees with the film thickness determined from XRR simulations. Consequently, we considered the rounded value of 16 nm as the film thickness. Figure 1b presents
the measured XRR fringes from the electrode coated with carbon for 275 min. The corresponding Kiessig analysis is presented in Fig. 1d. A film thickness of (229 ± 0.2) nm is obtained, from which we consider the rounded value of 230 nm as the film thickness.

Figure 1e presents the Raman spectroscopy measurements performed on the electrodes coated with 16 nm- and 230 nm-thin carbon films, respectively. Raman allows to analyze non-destructively the bonding configuration of all carbon structures (graphite, diamond, graphene, nanotube, and fullerenes) [18, 39–43]. Amorphous carbon films are assumed to possess intermediate structures between graphite (fully sp² hybridized) and diamond (fully sp³ hybridized). The Raman spectra of the carbon films (Fig. 1e) show broad emissions marked with the letters D, G, and 2G which resemble the typical Raman spectra of amorphous carbon with a low amount of sp³ structure, i.e., that of the so-called sp² hybridized low-density carbon. The vertical arrow in Fig. 1e points to broad peaks centered around 600 cm⁻¹ which are found for hydrogen-free carbon films [40].

GI-XRD confirmed the amorphous network of the carbon films. Only reflexes originating from the copper current collector are observed (Fig. 1f).

2.2 Electrochemical cell and cycling procedure

The electrochemical investigations were performed using a self-constructed three-electrode electrochemical cell, where distances between the electrodes attain large values of 30 mm without the need of a separator. Propylene carbonate (PC, Sigma-Aldrich, anhydrous, 99.7%) with 1 M LiClO₄ (Sigma-Aldrich, battery grade) was used as an electrolyte. The cell was assembled and disassembled within an argon gas-filled glovebox with O₂ and H₂O contents less than 1 ppm. The counter and reference electrodes are made of metallic lithium (1.5 mm foil, 99.9%, Alfa Aesar). Hence,
the electrochemical cell is a so-called LIB half-cell. If the carbon and Li counter electrode are electronically connected, a spontaneous Li insertion into the unliithiated carbon electrode happens. In this context, the carbon electrode is the positive electrode and the lithium counter electrode is the negative electrode. The Li\(^+\) insertion process into the carbon electrode (Li\(^+\) uptake) is then a discharge process and the Li\(^+\) extraction process from the carbon electrode (Li\(^+\) release) is a charge process. In the following, the galvanostatic Li\(^+\) insertion and extraction process into the carbon electrode is also denoted as constant current (CC) lithiation and delithiation, respectively. CC lithiation and delithiation were performed at room temperature with a Biologic SP150 potentiostat and the EC-lab software.

Figure 2a illustrates the meaning of the term “full lithiation up to Li-plating” which is used within this work. During CC lithiation, the voltage E\text{we} between the carbon film and the lithium-metal reference electrode is reduced theoretically to a minimum value of zero. As mentioned, overpotentials may push down the potential of the Li\(^+\) intercalation process to even negative potentials of E\text{we} \[34–37\] as presented in Fig. 2a. The first Li\(^+\)-insertion/extraction cycle in Fig. 2a was performed without a cut-off potential. This leads to a straight horizontal line marked with the first arrow which indicates Li deposition on the surface of the electrode, which is called Li-plating [44]. Li stripping is the remove of plated Li during the delithiation process, which is often incomplete as is the case in Fig. 2a. The lithiation process of the second cycle in Fig. 2a was performed with a cut-off potential of E\text{we} = −0.53 V which is just before the onset of Li-plating. This will be further denoted as full lithiation up to Li-plating. The differential charge and capacity curves were corrected by shifting the negative cut-off potential to the required higher and lower values for the Li insertion and release part of the curves, respectively. In that manner, the differential charge and capacity curves do not show negative potentials.

Figure 2b presents the test procedure applied in this work to investigate the performance of thin carbon films for LIBs. Consecutive blocks of five CC cycles with stepwise ascending current from 0.13 to 11.63 Am\(^{-2}\) were performed. Afterwards, the same procedure was reversed, i.e., with descending currents from 11.63 to 0.13 Am\(^{-2}\) (C-rate capability). During the next step, the carbon films were CC cycled for hundreds of cycles with the highest current of 11.63 Am\(^{-2}\). Finally, a few CC cycles with the lowest current of 0.13 Am\(^{-2}\) were performed to see if the capacity retains back to its value at the first cycles.

Figure 3 describes how d\(Q/dV\) plots are derived from CC measurements. Figure 3a presents the potential profile, i.e., E\text{we}(t), during the first CC cycle of the 16 nm-thin carbon film. Figure 3b presents the same potential profile but with reversed axes, i.e., t(E\text{we}). Figure 3c presents the differential of Fig. 3b multiplied with the current density I which results in the d\(Q/dV\) curves as given by the simple equation written in the legend of Fig. 3c (see also Eq. (7) in the appendix). It can be observed that the peaks in the d\(Q/dV\) curves (Fig. 3c) marked with the roman numbers I, II and III correspond to flat regions in the potential profile (Fig. 3a), indicating potentials of predominant Li\(^+\) uptake or release. The Li\(^+\) uptake (release) process corresponds to the negative (positive) ordinates. Note that d\(Q/dV\) curves can be compared to CV curves, because both of them represent the amount of charge (d\(Q\)) up-taken or released within a small potential interval d\(V\). The difference between d\(Q/dV\) and CV relies on how the charge d\(Q = d(I)t\) is build up. For the d\(Q/dV\) curves, there is constant current I. A d\(Q/dV\) intensity variation is then given by different time intervals dt needed to induce a potential interval d\(V\). For CV, the time intervals dt are constant and given by the potential ramp. Features in CV appear, because the current can vary during subsequent equal time intervals, i.e. d\(Q = tdI\). Note that the potential position of d\(Q/dV\) and CV peaks may slightly differ due to differences in
overpotentials (due to different currents). In general, it can be claimed that the shape of \( \frac{dQ}{dV} \) plots is similar to that of cyclic voltammetry measurements.

### 3 Results and discussion

#### 3.1 Electrode without carbon film

The electrode without carbon film was investigated to see whether the current collector participates in electrochemical cycling of the electrode. Figure 4a presents the potential profile of the first five CC cycles of the electrode without a carbon film, at the lowest Li\(^+\) current (Fig. 2b). During the first lithiation step seven times more Li\(^+\) is introduced than what can be extracted. This may stem from an irreversible Li\(^+\) consumption by reduction of surface copper oxides into Li\(_2\)O and copper metal, and an SEI layer formation by electrolyte reduction. Notice that the surface oxide reduction may belong also to the SEI layer formation. The Li\(^+\) uptake in the next cycles is strongly reduced, but there is a reversible Li\(^+\) uptake and release even if the amount of Li\(^+\) charge is very low (Fig. 4b, c).

Figure 4b presents the \( \frac{dQ}{dV} \) plots calculated from the potential profiles of the first, second and fifth cycle on the blank copper collector film. The area between the \( \frac{dQ}{dV} \) plot and the ordinate corresponds to the Li\(^+\) charge uptake (negative values) and release (positive values). The high irreversible Li\(^+\) consumption during the first cycle can be observed also in Fig. 4b. A sharp and strong peak (marked with A in Fig. 4b) appears at \(-0.8\) V. A second broader one (marked with B in Fig. 4b) is located at \(-0.6\) V and appears as a shoulder.
The dQ/dV curves of the second and fifth cycles are similar to each other. The strong peak A is no more present, a rest of peak B is still visible and seems to be responsible for the reversible lithiation/delithiation processes on the pure Cu electrode. The peak of Li⁺ release appears at ~2.5 V and is marked with C in Fig. 4b. The large potential difference between peak B and C of up to 2 V indicates cycling of strongly bonded Li, e.g., to an oxide. Peak A may correspond to the irreversible SEI formation including electrolyte and surface oxide reduction. The Li⁺ uptake (release) marked with B (C) may, at least partially, correspond to a reversible incorporation of Li₂O into the SEI [45]. Figure 4c shows that the Li⁺ release from the blank electrode during the cycling protocol of Fig. 2b is extremely low in comparison to that of the electrode with the carbon film. This indicates that the charge density associated with the Li⁺ release and uptake from the electrodes with carbon films stems not from the substrate.

3.2 Electrode with carbon films: C-rate capability and extensive cycling

Figure 5a presents the gravimetric charge capacity of the 230 nm-thin carbon film during the cycling protocol presented in Fig. 2b. The Coulombic efficiency is given in Fig. 5b. The C-rates correspond to every fifth cycle. The normalized capacity is displayed in percentage on right vertical axis of Fig. 5a. There, the capacity is divided by the highest possible capacity of graphite (372 Ahkg⁻¹). For the first five cycles, which were performed with the lowest Li⁺ current density, the capacity of the 230 nm carbon film is markedly higher than that of bulk graphite. The capacity of Li⁺ insertion in the first cycle amounts to an incredible high value of 1389 Ahkg⁻¹ which is out of range in Fig. 5a. The Li⁺ extraction process in the first cycle amounts only to 560 Ahkg⁻¹ (Fig. 5a). The Coulombic efficiency is 40% (Fig. 5b), meaning that 60% of inserted Li⁺ gets lost during the first cycle. The Li⁺ losses during the next four cycles are continuously reduced to approximatively 10% for the fifth cycle (90% efficiency, Fig. 5b). After 10 cycles, the Li⁺ loss is marginal and within the error limits (Fig. 5). The reason for the Li⁺ losses points to side reactions such as SEI formation which consumes lithium. Notice that during the first five cycles, although more Li is inserted than extracted, the capacity of Li⁺ extraction is higher than the maximal capacity of bulk graphite.

For more than ten cycles, the lithiation and delithiation capacity is equal within error limits (Fig. 5a). Correspondingly, the Coulombic efficiency tends to 100% which means almost reversible behavior (Fig. 5b). The high error limits in Fig. 5b are due to the fact that the lithiation and delithiation time intervals decrease to below 3 s for the highest current. The small lithiation time intervals for thin films lead to very high C-rates reaching 1587 C at the highest current, where the capacity reaches only 5% of that of the theoretical capacity of graphite (Fig. 5a). Higher currents often increase the overpotentials while pushing the lithiation potentials below the cut-off potential, reducing in that way the capacity. However, this is not the case in this work because of the protocol used (Fig. 2). This means that a wrong cut-off potential is not responsible for the strong stepwise decrease of the capacity with stepwise higher current density in Fig. 5a. It has to be a different process.

A straightforward explanation might be found in kinetic limitations. Li diffusion in amorphous carbon films may limit the rate of the lithiation process. When the current density delivers more Li than can be transported away from the surface by diffusion, the excess of incoming Li is deposited as Li metal on the electrode surface (Li-plating). Concerning this scenario, the Li-plating effect appears especially for high current densities before full Li intercalation is reached. Consequently, the carbon films are not fully lithiated at high currents. This explains the decrease in capacity with higher current as originating from a premature appearance of Li-plating due to limited Li migration inside the carbon films.

Fig. 5 C-rate capability of the 230 nm-thin carbon film. a Gravimetric charge capacity and b Coulombic efficiency for the cycling protocol presented in Fig. 2b. The C-rate was calculated by dividing 1 h by the lithiation time interval given in hours. The C-rate values are given in C-units in a (do not confound them with the coulomb unit of charge)
Figure 5a shows that full lithiation may probably be achieved only with the smallest current of 0.13 A m^{-2} which possess a C-rate below 1 C. Already, the next current of 0.44 A m^{-2} reduces the carbon film capacity below that of graphite, revealing that Li-platting occurs before full intercalation already at 0.44 A m^{-2} with a rate of 4 C. Figure 5 shows that the capacity reduction is of reversible nature (compare cycles 6–10 and 36–42 in Fig. 5a). At high currents, the carbon film is only partially lithiated which may preserve the carbon film from deterioration and may cause reversibility. Consequently, the Li diffusivity in the carbon film has to be low at room temperature, presumably due to Li traps which bond the Li atoms stronger to the host material. Cycling with lower currents restores the capacity in a step-wise and reversible manner (Fig. 5a). For the lowest current density, the capacity reaches that of graphite (Fig. 5a). The experiments on C-rate capability (Fig. 5) show no indication of film destruction which makes the carbon film to a good electrode candidate in LIBs.

Figure 6 presents the C-rate capability results for the thinner (16 nm-thin) carbon film. Figure 6a shows that the capacity of the thinner film does not change systematically with the strength of the applied current, as it is the case for the thicker carbon film. The capacity for Li insertion of the 16 nm-thin carbon film during the first cycle is again high and out of range in Fig. 6a. It amounts to about 3720 Ahkg^{-1} which is ten times more than that of graphite and exceeds even that of silicon (3579 Ahkg^{-1}). Lithium extraction produces a capacity of about 1360 Ahkg^{-1} during the first cycle, evidencing huge irreversible capacity losses. The Li\textsuperscript{+} charge loss during the first cycle (i.e., the difference of inserted and extracted charge) of the electrodes with 16 nm-thin and 230 nm-thin carbon film amounts to 1 Ahm^{-2} and 4.7 Ahm^{-2}, respectively. It is higher for the thicker carbon film, indicating side reactions not only at the electrode surface (SEI formation), but also irreversible reactions inside the electrode (probably Li trapping) may occur. This agrees with results obtained from NR measurements on 70 nm-thin amorphous carbon film deposited by magnetron sputtering [27, 28].

After cycling, the carbon film electrodes were disassembled from the electrochemical cell in the Ar gas-filled glove box. Visual inspection shows that the electrode surface is still intact. The electrode was washed in the electrolyte solvent, PC, for 10 min and subsequently for 5 min in acetonitrile. The washing step with acetonitrile removed the part of the 230 nm-thick carbon film from the current collector which was lithiated during cycling (Fig. S1c). A rest of non-lithiated carbon at the film periphery is still visible as a black circle (Fig. S1c). The 16 nm-thin carbon film could not be properly analyzed by visual inspection, because due to the low thickness, it cannot be discriminated from the current collector.

Figure 7 presents the capacities of all cycles for the 230 nm (Fig. 7a) and 16 nm (Fig. 7b) thin carbon film. Subsequently to the cycling procedure of Fig. 2b, the electrodes were cycled up to Li-platting for several hundreds of cycles with the highest current. The capacity attains again a very low value. Afterwards, further 27 cycles were performed with the lowest current for the 230 nm-thin carbon film (Fig. 7a). The capacity recovers again to that of graphite. This happens also for the thinner carbon film (Fig. 7b). Summarizing, the ion-beam sputter-deposited carbon thin films show a reversible capacity almost equal to that of graphite. The capacity decrease for high currents is very likely due to Li diffusion limitations. The maximum capacity of graphite is restored for cycling afterwards again with low current. A drawback is the presence of a large irreversible capacity loss during the first cycles similarly to that of hydrogen-containing carbon [3]. The irreversible capacity does not exclusively stem from surface effects (SEI formation) but also from reactions inside the films indicating Li trapping, because the Li loss increases for the thicker film. These Li losses appear to be independent from the sputter deposition method, i.e., ion-beam sputtering (this work) and magnetron sputtering (ref. [27, 28]). Defective carbon is believed to be the reason for the first cycle capacity loss [31].
3.3 Electrode with carbon films: differential charge and capacity plots

The charge and capacity values vs cycle number discussed above represent integrated values over the whole electrode potentials (Ewe). More insight can be obtained by unfolding the charge and capacity with respect to the electrode potential. The obtained differential charge vs potential plots (dQ/dEwe, called dQ/dV plots) and capacity vs potential plots (dC/dEwe, called dC/dV plots) show the partial charge and capacity contribution at each potential. Such plots are analyzed in this subsection to discriminate (i) the potential location of reversible and irreversible processes (Li bonding), (ii) if the processes take place at the surface or in the bulk of the carbon films, and (iii) the microscopic locations of the Li bonds, e.g., Li intercalation into graphitic (sp²) like nano-domains, or bonding of Li bonds to defects such as unsaturated carbon bonds, locally sp³ bonded carbon, and impurities [3, 4]. A decrease of intensity or even a disappearance of peaks in the differential charge curves may indicate the presence and location of irreversible Li bonds. Such an analysis is presented in Fig. 8.

We assume that the Li⁺ uptake for SEI formation (surface process) is independent on the carbon film thickness. Note that this is a crude approximation, because thicker films need longer times up to full lithiation for a given current, and in that way, thicker SEI layers may grow. On the other hand, bulk processes such as the Li⁺ insertion into carbon material should clearly depend on the carbon film thickness. Consequently, for a better visualization, the dQ/dV curves are divided by the amount of carbon present in the electrode, getting dC/dV (dC: partial capacity). These plots should help to identify the ability of the carbon material to accommodate Li⁺ per carbon atom in an irreversible or reversible way. Hence, a comparison of dQ/dV and dC/dV can discriminate surface processes and bulk processes. Li bonds within the bulk of the carbon films should manifest as equal differential capacity, whereas bonds at the film surface as equal differential charge. This analysis is presented in Figs. 9, 10.

Figure 8 presents the dQ/dV plots of the first, second, and fifth cycle for the 230 nm (Fig. 8a) and 16 nm (Fig. 8b) carbon film electrode. Negative (positive) values correspond to Li⁺ uptake (release). The area between the dQ/dV curve and y = 0 (i.e., the integrated total charge) reveals that the Li⁺ uptake is higher than the release during the first cycle. For the first cycle, there are three predominant Li⁺ uptake peaks marked with roman numbers I, II, and III. Peak I which is centered at ~ 1 V was measured also on magnetron-sputtered 1.1 µm thin carbon films [24] and is thought to appear from SEI formation [24]. The sharpness of peak II which is located around 0.5 V indicates a well-defined process. Such a peak was not measured for magnetron-sputtered carbon films [24, 27, 28]. Graphite show a peak around 0.65 V which is attributed to SEI formation [19]. CV on 100 nm-thin carbon films prepared by an electron beam deposition technique [16, 17] shows two peaks at 0.75 V and 0.5 V in the first cycle, which roughly can be assigned to the peaks I and II of the present work. Peak III of the present work at 0.3 V is a region of Li intercalation into graphite. The operando NR experiments revealed that the SEI formation and Li insertion into the carbon film proceeds at all potentials [27]. This may indicate that all peaks of Fig. 8a, b might be due to SEI formation and also due to Li insertion into the bulk of the carbon films. Delithiation (Fig. 8a, b) produces a broad peak centered at 1 V which indicates processes at various potentials, i.e., from various different Li-bonding sites.
During the second cycle (green dashed curve in Fig. 8a, b), the amount of incorporated Li\(^+\) becomes considerable smaller compared to the first cycle, in agreement with the decay of the capacity (Figs. 5, 6). All peaks become smaller and are smeared out, meaning that irreversible Li-bond formation takes place at all peaks (I, II, and III). The dQ/dV plots of the second and fifth cycle do not show peaks and are rather of rectangular shape which is similar to supercapacitors [46–48]. Interestingly, this pseudo-capacitance is of reversible nature and shows high values (~ 400 Ahkg\(^{-1}\)) (Figs. 5, 6, 8). This does not necessarily indicate that Li uptake happens exclusively at the film surface. The mechanism of reversible energy storage in pseudo-capacitive material is possible also at confined regions in the bulk of the electrode [48]. Another possibility is the presence of a variety of bond sites, as expected for an amorphous material. In an ideal battery, the electrochemical reaction occurs at a well-defined potential due to a well-defined Gibbs free energy of the reaction [48]. This is definitively not the case for the sputter-deposited amorphous carbon films. The lithiation and delithiation of the first cycle produces additional disorder in the carbon film which is reflected by the
broadening of the peaks. The dQ/dV curves of the higher cycles (Fig. 8) are similar to CV [17, 18, 21] and dQ/dV [26] curves reported for amorphous carbon films deposited by electron beam evaporation of a carbon target [17, 18] and magnetron sputtering [21, 26].

Figure 8c–f presents differential charge plots during cycling with ascending (Fig. 8c, d) and descending (Fig. 8e, f) currents corresponding to the C-rate capability experiments (Figs. 2b, 5, 6) of the thicker (Fig. 8c, e) and thinner (Fig. 8d, f) carbon film, respectively. Peak II does not appear for the thinner film (Fig. 8d, f). Higher currents shift the peak I to lower potentials and peak II disappears also for the thicker film. Surprisingly, the subsequent decrease of the currents (Fig. 8e) restores all of the Li+ uptake peaks (I–III). Higher currents shift the peak I to lower potentials and peak II disappears also for the thicker film. Surprisingly, the subsequent decrease of the currents (Fig. 8e) restores all of the Li+ uptake peaks (I–III). Also, three recognizable Li release peaks IV, V and IV not seen before appears for the thicker film. This indicates that all six peaks I–VI are build up by reversible Li storage. The insertion peaks I, II, and III may be correlated to the release peaks VI, V, and IV, respectively. The pair of peaks (I, VI) possesses the highest potential hysteresis. The Li+ release peak VI lies at ~ 2.5 V similar to peak C in Fig. 4b for the Li+ release from the blank current collector. Such a high-potential peak indicates the cycling of oxides, where Li is strongly bond. The thinner film shows a more pseudo-capacitive behavior, presumably due to a stronger confinement [48].

Figures 9 and 10 present in direct comparison the differential charge (Figs. 9a, c, 10a, c) and differential capacity (Figs. 9b, d, 10b, d) at relevant cycles of the C-rate capability experiments. At the first cycle (performed with the lowest current applied in this work) (Fig. 9a), the peaks (I, II, III) do not appear for the blank copper electrode and consequently they have to originate solely from the carbon film. Peak I is shifted by 0.2 V to lower values for the thinner film (Fig. 9a). This shift may be induced by a higher overpotential in the thinner than the thicker carbon film. The other peaks (II and III) do not shift at all. The lithiation processes II and III take place during the first cycle in a very similar way for both carbon films. The differential charge consumed during the processes I, II, and III is lower for the thinner compared to the thicker film (Fig. 9a), revealing that bulk processes appear at all three peaks, but are less pronounced for the thinner film. The differential capacity at the processes I, II, and III is lower for the thinner compared to the thicker film (Fig. 9a), revealing that bulk processes appear at all three peaks, but are less pronounced for the thinner film. The differential capacity at the processes I, II, and III is lower for the thinner compared to the thicker film (Fig. 9a), revealing that bulk processes appear at all three peaks, but are less pronounced for the thinner film. The intensity ratio of the peaks

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Fig. 9 Differential charge (dQ/dV) (a, c) and differential capacity (dC/dV) (b, d) curves during the C-rate capability experiment (Figs. 2b, 5, 6) for the 16 nm (uninterrupted curve) and 230 nm (dotted curve) thin carbon film, and the blank copper electrode (dashed line, intensity multiplied with 5 in a and 50 in c). a, b first, c, d fifth cycle with 0.13 Am−2. A color version of this figure can be viewed online.
(thinner vs thicker film) is below 7 which is lower than the ratio of the film thicknesses (230/16 ~ 14.4). Hence, surface processes are more dominant for the thinner film. Consequently, for the first cycle, both, surface and bulk processes contribute to all peaks (I, II, III) of the carbon films.

Figure 9c, d presents the differential charge (Fig. 9c) and capacity (Fig. 9d) of the fifth cycle with the lowest current, where the irreversible losses are strongly reduced (Figs. 5, 6). For blank copper, there is a charge uptake peak at ~0.7 V, and a release peak at ~2.4 V. The charge inserted and released from the thicker film becomes considerable higher than from the thinner film (Fig. 9c). This resembles a strong reduction of surface reactions in accordance with the reduction of irreversible Li bonds during the fifth cycle (Figs. 5, 6). This is also visible in the differential capacity plots (Fig. 9d). The differential capacity of the two films is very similar, revealing a strong reduction of the surface reactions. The peaks I and II are less pronounced and considerable broader. They are shifted to higher potentials, i.e., to ~1.2 V and ~0.8 V, respectively, for the thicker carbon film (Fig. 9d). Peak I is not present for the thinner film, or, alternatively, it is shifted to the position of peak II. The width of the peaks resembles Li-bonding sites of various locations.

Figure 10a, b presents the differential charge (Fig. 10a) and capacity (Fig. 10b) during cycling with the highest current. The Li insertion into the thinner carbon film behaves similar to that of graphite (Li insertion only below 0.4 V). The Li release is different to that of graphite by a Li release signal widespread over a large potentials window (0.5 V–2.9 V). A large potential hysteresis is present. Nevertheless, the Li insertion and release processes have the same strength, and are of reversible nature (Fig. 10a, b). Although the inserted and released differential charge shows a different shape for the thicker carbon film, the total charge is quite similar to that of the thinner carbon film (Fig. 10a).

Although, the thicker film shows 14 times more carbon mass (atoms) than the thinner carbon film, the total Li\(^+\) charge inserted and released is equal to that of the thinner film (Fig. 10a). This strongly reduces the capacity of the thicker carbon film as it can be observed in Figs. 5 and 10b. The intensity of the dC/dV curve of the 230 nm-thin carbon film (dotted curve) is multiplied by 10 in Fig. 10b for better visualization. This clearly shows that surface reactions take place. This must not necessarily be completely attributed to SEI layer formation, but can stem also from kinetic limitations in the thicker carbon film. As mentioned in the preceding subsection, a premature appearance of Li-plating
due to limitation of Li transport inside the thicker carbon films may be the reason for the quite low capacity of the thicker carbon film in Fig. 10b. In the case of the 16 nm-thin carbon film, the Li permeability is probably high enough to transport all incoming Li into the film interior, whereas for the thicker carbon film, the Li permeability is lower and only the surface near region is lithiated. This may indicate a higher Li permeability of carbon material in thinner films, as it was measured for amorphous silicon material in thin layers [49, 50].

Finally, Fig. 10c, d presents the differential charge (Fig 10c) and capacity (Fig. 10d) during cycling back to the lowest current (see Figs. 2b, 5, 6), where irreversible Li bonds are fairly diminished. The charge inserted into the thicker carbon film (Fig. 10c) is higher by a factor which is close to the film thickness ratio, as expected. This is observed also in Fig. 10d where the total capacity (the area between the curve and the $y = 0$ axis) equals for both carbon films emphasizing reversible cycling. This means that not only peak III but also all peaks I–VI are due to reversible bulk processes in the interior of the carbon film.

### 3.4 Concluding remarks and outlook

The differential charge and capacity curves of thick and thin carbon films reveal three predominant Li insertion peaks (I, II, III) located around 1.2 V, 0.8 V, and below 0.4 V as well as three predominant broad Li release peaks (IV, V, VI) which span over a large potential range from 0 up to 3 V and are often smeared out over that range. All peaks can be attributed to reversible but also to irreversible Li bonding to the active material of the electrode during the first cycles. The irreversible Li bonds are located at the surface (SEI layer formation) and also in the bulk of the carbon films (Li trapping). For higher cycle numbers, only reversible Li insertion is present with bonds located exclusively in the bulk of the carbon films.

Considering the dominant physical mechanism governing the reaction of lithium with carbonaceous materials as reviewed in the introduction, one may attribute the reversible Li bonds associated with peak III (which is located below 0.3 V) to Li intercalation and de-intercalation into domains of the carbon films with parallel stacked graphene sheets, i.e., to regions of carbon with sp² bonding configuration. XRD and Raman evidenced an amorphous network for the carbon films, indicating that the size of the sp²-bonded domains has to be below 2 nm. Peak III and IV have also a low potential hysteresis similar to graphite. Consequently, those peaks may be associated to the Li intercalation and de-intercalation process, respectively, into nano-sized parallel stacked graphene domains. Interestingly, the cycling of the thinner film at the highest applied current not only produces a high C-rate of 2150 C (Fig. 6) but also a reversible Li insertion with solely one peak III. This is in contrast to the thick carbon film where all Li insertion and release peaks are present (Fig. 10a, b). This indicates that the Li transport to the graphite-like nano-domains is easier in thinner carbon films. A peculiar arrangement of the nano-sized graphitic domains may be the reason for the faster Li kinetics in the thinner carbon film, or a higher porosity in the thinner film. However, especially the thinner carbon film shows pseudo-capacitance behavior during Li⁺ insertion with high reversibility also for fast cycling, presumable due to a stronger confinement [48]. The reversibility at high cycling rates is advantageous for LIB electrodes composed of multilayers possessing very thin carbon layers.

According to the literature discussion given in the introduction, the reversible Li bonds attributed to peak I and II correspond to bonding to defects, such as unsaturated carbon bonds in the amorphous structure, carbon domains with sp³-bonding configuration (maybe turbostratic carbon), and sites in the vicinity of impurities like hydrogen, oxygen, and nitrogen. The pair of peaks (I, VI) possess a potential hysteresis of 1.2 V which is larger than that of the pair of peaks (II, V) which amounts to about 0.3 V. Consequently, the pairs of peaks (I, VI) and (II, V) may originate from reversible Li bonds in the vicinity of impurities, and to reversible Li bonds to clean carbon regions with unsaturated carbon bonds, respectively. Hence, Li insertion proceeds by bonding first reversibly in the vicinity of impurities (peak I), followed by reversible bonding to unsaturated carbon bonds (or non-sp³ hybridized carbon bonds) (peak II), and finally reversible insertion between nano-sized parallel graphene sheets (peak III). The Li release follows then the reversed sequence.

Concerning future work, it has to be noted that there is no funded knowledge about the lithiation and delithiation mechanism, i.e., which processes are ongoing during the six predominant Li uptake and release peaks. Consequently, it is of interest to elucidate the exact processes (mechanisms). This can be achieved by measuring Li depth profiles with secondary ion mass spectrometry (SIMS) [51, 52] or NR [51] at different states of charge (SOC) and for different film thicknesses. Furthermore, $^6\text{Li}/^7\text{Li}$ isotope exchange experiments with SIMS would allow to determine Li diffusivities on the nm up to the mm scale in the electrode at different SOC and for different film thickness. Note that there is no detailed knowledge of how the Li insertion front proceeds into carbon, even not in graphite. CV experiments on graphite show that below a potential of 0.3 V vs Li reference electrode, several peaks appear in CV. They are attributed to the formation of various LiC phases with $x = 0.25/6, 0.33/6, 0.5/6, 1/6$ by lithium intercalation [14–16, 19]. This means that these certain phases are created preferentially. In such a case, the lithiation mechanism can proceed via a phase-front mechanism which sharply delimits a certain LiC zone from another Li$_x$C zone. For $x > y$, the Li$_x$C zone consumes
the Li,C zone. The Li concentration in the Li,C zones is small (maximum x = 1/6) and measurement techniques based on electron diffraction and spectroscopy may not discern between the different Li,C zones. Nevertheless, SIMS can detect traces of Li isotopes and the method might be suitable to discern the certain Li,C zones. Last but not least, NR is able to investigate operando of the thicknesses of films and even that of buried layers with nm resolution [27, 28, 51, 53] which is of crucial importance for safe LIB operation. Moreover, the first cycle capacitive loss may be eliminated by a prelithiation of the carbon films [31].

4 Conclusions

The electrochemical lithiation/delithiation cycling of 230 nm- and 16 nm-thin carbon films were investigated at room temperature. The carbon films were deposited by ion-beam sputtering and found to be amorphous with a sp² (graphite-like) bonding configuration. For C-rate capability investigations, a cycling protocol of stepwise increase of the current after each fifth cycle from 0.13 to 11.63 Am⁻², and the stepwise decrease of the current after each fifth cycle back to 0.13 Am⁻², was applied. The carbon films were subsequently cycled for further hundreds of cycles. The 230 nm- and 16 nm-thin carbon film shows similar cycling behavior. A literature survey on the dominant physical mechanisms governing the electrochemical reaction of lithium with carbonaceous materials important for LIBs was presented to enable a proper data interpretation. Beneath graphite-like carbon, hydrogen-containing carbon and black carbon, the sputter-deposited carbon films represent a fourth class of carbonaceous materials that reversible react with lithium.

Lithiation was done up to Li-plating. Overpotentials caused negative potentials with respect to the lithium reference electrode. This procedure guaranteed full lithiation for the lowest applied Li⁺ current of 0.13 Ahm⁻². At higher currents, Li transport limitations permit Li-plating to start before full lithiation is achieved, reducing in that way the capacity. This process is strongly enhanced for the thicker carbon film. The capacity decreases with current increase, reaching at the highest current of 11.63 Am⁻² only 5% and 30% of the theoretical maximum graphite capacity (372 Ahkg⁻¹) for the thicker and thinner carbon film, respectively. The thinner carbon film allows a faster distribution of Li in the film interior, indicating an increased Li permeability of the carbon material in thinner films. A reduction of the current restores the capacity, reaching 100% of the graphite capacity. Hundreds of further cycles with the highest current reduce again the capacity, which recovers again for the subsequent application of lower currents. Thin sputter-deposited carbon films withstand cycling with high C-rates. Both carbon film electrodes show irreversible Li losses during the first 5 cycles.

Further information about irreversible and reversible Li losses corresponding to Li bonding at the surface and inside the carbon films was obtained by analyzing the influence of carbon film thickness on the differential charge and capacity plots at relevant cycles of the C-rate capability experiment. The two types of carbon films reveal in the dQ/dV curves three strong predominant Li⁺ uptake peaks located at potentials of ~1.3 V (I), ~0.8 V (II), and below 0.3 V (III). At higher cycle numbers and at low current densities, also three predominant Li⁺ release dQ/dV peaks are resolved, located at ~0.2 V (IV), ~1.1 V (V), and ~2.5 V (VI). All the predominant Li⁺ uptake and release peaks are reduced during proceeding cycling, but they do not disappear, indicating that irreversible and reversible Li bonds are formed at potential of each of the Li⁺ uptake peaks. It was found that the irreversible Li bonds are not exclusively formed at the surface as SEI formation, but also from side reactions inside the carbon films (Li trapping). At higher cycle numbers, all six peaks are exclusively associated with reversible Li bonds, which are formed in the interior of the carbon films. The pair of peaks (I, VI), (II, V), and (III, IV) show potential hysteresis of 1.3, 0.3, and 0.2 V, respectively. With respect to available literature, we suggest that reversible Li bonds are initially formed presumably in the vicinity of impurities (such as hydrogen, oxygen, and nitrogen) (peak I), then at unsaturated (or sp³ hybridized) carbon bonds (peak II), and finally in graphitic like nano-domains (sp² carbon) (peak III). The Li release follows the reversed sequence. Reversible full Li⁺ insertion into graphitic nano-sized carbon domains is achievable at high C-rates (above 1000 C) only for the thinner carbon film. This indicates a higher Li permeability of the carbon material in thinner films. Thin carbon films may show more confined regions with fast Li kinetics which leads to reversible high intercalation pseudo-capacitance.

Summing up, amorphous carbon films deposited by ion-beam sputtering possess advantages and disadvantages for LIB operation. The disadvantages rely on strong irreversible capacity losses occurring during the first cycles and on Li uptake and release at potentials even higher than 1 V. The advantages rely on a good cycling capability even at high C-rates of thousands of C with a reversible pseudo-capacitance close to that of graphite. The carbon material in thinner films shows further the advantage of faster Li kinetics. The disadvantage of irreversible capacity may be partially resolved using proper coatings and prelithiation.

Appendix

From the potential profiles (e.g., the second cycle of Fig. 2a), the time intervals of lithiation and delithiation were determined and the gravimetric capacity, the C-rate, and the Coulombic efficiency, and their errors were calculated as follows.
The Li\textsuperscript{+} current density was calculated by

\[
J = \frac{I}{A} = \frac{1}{\pi r^2},
\]

and in that way also the obtained capacity and Coulombic efficiency has large errors for small time intervals of the Li\textsuperscript{+} extraction and insertion process.

The C-rate was calculated by dividing 1 h through the lithiation time interval given in hours.

The dQ/dV and dC/dV plots were obtained from the CC potential profiles \((Ewe(t))\) in the following way:

\[
\frac{dQ}{dV} = \frac{I}{dEwe} = \frac{I}{dEwe} = m \cdot \frac{dC}{dV}.
\]

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**Declarations**

**Conflict of interest** There are no conflicts to declare.

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**References**

1. Asenbauer J, Eisenmann T, Kuenzel M, Kazzazi A, Chen Z, Bresser D (2020) The success story of graphite as a lithium anode material—fundamentals, remaining challenges, and recent developments including silicon (oxide) composites. Sustain Energy Fuels 4:5387–5416
2. Salgado RM, Danzi F, Oliveira JE, El-Azab A, Camanho PP, Braga MH (2021) The latest trends in electric vehicles batteries. Molecules 26:3188–1–41. https://doi.org/10.3390/molecules26113188
3. Dahn JR, Zheng T, Liu Y, Xue JS (1995) Mechanisms for lithium insertion in carbonaceous materials. Science 270:590–593. https://doi.org/10.1126/science.270.5236.590
4. Stevens DA, Dahn JR (2001) The mechanisms of lithium and sodium insertion in carbon materials. J Electrochem Soc 148:A803–A811. https://doi.org/10.1149/1.1379565

5. Shi Q, Zhou J, Ullah S, Yang X, Tokarska K, Trzebicka B, Ta H, Rummeli MH (2021) A review of recent developments in Si/C composite materials for Li-ion batteries. Energy Stor Mater 34:735–754. https://doi.org/10.1016/j.ensm.2020.10.026

6. Wang J, Tong Y, Xu Z, Li W, Yan P, Chung YW (2013) Amorphous silicon/carbon multilayer thin films as the anode for high rate rechargeable Li-ion batteries. Mater Lett 97:37–39. https://doi.org/10.1016/j.matlet.2013.01.027

7. Sayed SY, Kalisvaart WP, Olsen BC, Luber E, Xie H, Burik JM (2019) Alternating silicon and carbon multilayer-structured anodes suppress formation of the c-Li3.75Si phase. Chem Mater 31:6578–6589. https://doi.org/10.1021/acs.chemmater.9b00389

8. Zhao Y, Wang J, He Q, Shi J, Zhang Z, Men X, Yan D, Wang H (2019) Li-Ions transport promoting and highly stable solid-electrolyte interface on Si in multilayer Si/C through thickness control. ACS Nano 13:5602–5610

9. Wang J, Li S, Zhao Y, Lv L, Wang H, Zhang Z, Feng W (2018) The influence of different Si: C ratios on the electrochemical performance of silicon/carbon layered film anodes for lithium-ion batteries. RSC Adv 8:6660–6666. https://doi.org/10.1039/C7RA1207C

10. Tong Y, Xu Z, Liu C, Zhang G, Wang J, Wu ZG (2014) Magnetic sputtered amorphous Si/C multilayer thin films as anode materials for lithium-ion batteries. J Power Sour 247:78–83. https://doi.org/10.1016/j.jpowsour.2013.08.087

11. Jimenez AR, Köpisch R, Wagner R, Rodehorst U, Kolek M, Nölle R, Winter M, Placke T (2017) A step toward high-energy silicon-based thin film lithium ion batteries. ACS Nano 11:4731–4744. https://doi.org/10.1021/acsnano.7b00922

12. Garino N, Biserini E, Bassi A, Bruno P, Gerbaldi C (2015) Mesoporous Si and multi-layered Si/C films by pulsed laser deposition as Li-Ion microbattery anodes. J Electrochem Soc 162:A1816–A1822. https://doi.org/10.1149/2.0531509jes

13. Dattaa M, Maranchib J, Chungs S, Eparc R, Kadakiad K, Jampnid P, Kumta P (2011) Amorphous silicon–carbon based nanoscale thin film anode materials for lithium ion batteries. Electrochim Acta 56:4717–4723. https://doi.org/10.1016/j.electacta.2011.01.124

14. Levi MD, Aurbach D (1997) The mechanism of lithium intercalation in graphite film electrodes in aprotic media. Part I. High resolution slow scan rate cyclic voltammetric studies and modelling. J Electroanal Chem 421:79–88. https://doi.org/10.1016/S0022-0728(96)04832-2

15. Aurbach D, Levi MD, Levi E, Schechter A (1997) Failure and stabilization mechanisms of graphite electrodes. J Phys Chem B 101:2195–2206

16. Markowski B, Levi MD, Aurbach D (1998) The basic electroanalytical behavior of practical graphite-lithium intercalation electrodes. Electrochim Acta 43:2287–2304. https://doi.org/10.1016/S0013-4686(97)0172-4

17. Kwon K, Kong F, McLarnon F, Evans JW (2003) Characterization of the SEI on a carbon film electrode by combined EQCM and spectroscopic ellipsometry. J Electrochem Soc 150:A229–A233. https://doi.org/10.1149/1.1582232

18. Kwon K, Evans JW (2004) Comparison between cyclic voltammetry and chronamperometry when coupled with EQCM for the study of the SEI on a carbon film electrode. Electrochim Acta 49:867–872. https://doi.org/10.1016/j.electacta.2003.09.038

19. Kang SH, Abrahama DP, Xiao A, Lucht BL (2008) Investigating the solid electrolyte interphase using binder-free graphite electrodes. J Power Sour 175:526–532. https://doi.org/10.1016/j.jpowsour.2007.08.112

20. Geng H, Peng Y, Qu L, Zhang H, Wu M (2020) Structure design and composition engineering of carbon-based nanomaterials for lithium energy storage. Adv Energy Mater 10:1903030–1903034. https://doi.org/10.1002/aenm.201903030

21. Narayanan A, Mugele F, Duits MHG (2020) Electrochemically Induced Changes in TiO2 and Carbon Films Studied with QCM-D. ACS Appl Energy Mater 3:1775–1783. https://doi.org/10.1021/acsaeem.9b02233

22. Ding R, Huang Y, Li G, Liao Q, Wei T, Liu Y, Huang Y, He H (2020) Carbon anode materials for rechargeable alkalai metal ion batteries and in-situ characterization techniques. Front Chem 8:607504–607520. https://doi.org/10.3389/fchem.2020.607504

23. Lu ZG, Chung CY (2008) Electrochemical characterization of diamond like carbon thin films. Diam Relat Mater 17:1871–1876. https://doi.org/10.1016/j.diamond.2008.03.03

24. Subramanian V, Karabacak T, Masarapua C, Tekic R, Lud TM, Wei B (2010) J Power Sources 195:2044–2049. https://doi.org/10.1016/j.jpowsour.2009.10.037

25. Nam SC, Lee JM, Pukha VE, Seo HO, Kim YD, Lee HJ (2014) Carbon anode thin films for lithium batteries. Curr Appl Phys 14:1010–1015. https://doi.org/10.1016/j.cap.2014.04.012

26. Fathi R, Sanderson RJ, Lucas LJ, Dahn JR (2014) The electrochemical reaction of lithium with high-capacity dense sputtered carbon. Carbon 74:249–254. https://doi.org/10.1016/j.carbon.2014.03.029

27. Kawaura H, Harada M, Kondo Y, Kondo H, Suganuma Y, Takahashi N, Sugiyama J, Seno Y, Yamada NL (2016) Operating measurement of solid electrolyte interphase formation at working electrode of Li ion battery by time slicing neutron reflectometry. ACS Appl Mater Interfaces 8:9540–9544. https://doi.org/10.1021/acsami.6b01170

28. Kawaura H, Harada M, Kondo Y, Mitsutani M, Takahashi N, Yamada NL (2020) Operating time slicing neutron reflectometry measurements of solid electrolyte interphase formation on amorphous carbon surfaces of a Li ion battery. Bull Chem Soc Jpn 93:854. https://doi.org/10.1246/bcsj.20200044

29. Ronneburg A, Trapp M, Cubitt R, Silvi L, Cap S, Ballauff M, Risse S (2019) Surface structure inhibited lithiation of crystalline silicon probe with operating neutron reflectivity. Energy Storage Mater 18:182–189. https://doi.org/10.1016/j.ensm.2018.11.032

30. Wu X, He G, Ding Y (2020) Dealloyed nanoporous materials for rechargeable lithium batteries. Electrochem Energy Rev (EEE) 3:541–580. https://doi.org/10.1007/s41918-020-00070-7

31. Xin F, Whittingham MS (2020) Challenges and development of tin-based anode with high volumetric capacity for Li-Ion batteries. Electrochem Energy Rev (EER). https://doi.org/10.1007/s41918-020-00082-3

32. Liu Y, Li W, Xia Y (2021) Recent progress in polyanionic anode materials for Li (Na)-Ion batteries. Electrochem Energy Rev (EER) 4:447–472. https://doi.org/10.1007/s41918-021-00095-6

33. Liu J, Yue M, Wang S, Zhao Y, Zhang J (2022) A review of performance attenuation and mitigation strategies of lithium-ion batteries. Adv Funct Mater 32:2107769–2107822. https://doi.org/10.1002/adfm.202107769

34. Schnabel M, Harvey SP, Arca E, Stetson C, Teeter G, Ban C, Stradins P (2020) Surface SiO2 thickness controls uniform-to-localized transition in lithiation of silicon anodes for lithium-ion batteries. ACS Appl Mater Interfaces 12:27017–27028. https://doi.org/10.1021/acsami.0c03158

35. Schnabel M, Arca E, Ha Y, Stetson C, Han SD, Stradins P (2020) Enhanced interfacial stability of Si anodes for Li-Ion batteries via surface SiO2 coating. ACS Appl Energy Mater 3:8842–8849. https://doi.org/10.1021/acsaeem.0c01337

36. Schroder KW, Celio H, Webb LJ, Stevenson K (2012) Examining solid electrolyte interphase formation on crystalline silicon
electrodes: influence of electrochemical preparation and ambient exposure conditions. J Phys Chem C 116:19737–19747. https://doi.org/10.1021/jp307372m

37. Evmenenko G, Waburton RE, Yildirim H, Greeley JP, Chan MKY, Buchholz DB, Fenter P, Bedzyk MJ, Fister TT (2019) Understanding the role of overpotentials in lithium ion conversion reactions: visualizing the interface. ACS Nano 13:7825–7832. https://doi.org/10.1021/acsnano.9b02007

38. Hüger E, Dörrer L, Schmidt H (2018) Permeation, solubility, diffusion and segregation of lithium in amorphous silicon layers. Chem Mater 30:3254–3264. https://doi.org/10.1021/acs.chemmater.8b00186

39. Dillon RO, Woollam JA, Katkanant V (1984) Use of Raman scattering to investigate disorder and crystallite formation in as-deposited and annealed carbon films. Phys Rev B 29:3482. https://doi.org/10.1103/PhysRevB.29.3482

40. Tamor MA, Vassell WC (1994) Raman “fingerprint” of amorphous carbon films. J Appl Phys 76:3823–3830. https://doi.org/10.1063/1.357385

41. Ferrari AC, Robertson J (2000) Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B 61:14095–14107. https://doi.org/10.1103/PhysRevB.61.14095

42. Ferrari AC (2007) Raman spectroscopy of graphene and graphite: disorder, electron–phonon coupling, doping and nonadiabatic effects. Solid State Commun 143:47–57. https://doi.org/10.1016/j.ssc.2007.03.052

43. Wang L, Zhang R, Jansson U, Nedfors N (2015) A near-wearless and extremely long lifetime amorphous carbon film under high vacuum. Sci Rep 5:11119. https://doi.org/10.1038/srep11119

44. Paul PP et al (2021) A review of existing and emerging methods for lithium detection and characterization in Li-ion and Li-metal batteries. Adv Energy Mater 11:2100372. https://doi.org/10.1002/aenm.202100372

45. Kohler T, Hadjixenophonos E, Joshi Y, Wang K, Schmitz G (2021) Reversible oxide formation during cycling of Si anodes. Nano Energy 84:105886. https://doi.org/10.1016/j.nanoen.2021.105886

46. Simon P, Gogotsi Y, Dunn B (2014) Where do batteries end and supercapacitors begin? Science 343:1210–1211. https://doi.org/10.1126/science.1249625

47. Brousse T, Belanger D, Long JW (2015) to be or not to be pseudocapacitive? J Electrochem Soc 162:A5185–A5189. https://doi.org/10.1149/2.0201505jes

48. Fleischmann S, Mitchell JB, Wang R, Zhan C, Jiang D, Presser V, Augustyn V (2020) Pseudocapacitance: from fundamental understanding to high power energy storage materials. Chem Rev 120:6738–6782. https://doi.org/10.1021/acs.chemrev.0c00170

49. Hüger E, Schmidt H (2018) Lithium permeability increase in nanosized amorphous silicon layers. J Phys Chem C 122:28528–28536. https://doi.org/10.1021/acs.jpcc.8b09719

50. Hüger E, Stahn J, Heitjans P, Schmidt H (2019) Phys Chem Chem Phys 21:16444–16450. https://doi.org/10.1039/C9CP01222B

51. Uxa D, Jerliu B, Hüger E, Dör rer L, Horisberger M, Stahn J, Schmidt H (2019) On the lithiation mechanism of amorphous silicon electrodes in Li-ion batteries. J Phys Chem C 123:22027–22039. https://doi.org/10.1021/acs.jpcc.9b06011

52. Hüger E, Jerliu B, Dör rer L, Bruns M, Borchardt G, Schmidt H (2015) A secondary ion mass spectrometry study on the mechanisms of amorphous silicon electrode lithiation in Li-ion batteries. Z Phys Chem 229:1375–1385. https://doi.org/10.1515/zpch-2014-0650

53. Jerliu B, Dör rer L, Hüger E, Seidlohofer BK, Steitz R, Geckle U, Oberst V, Bruns M, Schmidt H (2014) Volume expansion during lithiation of amorphous silicon thin film electrodes studied by in-operando neutron reflectometry. J Phys Chem C 118:9395–9399. https://doi.org/10.1021/acs.jp502261t

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