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Determination of the chemical diffusion coefficient of Li-ions in carbon-rich silicon oxycarbide anodes by electro-analytical methods

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ABSTRACT

The diffusion coefficient of Li-ions ($D_{Li}{}^+$) within carbon-rich silicon-oxycarbide ceramic anodes of specific chemical composition $SiO_{0.95}C_{3.72}$ is determined by potentiostatic and galvanostatic intermittent titration technique (PITT, GITT) and electrochemical impedance spectroscopy (EIS). The estimated values for $D_{Li}{}^+$ range between 10^{-9} and 10^{-11} cm^2 s^{-1}, dependent on the applied method. The observed variation of $D_{Li}{}^+$ is in a comparable range as reported for disordered carbons, well reflecting the Li-ion storage in the segregated free carbon phase in the amount of about 43 wt-% within the SiOC microstructure. However, in contrast to graphite and disordered carbons, the diffusion coefficient of lithium within carbon-rich SiOC is less potential dependent. This feature is discussed with respect to the particular morphology of the free carbon phase.

1. Introduction

The electrochemical properties of polymer- and sol-gel- derived silicon oxycarbide (SiOC) ceramics have been studied in the middle of the 1990's by Dahn et al. Accordingly, SiOC was identified as potential host material for Li-ions [1–6]. Within the last few years, among the various chemical compositions of SiOC compounds, stoichiometries with an exceptional high content of carbon (> 50 wt-%) were further considered as perspective anode material in terms of high gravimetric capacity, rate capability and reliable cycling stability [7–16].

The microstructure of carbon-rich SiOC consists of an unique nano-heterogeneous network topology, composed of two interpenetrating amorphous phases: *i)* a Si-O-C glassy phase composed of $SiO_{4-x}C_x$ ($x = 1$ - 4) mixed bonds, embedding a *ii)* free disordered carbon phase [7,17–20]. In dependence on the amount of free carbon content, either carbon nano-domains (low amount of free C) or a carbon percolation network (high amount of free C) is formed as demonstrated by electrical conductivity measurements and TEM analysis [18,21–24]. The nature of the free carbon can be further described as a mixture of disordered carbon, graphite nano-crystallites and graphene sheets [7,12,13].

Whereas Li-ion intercalation into graphite is a staged process, Li insertion into carbon-rich SiOC compounds occurs majorly in form of adsorption and surface storage within the free carbon phase, similar to the storage in disordered carbon electrodes. Major host sites are the edges of graphene sheets, interstitial and defect sites, micro-pores, graphite nano-crystallites and interfacial adsorption at carbon-crystallite surfaces. The Si-O-C glassy phase on the contrary is considered to play a minor role in terms of the reversible storage process [7,12,13]. Complementary, the storage of Li-ions within the phase-boundary of the Si-O-C glassy and free carbon phase, described by the nano-domain model, is discussed in the literature as well [25,26]. The question of the rate of the Li-ion transport within silicon oxycarbide of chemical composition $SiO_{0.85}C_{1.98}$ was initially addressed by D. Ahn within his PhD work [27]. In this work $D_{Li}{}^+$ values were determined by means of PITT (10^{-7} - 10^{-9} cm^2 s^{-1}) and GITT (10^{-8} - 10^{-10} cm^2 s^{-1}). Weidman et al. evaluated the Li-ion diffusivity within SiOC of the same composition ($SiO_{0.85}C_{1.98}$) by GITT to be 1.8 - 4.2 × 10^{-14} cm^2 s^{-1} [28]. For Si(B)CN-CNT electrodes, a Li-ion diffusivity of 10^{-9} - 10^{-12} cm^2 s^{-1} was analyzed by Bhandavat et al. [29,30].

The work presented in this article, relates to the determination of the chemical Li-ion diffusion coefficient within carbon-rich silicon oxycarbide of the specific composition $SiO_{0.95}C_{3.72}$ by different electro-analytical methods: *i)* potentiostatic intermittent titration technique (PITT), *ii)* galvanostatic intermittent titration technique (GITT) and *iii)* electrochemical impedance spectroscopy (EIS). All three techniques are well-established in the characterization of Li-ion battery electrodes and have been widely applied for a large variety of anode and cathode materials, i.e. graphite, disordered carbons, silicon, Li_xNiO_2, $Li_xCo_{0.2}Ni_{0.8}O_2$, etc. [31–39]. In addition we correlate the chemical diffusion coefficient with the unique morphological features of carbon-rich SiOC.

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Table 1
Elemental analysis data for the Si, O and C content. The weights and molecular fractions of silica, silicon carbide and free carbon were quantified according to reference [40].

	Si	O	C	SiO_2	SiC	Free C
wt-%	31.95	17.28	50.77	32.45	23.96	43.57
mol	1.14	1.08	4.23	0.54	0.60	3.63
mol-%	17.65	16.76	65.59	11.33	12.54	76.14
mol-% normalized	1.00	0.95	3.72			

2. Experimental

Carbon-rich SiOC was prepared by thermal conversion of commercially available polyorganosiloxane, namely *Polyramic RD-684a* (Starfire Systems Inc., USA). The polymer was thermally cross-linked at 350 °C for 2 h and then pyrolyzed at 1100 °C for 3 h under argon atmosphere for ceramization. Heating rates were set to 50 °C h^{-1} for cross-linking and 100 °C h^{-1} for pyrolysis. The heat treatment procedure was performed, using quartz equipment and standard Schlenk-technique. After pyrolysis the obtained sample was hand-ground to a fine powder and sieved < 40 μm for further handling.

The particle size distribution of the ceramic powder was measured by dynamic laser light scattering, using a Fritsch Analysette 22 COMPACT (Fritsch GmbH, Germany). The average particle size (D50-value) amounts 17 μm.

The chemical composition of the sample was determined by hot-gas extraction, using a Leco-200 carbon analyzer and Leco TC-436 N/O analyzer (both Leco Corporation, USA), whereas the amount of silicon in the sample was calculated as the difference to 100 wt-% of the sum of the wt-% values of carbon and oxygen, assuming negligibly amount of hydrogen and no other elements present in the sample. The analyzed composition of Si, O and C is presented in Table 1, including the corresponding molar fractions and equivalents of SiO_2, SiC and free C according to reference [40]. From this data the specific molecular formula $SiO_{0.95}C_{3.72}$ is derived for the compound with a molecular weight of 87.90 g mol^{-1}. Moreover, the density of the material was estimated as described by Martínez-Crespiera et al. and determined to be 2.09 g cm^{-3} [24].

For electrochemical measurements, electrodes composed of 85 wt-% SiOC active material, 5 wt-% Carbon Black SuperP (Timcal Ltd., Switzerland) and 10 wt-% polyvinylidene fluoride binder (PVdF, SOLEF Solvay, Germany) were prepared by tape-casting. The film thickness after drying of the tape was around 60 μm, with a loading of active material of about 2 mg cm^{-2}. Testing-cells of two-electrode Swagelok-type were assembled under protective argon-atmosphere, using metallic lithium (99.9% purity, Alfa Aesar, USA) as reference/counter electrode, 1 M $LiPF_6$ in EC:DMC ratio 1:1 (LP30, Merck KGaA, Germany) as electrolyte and Whatman glass fiber filter (Whatman, UK) as separator. Hermetically closed cells were cycled and analyzed with a VMP multipotentiostat (BioLogic Science Instruments, France) by potentiostatic and galvanostatic intermittent titration technique (PITT, GITT) and electrochemical impedance spectroscopy (EIS). PITT and GITT were performed within the potential range of 2 - 0.05 V, while in former potential steps of 50 mV at a current limit of 37 mA g^{-1} were applied. For GITT the current pulse were chosen to 37 mA g^{-1} for a duration of 15 min, followed by an open circuit voltage period of 4 h. EIS spectra were recorded at different states of charge within the frequency range of 100 kHz - 10 mHz. In order to realize an equilibrium state of the tested cell within EIS-sequences a holding time of 1 h was applied before each measurement.

Due to the little thickness of the tested electrodes of about 60 μm, the influence of Carbon black and PVDF on the electroanalytical response of SiOC could be excluded, since only for μm-thin electrodes PITT, GITT and EIS provide meaningful results for Li-insertion processes, as emphasized by Aurbach et al., [41] and references therein.

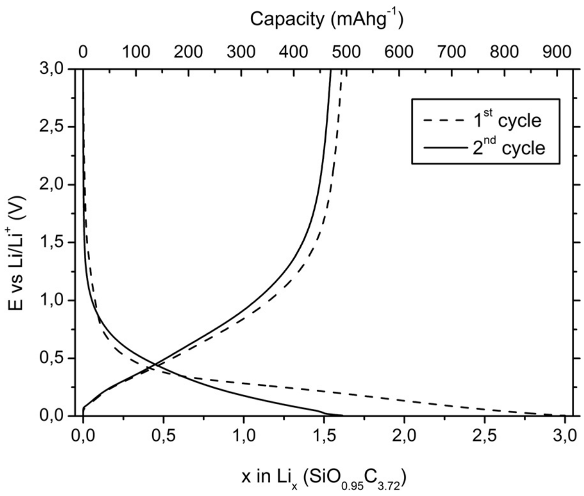

Figure 1. First and second galvanostatic discharge/charge curve of carbon-rich $SiO_{0.95}C_{3.72}$ at a current rate of 37 mA g^{-1}.

3. Results and discussion

General features of the galvanostatic discharging/charging curves (1st and 2nd cycle, 37 mA g^{-1}, 3 - 0.005 V) of $SiO_{0.95}C_{3.72}$ are presented in Figure 1. The obtained profile is in excellent agreement with our previous reports [11–13]. The anodic and cathodic curve progression exhibits significant similarities with the lithiation/delithiation characteristics of disordered soft or hydrogen containing carbons [42–44]. There are no distinct plateaus visible that indicate staged intercalation processes, but pronounced and continuously sloping and rising branches, illustrating Li-ion insertion and extraction within the free disordered carbon phase.

3.1. PITT

In potentiostatic intermittent titration technique, a constant potential is stepwise applied to the working electrode while the current response is analyzed. When the current drops under a defined value, the next potential step is applied. From the change in current and amount of charge transferred at each step (dQ), the Li-ion diffusion coefficient (D_{Li^+}) can be derived. The numerical integration of the transferred change at one potential step represents the differential capacity (C_{int}) according to equation 1.

$$C_{int}(E) = \frac{dQ(E)}{dE} \tag{1}$$

The corresponding differential capacity plot (C_{int} *vs.* E) of a cycled $SiO_{0.95}C_{3.72}$ electrode is shown in Figure 2. In the cathodic branch of the curve, electrochemical activity starts around 1.1 V, without any characteristic peaks developing during Li-insertion. This observation corresponds well to the cathodic branch of the galvanostatic second cycle in Figure 1. In anodic response two broad peaks appear around 0.35 and 0.7 V during Li-ion extraction, not resolved in the galvanostatic second cycle discharge in Figure 1. Whereas the staged process of Li-ion intercalation into graphite bears characteristic peaks in the differential capacity progression, the Li-ion insertion into carbon-rich SiOC compounds occurs in form of adsorption within the disordered carbon phase. A broad distribution of adsorption site energies leads to the observed curve characteristics and the broad extraction peaks [32,33].