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Determination of chemical diffusion coefficient of lithium ions in ceramics derived from pyrolysed poly(1,2-dimethylsilazane) and starch

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Abstract

The apparent chemical diffusion coefficient Li^+ ($D_{\text{Li}^+}^{\text{app}}$) in pyrolysed poly(1,2-dimethylsilazane)/starch (PSN/S) (weight ratio: 30/70) ceramic anode composite is determined by galvanostatic intermittent titration technique (GITT). The electrode material composition is $\text{C}_{6.00}\text{N}_{0.14}\text{H}_{0.47}\text{O}_{0.12}\text{Si}_{0.13}$. The calculated values of $D_{\text{Li}^+}^{\text{app}}$, depend on the applied potential, vary from 10^{-14} to 10^{-9} [cm^2/s]. The diffusion coefficient of lithium ions calculated in this work are similar with the values reported by other authors for carbonaceous anodes.

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1. Introduction

During last decades, lithium-ion batteries have been investigated and widely used. Lithium-ion batteries (LIBs) are used in small electric devices *i.e.* mobile phones and portable computers due to their relatively high charge/discharge rates. Moreover, LIBs start to meet requirements for new application such as electric vehicles where high power and high energy densities are required. To meet the need of this new trends, the rate capability of both the anode and the cathode materials must be improved [1]. It is well known that the factors which control the rate capability of lithium ion intercalation/deintercalation in the anode materials mainly depend on the bulk

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properties including diffusion of lithium ion within the compound and its electronic conductivity as well as the kinetics of the electrochemical processes at the interface. The carbonaceous materials, mainly graphite, are considered for the negative electrode in lithium ion batteries for electronic equipment application. The carbon anodes are not suitable for fast charge/discharge rate performance due to structural breakage within the bulk and surface appearing during extended cycling. These phenomenon influence on the lifetime of carbonaceous electrodes and limits its usage in LIBs. The lithium bulk diffusion in carbonaceous materials is still under investigation. This is due to fact, that the measurements of bulk transport properties of the particles, exhibiting non-isotropy and finite size, are very complex [2].

Recently, polymer-derived ceramics (PDCs) have attracted attention to be used as anode materials in LIBs. These materials are expected to exhibit high capacities and show stable cycling behaviour at relatively fast charge/discharge rates. The SiCN class of PDCs materials shows promising electrochemical properties with respect to the capacity and stability [3,4].

Polymer-derived SiCN materials are known to have an amorphous network consisting of silica, carbon, and nitrogen atoms and softly dispersed domains of nanocarbon clusters in the SiCN matrix [5]. The presence of free carbon in the SiCN materials is supposed to be an active site for lithium insertion while the amorphous structure of SiCN provides a pathway for lithium ion transfer [6,7]. The carbon content in ceramics may be divided into different zones. One may distinguish nano-domains (low amount of free carbon) and a carbon percolation network (high amount of free carbon). Both of these are a mixture of disordered carbon, graphite nano-crystallites and graphene sheets [8,9].

It is known that lithium ion insertion into highly crystalline graphite takes place according to the following scheme [10]:



The lithium ion insertion into polymer-derived ceramic compounds is related to adsorption and surface storage mechanism due to presence of free carbon phase. This behavior is consequence of the disordered structure of free carbon phase providing electronically and geometrically non-equivalent sites [11].

In the present work apparent chemical lithium ion diffusion coefficient ($D_{Li^+}^{app}$) of the SiCN material derived from polysilazane (poly(1,2-dimethylsilazane) mixed and pyrolysed with potato starch (PSN/S 30/70 900°C) calculated by galvanostatic intermittent titration technique (GITT) is shown. It was already shown that the presence of ceramics has a positive impact on the electrochemical properties of such composite material [12]. The GITT is considered to be a reliable technique to determine the $D_{Li^+}^{app}$ with highly resolved data for insertion compounds of varying potential with lithium content.

The $D_{Li^+}^{app}$ value for PSN/S 30/70 900°C, calculated by GITT, are compared with data obtained for PSN/S 30/70 700°C and with starch pyrolysed at 700 and 900°C.

2. Experimental

Commercially available polysilazane (poly(1,2-dimethylsilazane) (PSN 2M01 Gelest, M.W. 500-900) was mixed with commercially available starch (POCH Gliwice). The ratio polymer to starch (PSN/S) was 30/70. The mixture was hand mixing for 10 minutes to obtain uniformly distributed starch in the polysilazane. Next the composition was immersed in the ultrasonic bath for 1h followed another hand mixing procedure before thermal treatment. The mixture was filled in a ceramic crucible, put into a quartz tube, evacuated, subsequently filled with argon and finally heated under a steady flow of argon (Ar 5.0) (25 ml/min) in a programmable horizontal tube-furnace (Czylok, Poland) with heating rate of 100 °C/h. The polysilazane/starch blend was cross-linked at 230 °C for 2 h followed heating to the final temperature (700 °C and 900 °C) and hold at the final temperature for 2 h.

Pyrolysed samples were mechanically milled using ball mill (MM200, Retsch GmbH). Grinding has been carried out for 30 minutes, rpm = 1500. The composites' fine powders were mixed with binder solution containing polyvinylidene fluoride (pVDF, Solvay S.A) in acetone (POCH Gliwice) in weight ratio 9:1. No carbon black was



added. The slurry was solvent casted on the rough side of 10 μm thin copper foil (Schlenk Metallfolien GmbH & Co KG, Germany) and spread out with a metal hand blade. After tape casting procedure, the electrode strip was dried for 6 h at 100 $^{\circ}\text{C}$ in an oven (Glass Oven B-585 Büchi, Germany). Then the disks of 5 mm diameter (up to 2 mg of material) were cut of the tape and pressed for 30 sec under pressure of 950 MPa (9.7·10⁹ mg/cm²). After cut the discs were dried under dynamic vacuum in an oven (Glass Oven B-585 Büchi, Germany) for 24 h at 80 $^{\circ}\text{C}$. Such disks served as a working electrode in two-electrode and a three-electrode Swagelok type cell. The lithium foil (99.9 % purity, 0.75 mm thickness, AlfaAesar) was used as the counter and reference electrode for two-electrode half-cell configuration. The lithium wire (99.9 % purity, 2 mm diameter, AlfaAesar) served as a reference electrode for GITT measurements in T-shape Swagelok type cell. The glass fibre filter (Schleicher & Schüll, Germany) and 1M of LiPF₆ dissolved in mixed solvent which was composed of the equal volumetric amount from of ethylene carbonate (EC) and dimethyl carbonate (DMC) (LP30 Merck, Germany) were used as a separator and an electrolyte.

Chemical analysis of the composites was performed by CHNS/O analyzer (FLASH 2000 Series CHNS/O Analyzer, Thermo Scientific, USA). The silicon fraction was calculated as the difference to 100 % of the sum of the wt. %-values of carbon, nitrogen, hydrogen and oxygen. From this data the specific empirical formula C_{6.00}N_{0.14}H_{0.47}O_{0.12}Si_{0.13} is derived for the compound with a molecular weight of 80.00 g/mol.

The lithium amount was analyzed using a flame photometer (model BWB-1, BWB Technologies UK, Ltd.). Standard solutions of Li⁺ were used for calibration.

The galvanostatic intermittent titration technique (GITT) was performed with multichannel battery interface ATLAS – SOLLICH 0961 MBI (Poland) with the current pulse 18.6 mA/g for duration of 60 min, followed by an open circuit voltage period of 2 h.

3. Results and Discussion

The coulometric titration curves of PSN/S 30/70 900 $^{\circ}\text{C}$ electrodes for two first charging/discharging procedures are shown in Fig. 1. The shape of the curves is typical for insertion of lithium ion into disordered carbonaceous materials [13,14].

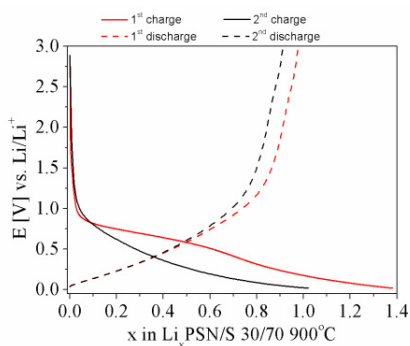


Fig. 1. Coulometric titration curve for lithium-PSN/S 30/70 900 $^{\circ}\text{C}$ material.

One may see a plateau at ~ 0.8 V typical for SEI formation. However, in the potential range from 0.05 to 0.5 V no plateaus ascribed to Li⁺ insertion into graphite are observed. This behaviour is characteristic for soft and hard carbons [15] with the presence of the hysteresis: lithium ion insertion occurring at ~ 0 V and lithium ion extraction seen at more positive potentials [16].

3.1. GITT

The galvanostatic intermittent titration technique (GITT) is one of the most reliable technique to determine the chemical diffusion coefficient of lithium ions (D_{Li^+}) with varying composition (x) in the anode materials [17–21]. Assuming that the lithium transport in the electrode is controlled by the diffusion process, in accordance with Fick's second law, the diffusion coefficient of lithium ions can be calculated from the equation given by Weppner and Huggins [17]:

$$D = \frac{4}{\pi} \cdot \left(\frac{V_M}{S \cdot F \cdot n} \right)^2 \cdot \left[I_o \cdot \left(\frac{dE}{d\delta} \right) / \left(\frac{dE}{d\sqrt{t}} \right) \right]^2 \text{ for } t \ll L^2/D \tag{5}$$

where: V_M is the mole volume of active material [cm^3/mol] (calculated as a molar mass (80 g/mol) divided by material's density (1.816 g/cm^3)), S is the surface area of the electrode [cm^2], F is Faraday's constant, n is number of electrons, I_o is applied current, $dE/d\delta$ is the slope of the coulometric titration curve (from 2nd step), $dE/d\sqrt{t}$ is the slope of the voltage change vs. square root of the time during the current pulse.

It is very important to control relaxation time during GITT measurements. Longer equilibrium time influences on the extent of self-discharge of the electrode [22]. It may cause that the chemical diffusion coefficients are not calculated properly.

For sufficient small current and straight relation E vs. \sqrt{t} the Eq. (5) may be simplified in a form [17]:

$$D = \frac{4}{\pi \cdot \tau} \cdot \left(\frac{m \cdot V_M}{M \cdot S} \right)^2 \cdot \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \text{ for } \tau \ll L^2/D \tag{6}$$

Here ΔE_s is the change of a steady-state (equilibrium) voltage at the end of two sequential open-circuit relaxation periods, ΔE_t is the total change in the cell voltage E during the current pulse, neglecting the IR drop.

The formula $\frac{m \cdot V_M}{M \cdot S}$ is known as a diffusion length, l , and thus the eq. 6 may be rewritten in a form given by Aurbach et. al. [23]

$$D = \frac{4 \cdot l^2}{\pi \cdot \Delta t_p} \cdot \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \text{ at } t \ll \tau \tag{7}$$

where Δt_p is time of the galvanostatic pulse duration.

The short-time domains ($t \ll \tau$) of GITT corresponds to the case of semi-infinite diffusion of ions in the electrodes' bulk.

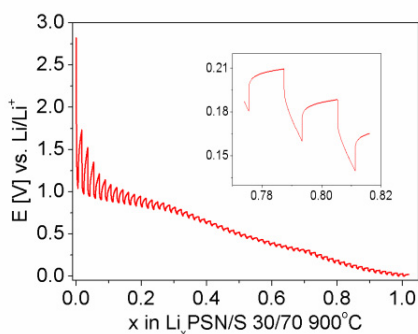


Fig. 2. Galvanostatic intermittent titration curve of PSN/S 30/70 900°C, current pulse 5 mA/g.

The values of $D_{Li^+}^{app}$ calculated from data given in Fig. 2 according to Eq. (6) are plotted in Fig. 3.

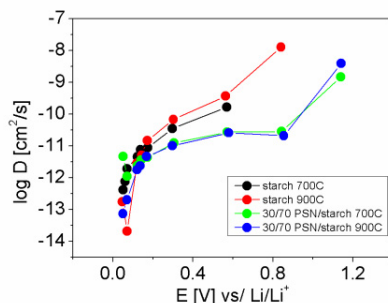


Fig. 3. Comparison of the Li-ion diffusion coefficients obtained by GITT as a function of the potential for different materials.

The chemical diffusion coefficient of lithium ions changes with the potential for the all studied materials. The highest value was calculated for $E = 1.14$ V and the lowest for $E = 0.05$ V for PSN/S 30/70 900°C are equal to $3.9 \cdot 10^{-9}$ cm²/s and $7.3 \cdot 10^{-14}$ cm²/s, respectively. The diminution of the $D_{Li^+}^{app}$ values with the potential decrease is in agreement with results obtained Aurbach *et al.* for graphite electrode [24]. The diffusion coefficients of lithium in carbonaceous materials obtained by different authors are in the range of 10^{-7} to 10^{-14} cm²/s [21,25].

In Table 1 the $D_{Li^+}^{app}$ values of studied material are given.

Table 1. Comparison of the $D_{Li^+}^{app}$ by GITT technique for different materials.

E [V]	log D [cm ² /s]			
	GITT			
	starch 700°C	starch 900°C	PSN/starch 30/70 700°C	PSN/starch 30/70 900°C
0.05	-12.39	-12.75	-11.33	
0.06	-12.13	-14.59	-11.10	-12.91
0.07	-11.72	-13.68	-11.96	-12.70
0.12	-11.34	-11.54	-11.62	-11.75
0.14	-11.12	-11.29	-11.45	-11.63
0.17	-11.06	-10.84	-11.37	-11.33
0.30	-10.46	-10.17	-10.91	-11.00
0.60	-9.78	-9.44	-10.56	-10.59
0.85		-7.89	-10.54	-10.68
1.14			-8.83	-8.41

The starch pyrolysed at 700°C and 900°C exhibits higher values of $D_{Li^+}^{app}$ in comparison with PSN/S materials at potential range more anodic than 0.12 V. However, at potentials below 0.07 V the lithium diffusion in starch derived materials is of two orders of magnitude lower. It may suggest that the presence of ceramic network enhances the lithium mobility in the bulk of ceramic already lithated.

4. Summary

Summarizing the evaluation of apparent diffusion coefficient of lithium ions, $D_{Li^+}^{app}$, in composite material with the composition of C_{6.00}N_{0.14}H_{0.47}O_{0.12}Si_{0.1} was done with galvanostatic intermittent titration technique (GITT). The variation of $D_{Li^+}^{app}$ values obtained from GITT are in the range from 10^{-14} to 10^{-9} [cm²/s] and are of the same order of magnitude as it is reported for carbonaceous materials. The diffusion of lithium ions in the material is potential dependent. The higher the insertion degree is, the lower the diffusion coefficient is. The small amount of incorporated ceramic backbone is found to have measurable impact on lithium diffusion with bulk of electrode when the potential excites certain value (0.07 V).

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