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High Rate Capability of SiOC Ceramic Aerogels with Tailored Porosity as Anode Materials for Li-ion Batteries

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ABSTRACT

Porous carbon-rich SiOC ceramic aerogels have been synthesized from a linear polysiloxane cross-linked with divinylbenzene (DVB) *via* hydrosilylation reaction in presence of a Pt catalyst and acetone as a solvent. The obtained wet gels are aged in solvent followed by drying under supercritical conditions using liquid carbon dioxide. The resulting pre-ceramic aerogels are subjected to pyrolysis at 1000 °C under controlled argon atmosphere to form the desired SiOC aerogel. The synthesized SiOC ceramics contain 43 wt% of free carbon, which is segregated within amorphous SiOC matrix. The high BET surface area up to 230 m^2g^{-1} of preceramic aerogels is only slightly diminished to 180 m^2g^{-1} after pyrolysis at 1000 °C. The electrochemical characterization reveals a high specific capacity of more than 600 $mAh\,g^{-1}$ at a charging rate of C (360 $mA\,g^{-1}$) along with a good cycling stability. At a rate of 10C (3600 $mA\,g^{-1}$) the specific capacities as high as 200 $mAh\,g^{-1}$ are recovered. The excellent properties of the materials are discussed with respect to their structural features. The porous nature of the carbon rich ceramics allows for fast ionic transport and helps to accommodate the structural changes which in turn allow a stable performance during repeated lithiation/delithiation.

1. Introduction

Lithium ion batteries (LiB) are considered as a promising solution for various energy storage applications owing to their compactness, light weight, high efficiency and longer life span compared to other rechargeable battery types [1]. These rechargeable battery systems are currently dominating the field of portable electronic applications but there are still many hurdles to reach the goal of high power applications such as in hybrid electrical vehicles (HEVs). Carbon based materials are one of the best host materials for reversible lithium storage. There is a good compromise between volume expansion and lithium storage leading to extended battery life. In particular graphite has been long used as an anode material due to low operating potential vs lithium and favorable cycling performance. However, graphite is facing its limitation in lithium storage capacity because of the formation of a well-organized stage structure LiC_6 offering a capacity of 372 $mA\,h\,g^{-1}$ [1–5]. Another crucial problem related to graphite is their limited rate capability during lithium insertion. There is a considerable discussion related to the reasons of these limits, mostly attributing the slower lithium insertion to the slow desolvation of ion at solid electrolyte interface (SEI) surface and SEI increasing resistance. However there is still no direct proof of the above hypothesis and the most valid explanation till now relates to the thermodynamic point of view, i.e. for any lithium-ion intercalating electrode (whether anode or cathode), the de-intercalation process should be more favourable than the intercalation process because the lithium-ions acquire greater freedom during de-intercalation (increase of entropy) [6]. In consequence, the rate of lithium intercalation to graphite is considered as a limiting step for the rate performance of this electrode, whereas lithium ions can be extracted with high rates without significant capacity losses.

In comparison to graphite, porous carbon compounds are known to offer higher capacities especially at higher charging/discharging currents [7–19]. In particular, mesoporous carbon compounds are reported to be an interesting anode material for high rate applications. The important features for these materials are their controlled porous structure with better interconnectivity between the pores allowing fast ion diffusion. In order to maintain the rate capability along with longer cycling life time, the host

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structure should also be mechanically flexible to allow uninterrupted insertion and extraction of lithium ions during the entire charging/discharging process.

Most common methods adapted for the synthesis of porous carbon materials are by using sacrificial templates [11,20]. Another possible way for the synthesis of porous materials is based on aerogel technique. Aerogels have got much more attention since the successful synthesis of silica aerogels by Kistler in 1931 [21]. Aerogels are tailor made porous networks with high surface area and relatively low densities. These materials are well known for different potential applications such as for thermal insulation, sensors, waste management, in capacitors, catalysts etc. due to their excellent properties such as high surface area, high porosity, low bulk density and low thermal conductivity [21–24]. However, the investigation of the use of carbon aerogels towards application as anode materials in lithium ion batteries is very limited [19,23,25,26].

Polymer derived ceramics (PDC's) such as SiOC, SiCN etc. have been analyzed in detail for lithium storage applications. Silicon oxycarbides are ceramic structures with silicon bonded to both oxygen and carbon simultaneously. The structure of SiOC beside the amorphous silicon oxycarbide network -in which Si atoms share bonds with O and C atoms simultaneously- contains an interconnected disordered free carbon phase which accounts for many of their excellent mechanical and electrochemical properties [27–44]. It came out from our previous studies on SiOC and SiCN ceramic materials [32,52] that free carbon content is an important factor determining reversible Li storage capacity and cycling stability. Both, reversible capacity and cycling performance are enhanced with increasing carbon content (increased C/SiOC ratio) in the ceramic matrix. However, certain equilibrium between the free carbon and the ceramic phase has to be maintained in order to achieve the material stability with respect to continuous lithium insertion/extraction. This equilibrium is reached at around a 1:1 weight ratio between free carbon and ceramic phase, but the exact value depends on the particular preceramic polymer and it's processing to SiOC ceramic.

In the present work, we focus on the electrochemical properties of carbon-rich SiOC ceramic aerogels prepared by pyrolysis of low-density preceramic aerogels, obtained cross-linking, a pre-ceramic polymer under highly diluted conditions. The cross-linking of the precursor is performed via hydrosilylation reaction, using divinylbenzene as crosslinking agent. The wet aerogels are supercritically dried using CO_2 and pyrolyzed at 1000 °C to produce the studied SiOC aerogel [45,46]. The synthesized porous SiOC ceramic is subjected to electrochemical characterizations and demonstrates promising properties in particular for high rate applications.

2. Experimental Part

2.1. Material Synthesis

Starting materials, a linear polyhydridomethyl siloxane (PHMS, MW = 1900), which contains Si-H bonds, and divinylbenzene, (DVB, technical 80%, mixed isomers) were purchased from Alfa Aesar (AlfaAesar, Ward Hill, MA, USA). Platinum divinyltetramethyldisiloxane complex, ~Pt 2% in xylene (Sigma-Aldrich, St. Louis, MO, USA) was used as catalyst for the hydrosilylation reaction between the Si-H moieties of the siloxanes and the vinyl groups of the crosslinker. In a typical preparation, PHMS is cross-linked with DVB in presence of acetone as solvent using the platinum catalyst (always 5 ppm relative to Si compound). In a typical preparation PHMS is cross linked with 200 wt% of DVB. The amount of solvent is calculated assuming the 80% of porosity of the final gel [45]. The cross linking is carried out at a temperature of 150 °C in an autoclave. The autoclave is then cooled down to room temperature and the gels are transferred to a beaker with excess of the acetone (Sigma-Aldrich, ≥99.9%). The wet gels have been kept for 1 week in a 100 mL flask filled with fresh acetone, renewing the acetone three times, in order to remove the catalyst and unreacted precursors. The wet gels are dried supercritically using solvent exchange with liquid CO_2. The dried gels are then pyrolysed using an alumina tubular furnace (Lindberg/Blue) under 150 mL/min of flowing argon. The samples are heated at a rate of 5 °C/min up to 1000 °C and maintained for 1 h at the maximum temperature. Cooling down to room temperature is done by turning off the furnace power. The pyrolysed sample is then milled in an agate mortar and sieved with a 40 μm sieve.

Table 1
Elemental composition of Si, C and O in final SiOC ceramics.

C (wt.%)	O (wt.%)	Si (wt.%)	Si C_x $O_{2(1-x)}$ (Wt.%)	Free Carbon (Wt.%)
43.04	27.08	29.88	60	40

2.2. Characterization

Elemental C and O are measured with Leco C and O analyzer. The porosity is analyzed using the N_2 adsorption technique with a Micrometrics equipment, ASAP Model 2010, Norcross, GA, USA (N_2 adsorption at 77 K). The specific surface area was determined using the BET equation [47] and the pore size distribution (PSD) was obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method [48]. The total pore volume (TPV) was calculated as TPV = VaD, where Va is the volume adsorbed at p/p_0 0.99 and D is the density conversion factor (0.0015468 for nitrogen as adsorbate gas). The pore size distribution (PSD) was obtained using the Barrett–Joyner–Halenda (BJH) method. Assuming that the pores are cylindrical and open at both ends, the average pore size, expressed in nanometres, of a given sample is calculated using this equation, 4000TPV/SSA ($4V_{total}/S_{BET}$). The microstructure of the samples is studied using a Supra 40 Zeiss FE-SEM (Carl Zeiss NTS GmbH, Oberkochen, Germany).

Electrochemical characterization is carried out using a Swagelok® type cell assembly with lithium metal as the counter/reference electrode (99.9% purity, 0.75 mm thick, Alfa

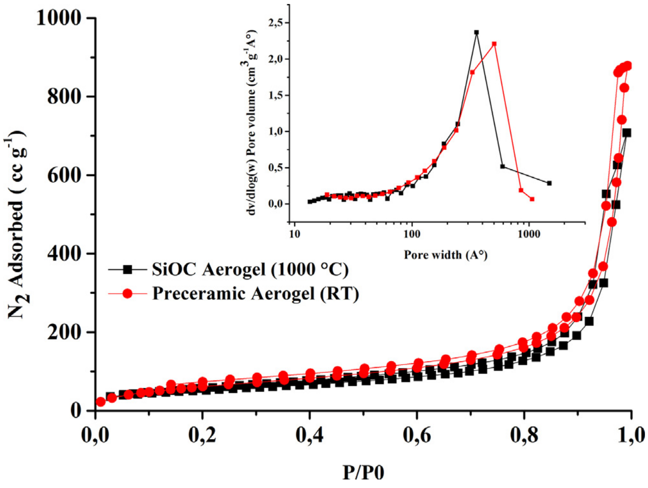

Fig. 1. Adsorption/desorption isotherm of samples before and after pyrolysis. Inset shows the pore size distribution, the data for plotting is taken from the desorption branch of isotherm.