Edge/basal/defect ratios in graphite and their influence on the thermal stability of lithium ion batteries

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HIGHLIGHTS

- Edge/defect and basal ratios has been obtained for graphite samples using DFT.
- Effect of extended heat treatment of industrial graphite has been studied.
- Ethylene carbonate improved thermal stability for graphite with high surface area.
- DFT combined with ICL could be used as a tool to predict thermal stability.

ARTICLE INFO

ABSTRACT

Raw graphite can be processed industrially in large quanta but for the graphite to be useful in lithium ion batteries (LIB's) certain parameters needs to be optimized. Some key parameters are graphite morphology, active surface area, and particle size. These parameters can to some extent be manipulated by surface coatings, milling processes and heat treatment in various atmospheres. Industrial graphite materials have been investigated for use as anode material in LIB's and compared with commercial graphite. These materials have been exposed to two different milling processes, and some of these materials were further heat treated in nitrogen atmosphere above 2650 °C. Brunauer-Emmett-Teller (BET) theory combined with density functional theory (DFT) has been employed to study the ratio of basal to non-basal plane and to determine the relative amount of defects. Thermal properties have been investigated with differential scanning calorimetry (DSC). High ethylene carbonate (EC) content improved the thermal stability for graphite with high amount of edge/defect surface area, but showed no improvement of graphite with lower amount of edge/defects. High irreversible capacity loss (ICL) combined with low surface area improved the thermal properties. DFT combined with ICL could potentially be used as a tool to predict thermal stability.

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1. Introduction

Lithium ion batteries (LIB) have been used commercially since the early 90's when Sony bought the Goodenough patent on $LiCoO_2$ [1] and used it to make $LiCoO_2$/hard carbon batteries. The choice of using lithium ion batteries is mainly due to its high energy density (low weight and high energy). Lithium-ion batteries is therefore the energy storage technology of choice for use in electric vehicles (EV), and its utilization in other large-scale applications is increasing, like stationary energy storage from renewable sources (wind and PV panels), and ships. These large-scale applications pose new challenges with regards to safety, cycle life and operating conditions. In particular thermal stability is a critical issue for application of lithium-ion batteries in road vehicles and maritime applications.

Graphite has been the main choice as anode material in lithium ion batteries because of its availability, stability, capacity and low cost. The electrolytes most commonly used have been the combination of cyclic carbonates, like ethylene carbonate (EC) and propylene carbonate (PC), together with linear carbonates, like diethylene carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC). However, as the intercalation potential is outside the electrochemical stability window for all known electrolytes, there is an irreversible capacity loss (ICL) during the first cycle due to the reduction of electrolyte species. After the

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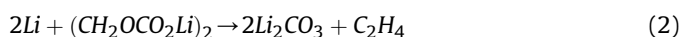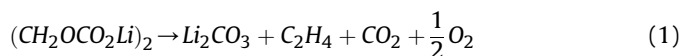E-mail address: carl.foss@material.ntnu.no (C.E.L. Foss).

reduction, a passive film is formed, preventing further reduction and increasing the stability of the graphite/electrolyte interface. This film is commonly termed the solid electrolyte interphase (SEI) [2]. Prior to this film formation, solvent species could co-intercalate into the graphite structure, causing exfoliation [3], but for electrolytes containing EC (and not PC), severe exfoliation is prevented.

The reduction product of EC, lithium ethylene dicarbonate $(CH_2OCO_2Li)_2$ (referred to as LEDC), and Li_2CO_3 are among the most efficient passivating species due to their small size and polar nature [4]. EC is therefore known to be a vital electrolyte component when it comes to the formation of the SEI. The composition of the SEI has been reported to be a complex mixture of compounds, which in addition to EC reduction products may contain CH_3OCO_2Li (lithium methyl carbonate, LMC), $CH_3CH_2OCO_2Li$ (lithium ethyl carbonate, LEC), Li_2CO_3, Li_2O, LiF, and $Li_xPF_yO_z$ [5]. It has also been established that the composition of the SEI depends on the surface structure of the graphite, as the edge planes, through which lithium intercalates [6–8], are rich in salt reduction products, whereas the basal planes are dominated by the solvent reduction products [9].

The surface properties of the graphite, both total Brunauer-Emmett-Teller (BET) surface area and the total amount of active surface area (ASA), have proven to be important parameters with regards to the first cycle irreversible capacity loss (ICL) [10,11], as well as formation of a stable and conductive SEI layer. However, a more recent study by Placke et al. [12] implemented the use of density functional theory (DFT) [13,14] for the evaluation of nitrogen adsorption data, allowing for the determination of the ratio of non-basal planes (edge/defects) vs. basal planes of the surface of the graphite. In their study, variations in the amounts of defects with heat treatment of the graphite in oxygen atmosphere, was studied. Furthermore, upon cycling of the graphite anodes, subject to various heat treatments, a linear correlation between ICL and BET surface area was not obtained, as previously reported [15], but rather a strong correlation between non-basal planes and ICL was found.

On the other hand, a higher percentage of edge planes could be advantageous for cycling at higher charge rates, and an increased amount of edge planes compared to basal planes has been found to reduce the charge transfer resistance [16].

Additionally, the surface properties can have a large effect on the thermal properties. Flaky morphology showed a much earlier onset temperature for exothermic reaction upon heating compared to round particle morphology [17]. This was attributed to an insufficient SEI formation, leaving many sites available for electrolyte reactions. This conclusion was based on the fact that the first exothermic reaction in anode materials for lithium ion batteries is related to the conversion of meta-stable SEI species to more stable species [18], according to Eqs. (1) and (2)

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + \frac{1}{2}O_2 \qquad (1)$$

$$2Li + (CH_2OCO_2Li)_2 \rightarrow 2Li_2CO_3 + C_2H_4 \qquad (2)$$

Reaction in Eq. (2) has been suggested to be more likely, as no exothermic peak was observed for de-lithiated samples in the temperature range of 80–120 °C [19]. As it turns out, the state of charge (SOC) (or degree of lithiation) can have a large impact on the thermal response of the anode material, and studies have shown that there is generally a higher thermal response for samples with high state of charge (high concentration of lithium) [18,20]. The carbon anode has also been shown to be responsible for most of the heat evolved in the early temperature range (80–180 °C) [21], and may hence trigger thermal runaway in the battery [22]. Studying fully lithiated carbon anodes could therefore be very useful to

determine the overall thermal stability of a battery system. Conversion of meta-stable species by ageing at various temperatures also improved the thermal stability (increased the onset temperature for exothermic reactions) [17]. XPS studies of aged electrodes at elevated temperatures has shown an increase in LiF species (in $LiPF_6$ containing electrolytes) with storage temperature [23]. In addition, Li_2CO_3 can also be formed according to Eqs. (1) and (2) above [18]. It is clear that the properties of the SEI highly influence the thermal properties of the anode. The SEI is again highly influenced by surface area and structure [9,11,12,24] and formation conditions [25] in addition to the electrolyte solvent [26].

The scope of this paper is to investigate the effect of the carbon surface structure on the thermal stability of the cycled anodes. Different graphites, including both commercial battery grade graphites, as well as non-commercial graphites, exposed to different milling processes and heat treatment, were included in the study. The surface structure (relative area of basal, edge and defects) was determined from nitrogen adsorption evaluated by a DFT model. The graphites were evaluated with respect to ICL and changes in thermal stability. It is for example expected that both milling type and varying heat treatment (in N_2 atmosphere) will have an effect on the cell performance. As little is known about the effect on thermal stability of the ratio between non-basal planes and basal planes, the results will thus give important knowledge regarding the safety of the battery, and how to optimize the graphite anode with respect to thermal stability.

2. Experimental

Graphite SLP30 was used as received from TIMCAL™. Graphite Cpreme G8 and P5 were used as received from CPREME. Graphite A2, H2 and A2-2650, H2-2650, supplied by Elkem Carbon, have undergone varying degree of heat treatments (HT). Both A2/H2 and A2-2650/H2-2650 have undergone a graphitization process by heat treatment in N_2 atmosphere between 2300 and 3000 °C. However, for the A2-2650 and H2-2650 the minimum temperature has been set at 2650 °C, whereas for A2 and H2 the minimum temperature was set to 2300 °C. The difference between A2 and H2 is mainly the milling method. The A-samples were grinded by use of an Alpine mill (jet milling) while H samples were grinded by use of a Hicom mill (high –intensity tumbling mill).

The graphite electrodes were prepared by tape casting slurries consisting of 37 g active graphite material (SLP30/G8/P5/A2/H2), 2 g PVDF (Kynar, reagent grade), 1 g Super P (TIMCAL™), and 60 g 1-methyl-2-Pyrrolidinone (Sigma-Aldrich >99.5%) onto a 10 μm thick Cu-foil current collector from Circuit foil Luxembourg. The tape caster was a "K Control Coater" from Printcoat instruments. The casts were dried in a vacuum oven at 120 °C overnight.

The electrolytes were made using 4:3:3 or 1:2:2 wt ratio of ethylene carbonate (Sigma-Aldrich >99%), ethyl methyl carbonate (Merck, >99%), and dimethyl carbonate (Sigma-Aldrich, >99%). All solutions are with 0.9 M $LiPF_6$ (Aldrich, >99.99%) electrolyte salt unless otherwise specified.

The electrochemical measurements were performed with coin cells from Hohsen Corp which were assembled and sealed inside an argon-filled glove box (O_2 and H_2O < 0.1 ppm). The cells consisted of a graphite working electrode (2.01 cm^2) with a loading of about 3 mg/cm^2, separator (Celgard® 2320), and 0.75 mm thick lithium foil (1.54 cm^2) as counter electrode. All potentials are reported vs. Li/Li$^+$ unless otherwise specified. The cells were initially charged with a model 4200 potentiostat from Maccor at a constant current of 10 mA/g until 5 mV vs. Li/Li$^+$, followed by a constant current of 5 mA/g until the current dropped to 5 mA/g to ensure complete lithiation of the graphite. The cells were then discharged with a constant current of 10 mA/g until 1.5 V. The subsequent cycles were