NATURAL GRAPHITE AS ANODE FOR LITHIUM-ION BATTERIES

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ABSTRACT

This article is aimed on preparing and measuring the negative electrode base on natural graphite.

1. INTRODUCTION

In the world there are two trends in anode materials for Li-ion batteries nowadays. The first one tries to replace synthetic carbon by natural carbon, which is much cheaper than synthetic one and has similar properties [1]. Mesocarbon microbeads belong to a typical representative of synthetic carbon. His properties such as high reversible capacity (320 mAh/g), low irreversible capacity (30 mAh/g), low potential versus metal lithium (below 0.2 V) and good cyclability are very suitable for Li-ion batteries.

The second one employs silicon as anode material instead of carbon and therefore offers more than 10 times higher capacity (4200 mAh/g) [2] than graphite but large volume expansion during lithium ions intercalation leads to destruction of silicon matrix. This problem was partially solved by using silicon nanowires [3] but still the silicon nanowires exhibit high irreversible capacity (1000 mAh/g). Silicon also has higher voltage versus metal lithium (0.4 V) than graphite which decreases the total voltage of Li-ion battery. The work is aimed at the first way.

2. EXPERIMENTAL

The negative electrode was prepared in the following way: The electrode material was prepared by mixing the natural graphite CR 5995 (Maziva s.r.o., Týn n. Vlt., fig.1) with PTFE at weight ratio of 95:5. A small amount of ethanol was added to the mixture for making the proper paste. The resultant paste was coated on the nickel mesh than pressed and dried at 150 °C for 1 h.

The three electrode cell was assembled in the glove box MBRAUN LABMASTER ($H_2O<5$ ppm $O_2<5$ ppm, fig.2) to examine galvanostatic charge/discharge behaviors. A piece of lithium metal (purity 99.9 %) was used as a counter and reference electrode. The working (negative) electrode is described above. 1 M LiClO₄ (purity 95 %) in EC-DEC [ethylene carbonate, diethyl carbonate (purity 99.9 %)] was used as electrolyte. The electrode was

charged/discharged between 0 V and 1.5 V (vs.Li) at a constant current of 100 mA/g and 300 mA/g. The AUTOLAB PGSTAT 30 was used for the measurement.



Fig 1: SEM picture of graphite CR 5995



Fig 2: Glovebox Mbraun Labmaster

3. RESULTS AND DISCUSSION

The results are shown in the table 1 and in the figure 2, 3. The results demonstrate that the natural graphite shows promising reversible capacity at the first cycle, which is 82 % capacity related to the composition of LiC_{6} . Irreversible capacity is relatively high but only quarter of that can be contributed to SEI formation.

3.1. SOLID ELECTROLYTE INTERFACE

SEI is a thin film (several nm) consists of decomposition products of electrolyte solvents such as EC (eq.1, 2) [4] which are permeable to Li^+ cation, but are electronically insulating and prevent further electrolyte decomposition. The stability of SEI determines safety, power capability and cycle life of batteries.

$$(CH_2O)_2CO + 2e^- + 2Li^+ \longrightarrow Li_2CO_3 + C_2H_4(g)$$

$$\tag{1}$$

$$2(CH_{2}O)_{2}CO + 2e^{-} + 2Li^{+} \longrightarrow LiO_{2} + CO - CH_{2}CH_{2} - OCO_{2}Li + C_{2}H_{4}(g)$$
(2)

Tab. 1:Graphite CR 5995

Reversible capacity 1st cycle (100 mA/g)	305 mAh/g
Irreversible capacity 1st cycle	111 mAh/g
Irreversible capacity 1st cycle due to SEI formation	25 mAh/g
Coulombic efficiency 1st cycle	73 %
Coulombic efficiency 10th cycle (300 mA/g)	98 %
Reversible capacity 4th cycle (300 mA/g)	50 mAh/g
Reversible capacity 20th cycle (100 mA/g)	216 mAh/g



Fig 3: Summarized properties of graphite CR 5995. Crosses: coulombic efficiency, squares: current 100 mA/g, triangles: 300 mA/g



Fig 4: Galvanostatic charging – discharging curves of graphite CR 5995

4. CONCLUSION

The results illustrate that the natural graphite is a promising candidate for anodes in Liion batteries but some obstacles such as capacity fading have to be removed.

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