ADVANCED COMMERCIAL AND EXPERIMENTAL GRADES OF GRAPHITE FOR LITHIUM-ION BATTERIES

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We have investigated the electrochemical characteristics of more than 40 grades of natural and synthetic graphite from the different manufacturers for development of optimal carbons for lithium-ion cells.

The first series of experiments were performed in T-type 3-electrodes Li/carbon cells with surplus of electrolyte. The best results have shown grades LBG-73 **(1)** and LBG-25 **(2)** from Superior Graphite Co.(SGC), Chicago, USA, which demonstrated the utilization coefficients $\mu \cong$ (98.1…100)% and the 1st cycle loss of capacity $\Delta \cong$ (9.71…10.3)%.

According with our team recommendation SGC has synthesized also two experimental modified graphite grades, which demonstrated such electrochemical parameters:

- 3wt% B-treated graphite (grade SO # 3-38-18=2900 RG): $\mu \cong$ 90.5 %; $\Delta \cong$ 9.46 % **(3)**;
- 3wt% Si-coated LBG-25 graphite (grade SO # 3-43-18): $\mu \cong$ 106 %; $\Delta \cong$ 12 % **(4)**.

Boronated graphite **(3)** demonstrates a decrease of specific capacity. Nevertheless, such type of graphite has a minimal 1st cycle loss of capacityΔ. It seems that modification graphite by boron and estimation of optimal boron concentration would be useful at the further stages of prolonged cycling with a purpose of increasing graphite stability.

Maximum specific discharge capacity (of about 400 mA·h/g) and utilization coefficient ($\mu \cong$ 106 %) have demonstrated Si-coated graphite **(4)**.

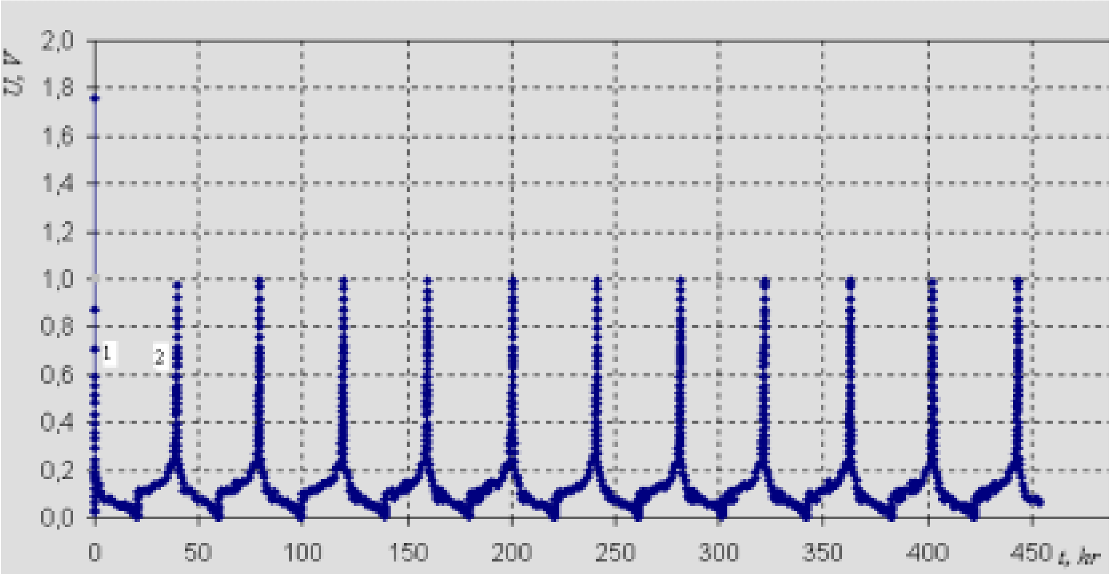
For the second series of experiment graphites **(1), (2)** and **(4)** with a large discharge capacity were selected. *The basic difference of the given stage* was investigation of initial electrochemical characteristics of graphites inside of 2-electrodes 2016 Graphite/Li coin cells in the conditions of relatively limited stock of electrolyte, close contacts and in real cases (∅ 20 mm, thickness of 1.60 mm). All negative electrodes were prepared on the special Cu foil (thickness of 10 micron) and contained 10% of PVDF binding additive. Li foil with a thickness of 0.85mm was a counter electrode. 2 separators of Celgard type with a thickness of 0.10 mm were used in this construction. A standard LP-30 electrolyte from Merck company with composition 1M $LiPF_6$ + EC:DMC (1:1 w/w) was used as a working electrolyte.

The typical galvanostatic charge-discharge curves of such coin cells (a) at C/20 rate for the initial deep cycling in diapason of potential from 0.01 V to 1.0V, as well as the changes of capacity during such cycling (b) have shown at the Fig.1. Curves have a similar character for all types of investigated graphite, demonstrate a small 1st cycle loss of capacity and stabilization of charge and discharge capacities, at least in the beginning of cycling.

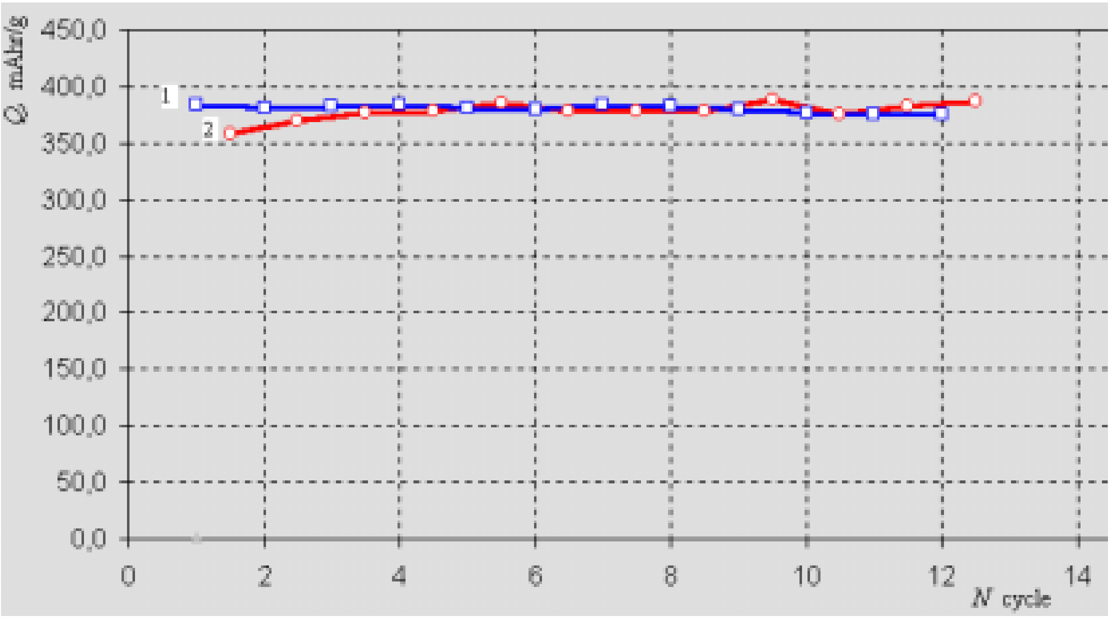
The quantitative characteristics of best graphite grades in the condition of above 2016 coin cells are generalized in the Table. The investigations of graphite characteristics in developed 2016 coin cells confirm general conclusions from the first series of experiments.

Maximal discharge capacity in 2016 coin cells (412 mA·h/g) has demonstrated Si-coated graphite (grade SO # 3-43-18). It's utilization coefficient $\mu \cong$ 111% even higher than in T-type electrochemical cell, but Δ is also higher (of about 21%). SGC's commercial grades LBG-73 and LBG-25 demonstrates a little bit smaller capacity (μ of about 100%) and insignificant $\Delta \sim$ 7…8%.

Thus, up to now all above three grades of graphite remain the promising active materials. The paper will contain explanations of possible mechanisms of high capacity of Si-coated graphite.



a)



b)

Fig. 1 *a) Galvanostatic charge (1) – discharge (2) curves of LBG-73 grade of graphite at C/20 rate in 2016 coin cell. Electrolyte: EC:DMC + 1M $LiPF_6$. Counter electrode – Li foil*

b) Charge (1) and discharge (2) specific capacity of SL 20 graphite during cycling at C/20 rate in 2016 coin cell. Electrolyte: EC:DMC + 1M $LiPF_6$. Counter electrode – Li foil

Table. *The results of initial galvanostatic cycling of experimental 2016 coin cells with different types of graphite from SGC at C/20 rate (ΔU = 0.01…1.0V).*
Electrolyte – LP-30 from Merck (EC:DMC + 1M $LiPF_6$). Counter electrode – Li foil

Cell series	Graphite grade (main peculiarities)	Mode	Specific capacity of graphite (mAh/g) during the initial cycling:				Average discharge capacity (mAh/g)	Utilization coefficient μ (%)	1st cycle loss (%)
			Cycle 1	Cycle 2	Cycle 3	Cycle 4			
1*	LBG-73 (D_{50} = 43 μm; S = 2.85 m^2/g)**	Charge	383	381	383	384	368	98.9	7.83
		Discharge	353	368	376	376			
2*	LBG-25 (D_{50} = 18 μm; S = 4.90 m^2/g)**	Charge	384	380	382	384	370	99.5	6.77
		Discharge	358	370	376	377			
3*	SO # 3-43-18 (LBG-25 + 3% Si)	Charge	536	431	419	404	412	111	21.4
		Discharge	421	407	412	410			

- ** Results for an average sample in a series from 3-5 coin cells*
- ***According to the Catalogue of SGC's Purified Battery Grade Graphites' Characteristics*

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