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THE INFLUENCE OF GRAPHITE MATERIALS ON POWER PERFORMANCE OF LITHIUM-ION CAPACITORS

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A well-designed lithium-ion capacitor (LIC) can reach higher energy and power density than traditional supercapacitors [1]. The research in the field of lithium-ion capacitors is focused on the development of systems with higher power and energy density and longer cycle life. For this purpose, in the last years, an intensive effort has been made to test many electrode materials for LIC. The anode materials have been transferred from the technologies of lithium-ion battery. Synthetic graphites, such as mesocarbon-microbead (MCMB) have been used commercially by many battery companies as anode materials in lithium-ion batteries because they have shown a reversible electrochemical behavior and a low, flat potential curve for the lithium intercalation/deintercalation process [2]. However, the lower-cost natural graphite materials are of more interest. In the current work, the natural graphite materials with different physicochemical characteristics were considered for implementation in a lab cell.

Electrochemical performance of an LIC can be improved in several ways. A common approach is to try to find new materials with superior electrochemical properties. Minimizing the amount of inactive material (less weight impact) is another way to increase the specific energy and power in an LIC. The development of new smart designs and concepts that can add other values to the LIC is also a viable approach.

This work is to present the results of screening tests that were performed on a large number of low-cost materials. These materials were screened for their potential to have a positive impact on the high-power application. As part of this effort, we developed and employed a set of standard test protocols to evaluate all of the materials. Also, this work is dedicated to optimization of graphite electrodes in order to fulfill the requirements for use in an asymmetric supercapacitor such as LIC.

Experimental

Versatile electro-chemical testing of different anode materials was conducted in order to estimate their possible application for lithium-ion capacitors. Electrodes were composed of 89-91% of relevant-type graphite , 8% of the binder – polyvinyliden fluoride (PVDF) and 1-3% of carbon percolators. Slurries for electrode casting were prepared from a mixture of the graphite and PVdF dissolved in 1-methyl-2-pyrrolidinone (NMP). They were spread onto a Cu foil with different thickness and dried under vacuum at 120^{o}C for 12 h. After drying, the electrodes were compressed by roll press. The thickness of active mass after rolling was varied within a wide range from 40 to 100 μm. The density of graphite layer was about 1.0-1.6 g/cm^3. The 2025 type of half-elements with lithium electrode were assembled using the electrodes with an operating area of 1,77 cm^2. All these elements were assembled in the argon box (M Braun, USA) with a water content of < 1 ppm. Electrochemical investigations were performed using the multi-channel potentiostat/galvanostat VMP3 from Princeton Applied Research (UK). The electrochemical performance of materials was examined using a range of measurement techniques. Electrochemical cycling was used to establish capacity and power characteristics.

Results and Discussion

In this work, many kinds of carbonaceous materials were investigated in order to find the best materials. The common list of tested carbonaceous materials is presented in Table 1.

Table 1. Commercial types of carbonaceous materials

Type of materials	Commercial grade	Country	Company
Natural graphite	SLC1512P, SLC1520P, SLC1520T, SLA1518, ABG1005	USA	Superior Graphite Co.
	LGN1212	USA	American Energy Technologies Company
Synthetics graphitic materials	MCMB (TB-17), MT-1	USA	MTI
	KS6, SLP30, SLP50	Switzerland	Lonza (TIMICAL Group)
	LGS1228, LM1226, LGS1211	USA	American Energy Technologies Company
Hard carbon	Carbotron-P	Japan	Kureha Chemical Industry Co.

All samples could be defined as spherical (for example, SLP30) or exfoliated (ABG 1005, KS6) types of graphite materials. The materials manufactured by Superior Graphite Co., USA (SLC1512P, SLC1520P, SLC1520T, SLA1518) were prepared from natural crystalline flake graphite obtained via flotation of graphite concentrate and purified by subjecting it to the uniform zone of heat treatment at temperatures above 2.500 ^{o}C. The purified flake, in the subsequent stages of processing, was reduced in size by milling and classification technologies. As example, Fig. 1 shows SEM micrographs of graphite with prismatic and potato-shaped particles. The particles show only a small variation in shape. The sphericity of the potato- shaped particles is not such regular as that of mesocarbon micro- beads (MCMB) because the original natural graphite has a prismatic (flake-like) structure .

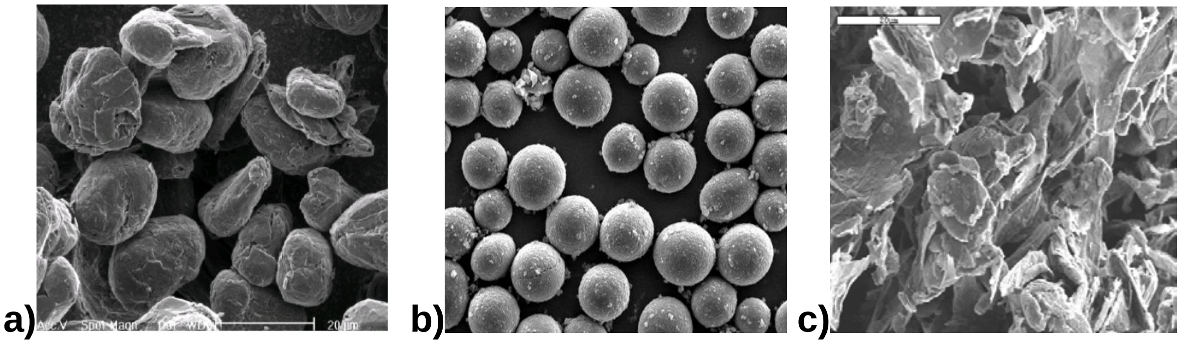

Figure 1. *SEM micrographs of different- type graphite materials: a) SLC1520P graphite; b) TB17 MCMB c) ABG 1005 graphite*

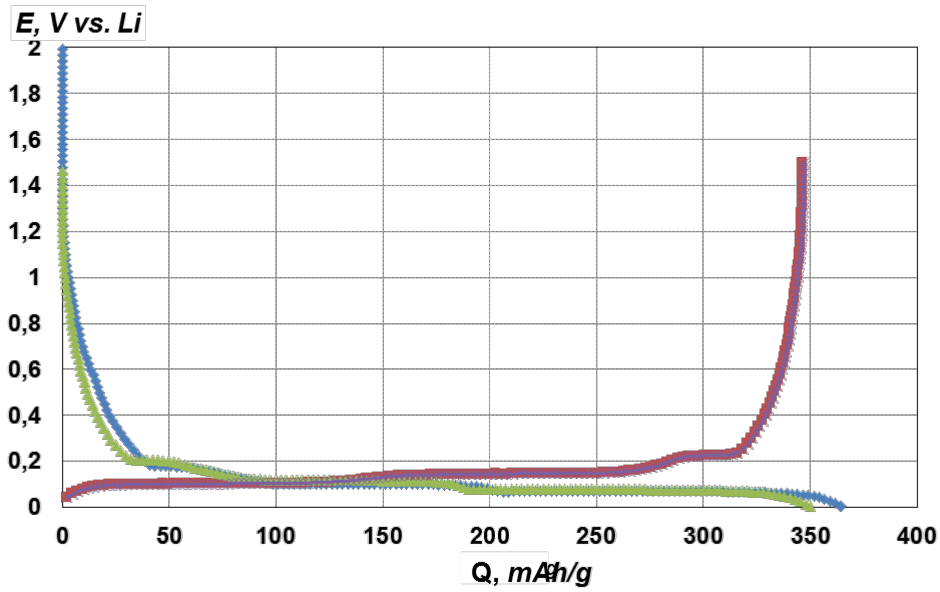

Figure 2. Charge and discharge profile of the half - element based on the reference SLC1520P graphite at the current density C/10

The electrochemical investigation of all anode materials was started with the first lithiation performed against metallic lithium. Fig. 2 shows initial charge/discharge curves for the SLK1520P graphite sample from Superior Graphite Co in the 2025 type half-elements. In the investigation, the coin cells were used for optimization of anode materials. The reversible capacity of SLC1520P graphite at the first cycle was of Q ~ 358 mA·h/g; this is quite close to the theoretical capacity. Irreversible loss of capacity at the first cycle came to 18 mA·h/g. The same test was done for different commercial types of carbonaceous materials. Some physical-chemical characteristics of selected samples are included in Table 2. Also, the values of reversible and irreversible capacity of all samples are presented in table 2. It is necessary to note that the lowest irreversible capacitance suggests the choice of Superior Graphite Co. Irreversible capacity is correlated to the surface area of a material, thus the more promising materials are the ones with a relatively low surface area and spherical or potato- shaped particles. For example, the SLC1512P has a lower specific surface area, thus a minimal irreversible capacity.

Table 2. Characteristics of anodes based on different types of graphite

Carbon	**Type of graphite**	**Reversible capacity, mAh/g**	**Irreversible capacity, mAh/g**	**Particle size, D 50, μ**	**BET surface area, m^2/g**
SLC1512P	Surface coated spheroidal natural flake	359	19	12,01	1,52
ABG1005	Expanded natural flake	327	106	6,5	16,5
KS6L	Synthetic graphite	363	114	6	22
TB17 MCMB	Artificial synthetic materials	309	25	26	0,86
SLP30	Highly crystalline structure artificial graphite	358	50	32	7
SLC1520P	Surface coated spheroidal natural flake graphite	358	18	17,99	0,96

It is well known that the reversible specific capacity decreases with increasing the current rate. In this work, selected graphite materials have been studied at various current densities in the cells using a Li metal counter electrode. Figure 3 shows discharge capability of graphite materials obtained as a function of discharge rate. Different graphite anodes were tested using the CR2025 coin half-cells. Discharge capability was determined at different C-rates with a charge of C/5 in the voltage range: 0.001-1.50 V vs. Li.

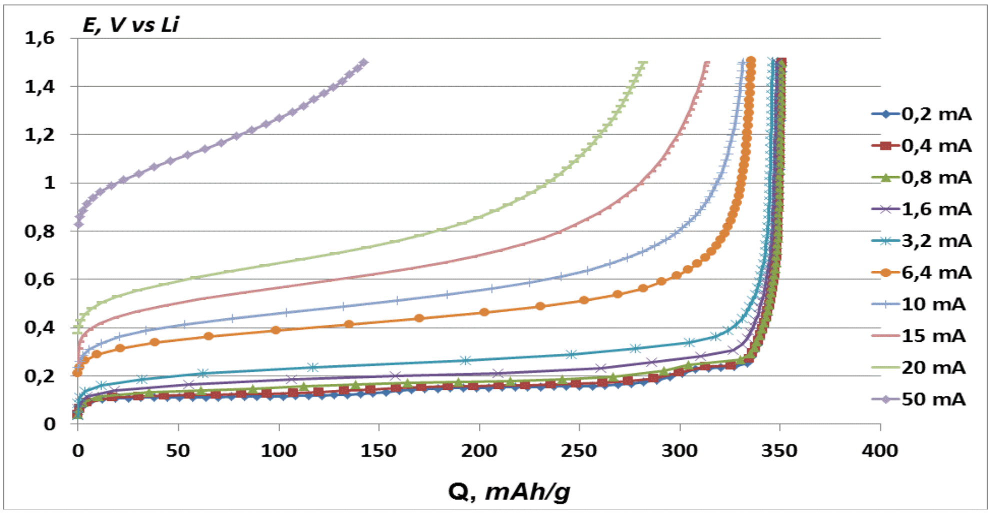

Figure 3. *Discharge capability graphite materials SLP-30 at different C-rates with a charge of C/5 in the voltage range 0.001-1.50 V vs. Li*

Such graphite materials as KS-6 and SLP-30 show more than 90% of capacity retention at 3C rate. However, high-rate capacity for the SLC1520P and MCMB (TB-17) graphite decreased. The other graphite materials presented in table 2 showed lower discharge capability than that of SLC1520 or MCMB. Therefore, such graphite materials as KS-6 and SLP-30 were selected for application in the LIC.

Conclusions

In this work different grades of carbonaceous materials were tested. Electrochemical high-rate and pulse measurements were applied to various types of graphite active materials for power-oriented lithium-ion capacitors. The results indicate the impact of graphite materials at high-power drain in real designed power devises. Surface coated spheroidal natural flake such as SLK1520P shows better electrochemical performance at low current density than other grades of graphite due to lower specific surface area. Nevertheless, these materials show some drawbacks regarding power performance. It was found that graphite KS-6 and SLP-30 from Timical shows the superior gravimetric capacity, density when high-current rates are used.

References

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