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Benchmark study on high performing carbon anode materials

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Abstract

Four state-of-the-art carbon graphite morphologies, beads, fibers, flakes and potatoes have been benchmarked with respect to materials properties and electrochemical performance. All four anode materials exhibit various degree of graphitization and performance. Fibers have a higher degree of turbostratic structure. Flakes consist of a binary phase mix. Potatoes and beads have reached an intermediate degree of crystallinity. Although graphite flakes still show the highest performance in early cycles, new materials challenge not only in-cell capacity, but also rate capability and cyclability. © 2001 Published by Elsevier Science B.V.

Keywords: Rechargeable lithium battery; Carbonaceous anode; Graphite

1. Introduction

Lithium-ion batteries dominate the portable power industry for laptop computers and mobile telephones. The lithium-ion battery technology is rapidly advancing and major improvements are focusing on battery capacity and safety. Recent successes have been based on integrated system design by combining novel active materials and developing solid processing parameters. One key element to enhanced lithium-ion battery performance is the selection and processing of active anode materials. In this paper, we present benchmarking data on state-of-the-art active carbon anode materials.

The battery manufacturers have not yet reached consensus on which anode material represents the best choice. Although, graphitic carbon is most widely used, there are still several phase, morphology and size variations for graphite materials found in the market place today. The most important developmental driver remains lithium-intercalation capacity, closely followed by processing and safety properties. Graphite's theoretical maximum capacity based on the intercalated composition LiC_6 of 372 mAh/g is somewhat lower than the capacity exhibited by many non-graphitic carbons that reach >450 mAh/g. However, good cycle life of graphite-based anodes in addition to high first cycle efficiency makes graphite an attractive choice.

Benchmarking active carbon materials focuses on their performance in a battery system and must, therefore, also

include optimization of components and processing. Surface termination and morphology play crucial roles in performance and processing. For example, a material's morphology will define both surface area and reactivity with electrolyte and Li^+ in a battery system, as well as determine the level of compressibility, which affects volumetric capacity of the cell and consistency of electrodes (hence reliability and potentially safety).

2. Experimental

X-ray diffraction (XRD) was measured on a Shimadzu XRD-6000 unit (Kratos Analytical) equipped with a monochromator, using Bragg–Brentano geometry and $\text{Cu K}\alpha$ radiation.

Benchmark samples were prepared in a 90:5:5 wt.% solids ratio of active material, PVDF binder (Kureha KF-#9130) and conductive carbon (acetylene black). Electrodes were solvent coated from a slurry with 1-methyl-2-pyrrolidinone solvent onto 18 mm thick copper foil. The slurry viscosities were in the range of 8000–12 000 cP. Coatings were dried at 130°C for 40 min followed by densification at 1500 kg/cm². Electrodes were dried overnight in a vacuum oven to eliminate any remaining solvents. Cells were assembled as the cathode with Li metal foil as anode, glass fiber disc as separator and 1 M LiPF_6 in 1:1 EC/DMC (EM Industries) electrolyte. Consistency in coin cell production was monitored with electrochemical impedance spectroscopy. Forced time testing protocols utilizing a variation of C/8–2C charge and

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discharge rates were utilized to quickly differentiate the four carbon samples.

3. Results and discussion

Four different pitch-based carbon materials with various morphologies were included in this study (Fig. 1, Table 1). As particle size and shape highly impact packing density and

volumetric capacity, we have included a 50% diameter measurement for comparison between samples. It is important to note that this number does not capture the size distribution displayed by scanning electron microscopy (Fig. 1). The first sample consists of graphite beads, which are mostly spherical in shape with diameters ranging from 10–50 μm . The second sample is a graphite fiber with lengths of 10–50 μm and cross-sections of about 10 μm . The third sample is a graphite flake material, which has been

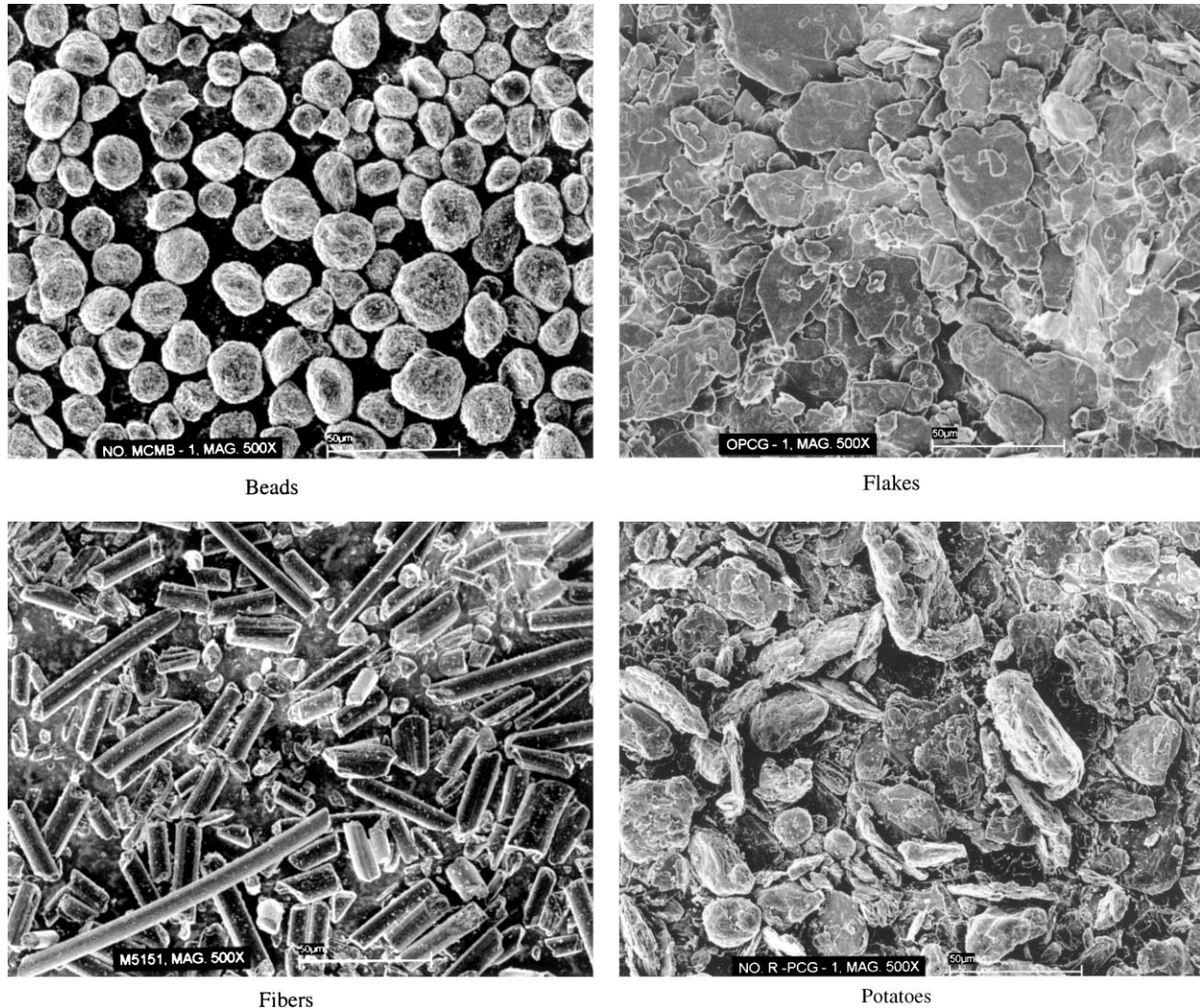


Fig. 1. SEM images showing four different morphologies of graphite particles used as the active anode material in Li-ion batteries today.

Table 1
Materials characterization of state-of-the-art anode materials

Graphite sample	$d(0\ 0\ 2)$ (nm)	L_c (nm) (from 0 0 2)	L_a (nm) (from 1 1 0)	Intensity ratio $I_{(1\ 0\ 1)}/I_{(1\ 0\ 0)}$	Particle size, 50% diameter (μm)	Specific surface area (m^2/g)
Beads	0.3367	21	76	1.74	21.6	1.08
Fibers	0.3368	17	66	1.36	17.9	1.30
Flakes	0.3351 (0.3401)	>100	>100	3.7	22.0	2.97
Potatoes	0.3366	16	73	2.06	19.1	2.42

Table 2
Initial electrochemical results

Graphite sample	Electrode density (g/cc)	First cycle specific capacity (mAh/g)	First cycle in-cell capacity (mAh/g)	First cycle in-cell capacity (mAh/cc)	First cycle coulombic efficiency (%)	18th cycle 2C rate (%)
Beads	1.65	346	311	513	89	99
Fibers	1.61	325	293	471	89	99
Flakes	1.91	370	333	637	89	96
Potatoes	1.43	350	315	451	88	99

coated with non-graphitic carbon. These flakes measure from 5–50 μm across and have a thickness less than 1 μm . The fourth sample consists of ground graphite particles, leading to a motley distribution of sizes and shapes, somewhat like small potatoes, resulting in effective spherical diameters similar to that of the graphite beads (synthesis parameters described in [1–3]).

XRD analysis shows that all of these materials are graphitized, although the extent of graphitization varies. Table 1 summarizes XRD parameters for the four different types of carbons. The differences seen in the XRD data reflect differences in the atomic structure of the carbon materials, which can, therefore, be expected to exhibit differences in electrochemical cycling. Structural parameters such as crystallite size (L_c and L_a , Scherrer equation), $d_{(0\ 0\ 2)}$, and peak intensity ratio $I_{(1\ 0\ 1)}/I_{(1\ 0\ 0)}$ can be used to monitor extent of graphitization. Fibers appear less graphitized compared to the three other morphologies. This may be attributed to a larger amount of defects in the crystal structure created in the spinning process, creating a barrier for the graphitization reaction. The coated flakes have a binary carbon composition, which is evident by the two numbers for $d_{(0\ 0\ 2)}$.

All materials included in this benchmark study show good performance for lithium-ion battery technologies (Table 2). However, all material types exhibit strength in various areas. The variation in specific capacities for the different graphitic materials (325–370 mAh/g) is even more pronounced in volumetric energy density (451–637 mAh/cc). It is interesting to note that no strict relationship between gravimetric and volumetric energy density exists. This is nicely illustrated in the “potato morphology” graphite, which shows high gravimetric capacity with low volumetric electrode values. A property that is going to play an even greater role in the future is the first cycle efficiency (all are 88–89%), for which there are large opportunities for differentiation.

Large differences between the four carbon samples are observed in the electrochemical cycling using forced time testing protocols (Fig. 2). Flake morphologies are known to exhibit closer to theoretical maximum values in capacity, due to their higher degree of graphitization. This advantage is compromised by decreased long-term cyclability and lower rate capability, both of which are greatly improved in fiber graphites. The mesophase microbeads and potatoes

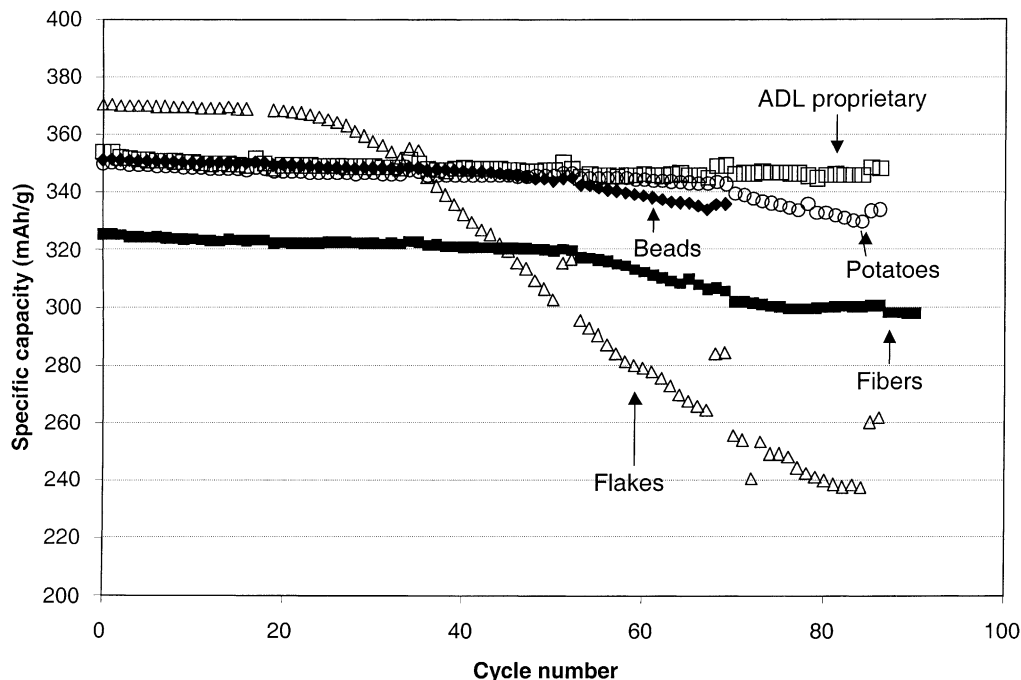


Fig. 2. Forced time testing capacity plots for five different graphite materials.

are well graphitized, resulting in capacities approaching those of the flakes. Although, a high level of graphitization is preferred for high specific capacity, other parameters such as electrode density, cyclability and process window may dominate the performance. Recently, manufacturers of carbons have introduced materials doped with boron, the addition of which has the beneficial impact of increasing the degree of graphitization and increasing capacity. Some

of these materials are now under active evaluation in our laboratories.

References

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