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Comparison of the Electrochemical Properties of Several Commercial Graphites with a Templated Disordered Carbon

Ronald A. Guidotti* and F. W. Reinhardt
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0614

and

Giselle Sandí
Argonne National Laboratory
9700 South Cass Ave.
Argonne, IL 60439-4803

** Author to whom all correspondence should be addressed*

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Argonne National Laboratory, 9700 South Cass Ave.
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Abstract

A templated carbon was prepared by the pyrolysis of pyrene impregnated into pillared clay (PILC). The electrochemical performance of this was evaluated with the goal of using this material as an anode in Li-ion cells. The reversible capacity was measured as a function of C rate and the cycling characteristics were determined for various intercalation protocols. The performance of this material was compared to that of several commercial graphites tested under the same conditions. The PILC carbon shows great promise as a Li-ion anode if the fade and first-cycle losses can be controlled.

Introduction

A large number of carbon materials are being studied and developed for use as anodes in Li-ion cells. The maximum theoretical reversible capacity of typical graphitic carbons is 372 mAh/g of C, for the formation of LiC_6. "Hard", non-graphitic carbons, on the other hand can exhibit reversible capacities much greater than this, due to their unique disordered structure. Many organic precursors have been studied by researchers, including various resins, cotton, woods, sucrose, cork, and the like. Depending on the pyrolysis conditions, a wide range of properties is obtained. Generally, most of these materials have capacities in excess of 400 mAh/g but suffer from equally large first-cycle irreversible losses. However, the pore structure of these materials is not readily controllable.

Argonne National Laboratory has developed a unique process to prepare disordered carbons with a controlled pore size to enhance Li-ion diffusion in the carbon structure.[1-4] By using inorganic matrices as templates, organic precusors are impregnated from the liquid or vapor phase into aluminosilicate PILC hosts and are pyrolyzed under controlled conditions to produce disordered carbons. The aluminum-oxides supports within the clay prevent the collapse of the structure during heat treatment. After removal of the inorganic template by demineralization, a porous layered carbon results with a well-defined pore structure. By choosing the appropriate inorganic matrix, a range of pore sizes can be readily obtained.

In this work, we report on the electrochemical performance of a disordered carbon prepared with pillared clay as the inorganic matrix and pyrene as the organic precursor. The performance of this disordered carbon was compared to that of a graphite from Osaka derived from mesocarbon microbeads (MCMB2528) and a fine-grained graphite from Lonza (KS-6). The cycling behavior and the rate capabilities over a range of 0.1 C to 3.2 C were determined and the effect of intercalation rate on the reversible capacities was examined.

Experimental

Materials – The pillared clay was stirred with a 0.1M solution of pyrene (Aldrich) in benzene overnight at room temperature. The impregnated clay was then filtered and sealed into a stainless steel tube that had been previously purged with nitrogen. The tube was then heated at 700°C for four hours. After depressurization of the tube, the carbon-loaded clay was then subjected to treatment with HF solution at 0°C to remove the mineral constituent. The final carbon was oven dried at 120°C overnight. The average diameter of the holes in the carbon was about 15 Å, which should provide a wide channel for Li-ion diffusion.

The MCMB 2528 graphite was obtained from Osaka Gas; the KS-6 graphite was obtained from Lonza (now Timcal). The electrolyte solution for the characterization tests was 1M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DMC) in a 1:1 volume ratio (Merck). The water content of the solution was typically <40 ppm as measured by Karl-Fischer titration. Li foil (Foote Mineral) was used for the counter and reference electrodes.

Cells – Swagelok® perfluoroalkoxy (PFA) tees were used to test the carbons. The anode was made with the carbon powder, 15 w/o polyvinylidene fluoride (PVDF) (Kynar 461) as a binder, and 5 w/o Super 'S' carbon as a conductive additive and was pasted onto a Cu-foil substrate using *N,N*-dimethylformamide. The anode discs were 1.27 cm in diameter (1.27 cm^2 area) and were separated from the 0.25-mm thick Li counter electrode by two Celgard 2500 separators. A Li foil was used as a reference electrode. The mass of active carbon ranged from 3 to 6 mg. Cell assembly was conducted in a dry room maintained at a dew point of less than -60°C. The polypropylene cells were evacuated and backfilled with electrolyte solution in a glove box where the moisture and oxygen content were <1 ppm each. After filling, the cells were allowed to stand overnight before testing.

Apparatus – Galvanostatic testing of the cells was performed using an Arbin Corp. Battery Test System. The cells were cycled galvanostatically between 2 V and 0.01 V versus Li/Li^+ using the schedule of Table 1, where the same rate was used for intercalation and deintercalation. The cells were then subjected to an additional 18 cycles, for a total of 50 cycles, using the schedule of Table 2. A 10-min wait was imposed between each charge and discharge, to allow the cell chemistry to relax. Each test was repeated twice.

Results and Discussion

The coulombic efficiencies for the PILC carbon and the two graphites are compared in Figure 1 when cycled at the C/5 rate. The coulombic efficiencies for the PILC carbon and the two commercial graphites are compared in Figure 1. The first cycle efficiency was the greatest for the MCMB 2528 graphite. The PILC carbon showed a low first-cycle efficiency of only 41%, which very likely results from having a much higher internal surface area than the graphites. This carbon also showed the lowest efficiency for the full 20 cycles. The efficiencies for the two graphites were comparable after seven cycles.

Table 1. Protocol for 32-Cycle Test for Same Rate of Intercalation and Deintercalation.

No. Cycles	Intercalation Rate	Deintercalation Rate
20	0.20 C	0.20 C
3	0.10 C	0.10 C
3	0.40 C	0.40 C
3	0.80 C	0.80 C
3	1.60 C	1.60 C

Table 2. Protocol for 18-Cycle Test where Intercalation Rate was Fixed at C/10 for All Intercalation

No. Cycles	Intercalation Rate	Deintercalation Rate
3	0.10 C	0.10 C
3	0.10 C	0.20 C
3	0.10 C	0.40 C
3	0.10 C	0.80 C
3	0.10 C	1.60 C
3	0.10 C	3.20 C

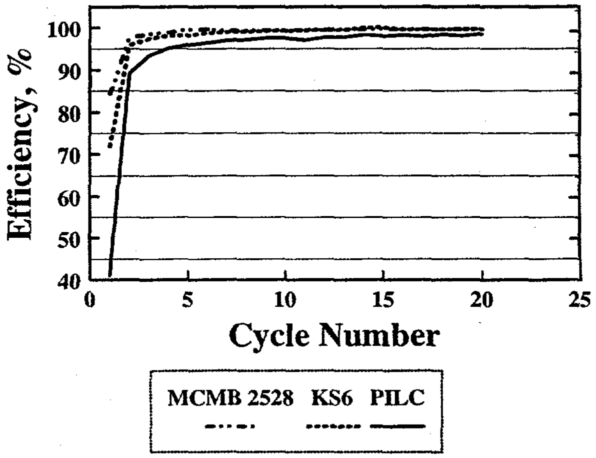

Figure 1. Comparison of Coulombic Efficiencies for PILC Carbon and Commercial Graphites Cycled at 0.2 C Rate.

The reversible capacities at the 0.2 C rate are compared in Figure 2. The PILC carbon had the highest reversible capacity initially—566 mAh/g on the first cycle. However, the fade for this material on cycling was high, so that by the 20th cycle, its reversible capacity was comparable to that of KS-6, which actually increased slightly with cycling. By the 20th cycle, it showed a reversible capacity of 368 mAh/g, which is close to the theoretical for LiC_6. Under these same conditions, there was a slight fade observed with the MCMB 2528 sample.

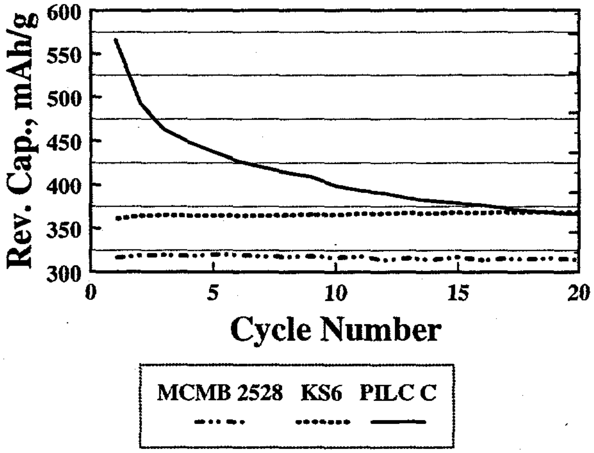

Figure 2. Comparison of Reversible Capacities of PILC Carbon and Commercial Graphites Cycled at 0.2 C Rate.

The degree of fade for the PILC carbon was not noted in earlier work.[1] That may be related to the manner in which the samples were prepared in this work. In the earlier work, the sample contained less binder (only 5%) than in this work (15%). Also, the samples were pressed into pellets at 5,000 psig, while in this work, the samples were simply doctor bladed. Also, a reference electrode was used in this work with a cutoff potential of 0.01 V, while the previous work was done in coin cells to a cutoff voltage of 0 V. The earlier work also used a lower C rate (C/20) for cycling. The slight difference in electrolyte composition between the two studies is not felt to contribute significantly to these observed differences.

The effect of C rate on the reversible capacities is shown in Figure 3 for the same rate of intercalation and deintercalation. (The data for 0.2 C are taken from the 20th cycle.) The rate capability of the KS-6 graphite was greater that of the MCMB 2528 graphite, which also dropped faster with increasing rate. The KS-6 and MCMB 2528 graphites similar coulombic efficiency for all C rates, which averaged over 99.6%. The capacity of the PILC carbon was the largest of the three carbons at the lowest C rate and the highest C rate. It showed the smallest drop with increase in C rate at the higher C rates but had a slightly lower coulombic efficiency. This is most likely a reflection of a higher surface area (6.05 m^2/g by BET) typical for such disordered carbons.

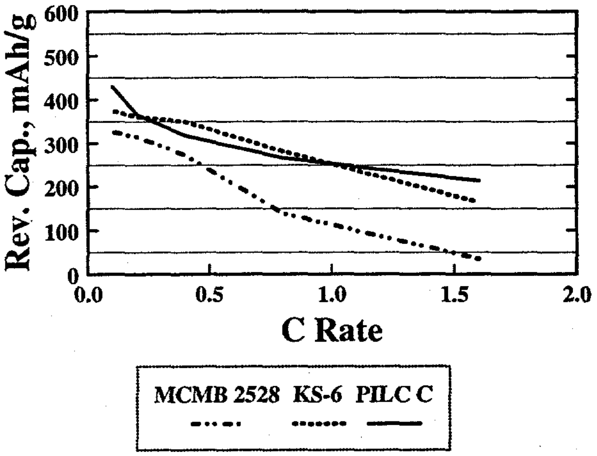

Figure 3. Reversible Capacities as a Function of Rate for Same Intercalation/Deintercalation Rate.

When the test protocol of Table 2 was used for the next 18 cycles, the performance differences between the two graphites was minimized. These test results are shown in Figure 4.

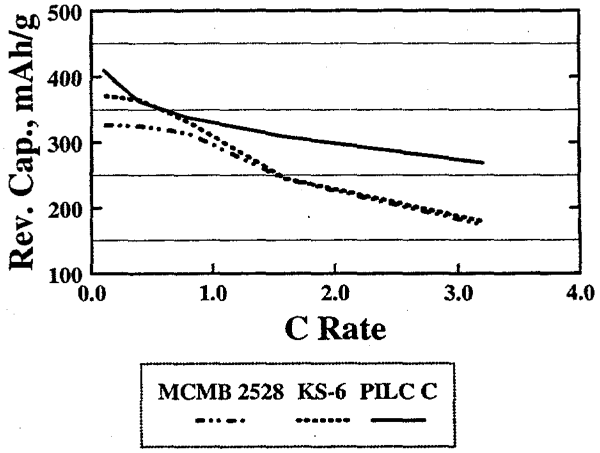

Figure 4. Reversible Capacities as a Function of Rate for Intercalation at Fixed 0.1 C Rate.

Slowing the intercalation rate to 0.1 C allowed the deintercalation to proceed at a higher rate. At a rate of 1.5 C and higher, the two graphites behaved identical. The PILC carbon, in contrast, had the highest rate capability of all the carbons and showed the least effect of rate on the reversible capacity.

The effect of intercalation rate on the reversible capacities is shown in Figures 5, 6, and 7 for the MCMB 2528 graphite, the KS-6 graphite, and the PILC carbon, respectively. The effect on the rate capability was most pronounced for the MCMB 2528 graphite. These data show that the manner in which the carbons are cycled (e.g., intercalation rate) can have dramatic effects on the reversible capacities that are obtained on deintercalation.

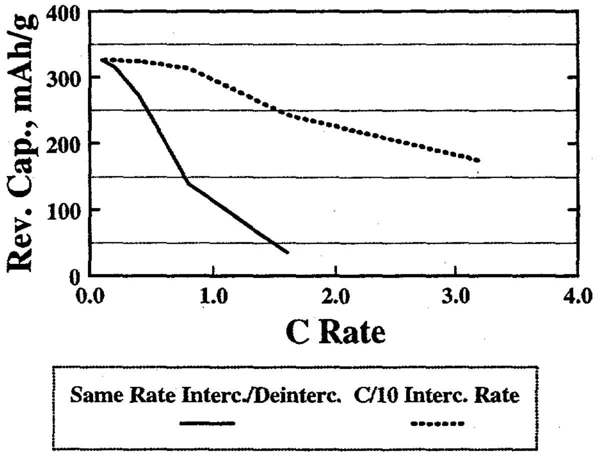

Figure 5. Effect of Intercalation Rate on the Rate Capability of MCMB 2528 Graphite.

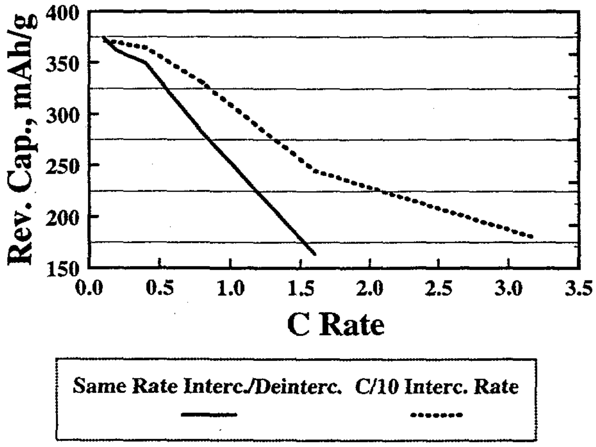

Figure 6. Effect of Intercalation Rate on the Rate Capability of KS-6 Graphite.

Conclusions

Pillared-clay substrates can be used for the preparation of templated carbons using organic precursors. This allows control on the dimensions of the channels in the carbon for enhanced Li-ion diffusion. A PILC carbon derived from pyrene has a much higher reversible capacity than commercial graphites such as MCMB 2528 and KS-6. First-cycle reversible capacities over 565 mAh/g can be attained. However, this is at the expense of a low coulombic efficiency of only 41%. This material also shows a high fade with cycling at a 0.20C rate (same rate of intercalation and deintercalation). The overall rate capability of the PILC carbon is far superior to that of the graphites and may be a result of a higher intrinsic surface area. Such material still shows great promise, however, if the first-cycle losses and fade observed during cycling at a 0.2 C rate can be successfully addressed and if they can be made economically in commercial quantities

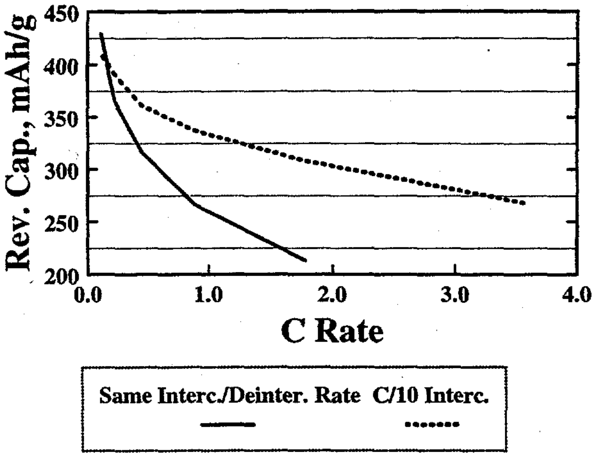

Figure 7. Effect of Intercalation Rate on the Rate Capability of PILC Carbon.

The manner in which the carbons are prepared and tested can have a significant impact on the performance that is obtained. Intercalation at a fixed 0.10 C rate during cycling tests at increasing rates increases the reversible capacity that can be realized compared to use of the same rate for intercalation and deintercalation. This is true for all the carbons tested and especially so for the MCMB 2528 graphite.

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