SAND99-1703C

THE EFFECTS OF LASER SURFACE RECONSTRUCTION OF DISORDERED CARBONS ON PERFORMANCE

Ronald A. Guidotti* and William R. Even**
Sandia National Laboratories
*P.O. Box 5800, Albuquerque, NM 87185-0614
**P.O. Box 969, Livermore, CA 94551

ABSTRACT

The reconstruction of the surface of disordered carbons was examined by heating carbons derived from polymethacrylonitrile (PMAN) and divinylbenzene (DVB) with a pulsed infrared laser in an argon or helium atmosphere, both fluidized and under static conditions. By graphitizing the outer surface of the carbons, it was hoped to reduce the high first-cycle losses associated with such disordered materials in Li-ion cells. The power to the sample was varied to observed the effects on surface morphology and electrochemical performance in 1M $LiPF_6$/ethylene carbonate-dimethyl carbonate. The use various reactive atmosphere such as ethylene, 2-vinylpyridine, pyrrole, and furfuryl alcohol were also evaluated as an alternative means of hopefully forming a thin graphitic layer on the carbon particles to reduce first-cycle irreversibility. While some improvement was realized, these losses were still unacceptably high. The laser heating did improve the rate capabilities of the carbons, however. More work in this area is necessary to fully understand surface and bulk effects.

INTRODUCTION

Disordered carbons have been extensively studied as intercalation anodes for Li-ion batteries. Their main attraction is their reversible capacities, which are much greater than the 372 mAh/g that is theoretical possible with ordered graphites. Unfortunately, these disordered materials have much higher first-cycle irreversible capacity losses than do the graphites—sometimes greater than the reversible capacities. In earlier work, we examined the possibility of laser heating, surface reconstruction of disordered ("hard") carbons derived from polymethacrylonitrile (PMAN)-divinylbenzene (DVB) copolymers (1). The intent of that work was the graphitization of the surface of the disordered carbon, thereby reducing the first-cycle irreversible losses, while at the same time taking advantage of the higher intrinsic reversible capacities of disordered carbons. Because of the promising results of that previous work, we have extended that study in the present investigation to include higher laser-power levels. The effect of the gas atmosphere surrounding the sample was examined, including the presence of a number of organic, potentially in-situ graphite-like coatings. This paper will present the results of this follow-on work.

DISCLAIMER

EXPERIMENTAL

Materials

The preparation of the disordered carbons used in this work has been previously described (2). Basically, an inverse emulsion polymerization of methacrylonitrile with divinylbenzene was used to produce a cellular carbon precursor. The final polymer was oxidatively stabilized and then pyrolyzed at 700°C under argon or an argon-5% hydrogen mixture to form the final PMAN carbon. Although this process does not optimize initial carbon capacity, it served as the starting point for a material tailored for laser-reconstruction experiments.

Laser Heating

A schematic diagram of the experimental setup used for laser heating of the experimental samples is shown in Figure 1. Provisions were made to allow either a static atmosphere or a dynamic one, where various gases could be flowed through the sample holder while the sample was heated. To assure that the carbon powders were not transported throughout the system, frits were used and the flow direction reversed on a two-second interval. The samples were examined by transmission electron microscopy (TEM), to determine the effect of surface ordering imparted by laser heating or materials deposition. The samples were heated at various power levels in the quartz cuvette using a Nd/YAG laser with an instantaneous pulse power density of 60 MW/cm^2 or an integrated power of 6 watts at 10 Hz. The pulses were deposited at various rates to allow for variation in integrated power dose and, therefore, graded reconstruction. Deposition rates varied from 1 to 10 Hz, accumulated to 100 sec per face, with each face exposed twice. Carbon powders were loaded in an argon glovebox with <10 ppm oxygen. Tests were conducted under flowing helium or nitrogen in the inert mode (alone) or active mode, saturated with furfuryl alcohol, pyrrole, or 2-vinylpyridine. Complementary tests were also performed under an atmosphere of flowing ethylene, since pyrolysis or postheating under ethylene was reported to reduce the first-cycle irreversible losses in some disordered carbons (3). After reconstruction, specimens were taken for physical analysis and balance loaded under high-purity argon for shipment to Albuquerque, NM, where the electrochemical testing was performed.

Electrochemical Characterization

Material. A ½" polyfluoroalkoxy (PFA) Swagelok® tee cell was used for electrochemical characterization of the samples. The samples were "doctor bladed" onto a copper foil and contained 85% carbon, 15% polyvinylidenedifluoride (PVDF) as a binder and 5% Super 'S' carbon black as a conductive additive. The electrolyte was 1M $LiPF_6$ in 1:1v/v of ethylene carbonate (EC)-dimethyl carbonate (DMC) (Merck). The water level was typically <40 ppm as determined by Karl Fischer titration.

Test Protocol. The samples were subjected to two test protocols. The first protocol involved 32 cycles and is shown in Table 1. The first 20 cycles gives a measure of the tendency for fading. The remaining cycles provide information on the rate capability. The same rates were used for intercalation and deintercalation. The second test protocol involved an additional 18 cycles, for a total of 50 cycles. It is shown in Table 2. In this protocol, the intercalation rate was fixed at C/10 to maximize Li charging. Some samples

were also subjected to cyclic voltammetry tests at a scan rate of 1 mV/s between voltage limits of 3 V and 0.010 V.

RESULTS AND DISCUSSION

Effect of Power Level and Atmosphere

The power level and the atmosphere surrounding the carbon samples had a significant impact on the heat-transfer process and the subsequent degree of ordering of the carbon surface. The effect on the first-cycle irreversible and reversible capacities of 700°C PMAN carbon is shown in Table III, along with the corresponding fade data.

The first-cycle reversible capacities increased with increase in the laser power in a static-argon environment, but the first-cycle irreversible capacities were still high. The first-cycle coulombic efficiencies also improved with increase in power level, as generally did those for the 20^{th} cycle. There was a slight reduction in the fade only at the highest power level.

The use of helium instead of argon at the highest power resulted in a slight increase in the first-cycle irreversible losses, a slight decrease in the first-cycle coulombic efficiency, and a corresponding decrease in the reversible capacity for the 20^{th} cycle relative to argon. There was also a slight increase in the fade. Under flowing helium, the first-cycle reversible capacity further decreased. This is related to the heat transfer that takes place in helium, which is a much better thermal conductor than argon. This increased conductivity results in condensation of materials ablated from the extreme outer surface of the carbon particle. The carbon vapor condensate is extreme disordered and has a very high surface area, likely exacerbating the loss mechanisms (see Figure 2 inset).

The TEM photomicrograph of Figure 2 shows the surface ordering that typically resulted after laser heating in static argon at the highest power level. The graphene sheets at the surface of the carbon particles are readily seen.

The effect on the rate capabilities of laser heating are presented in Figure 3 as a function of laser power for intercalation/deintercalation at the same rate for both argon and helium environments. There was a gradual increase in the rate capability at increasing laser power. The coulombic efficiency showed a concomitant improvement but the irreversible capacity showed a similar increase, except at the highest power level, as shown in Figure 4. The use of static argon gave the best results. The degree of surface reconstruction was less for the samples heated under helium due to larger heat losses to the surrounding environment. When the intercalation rate was fixed at C/10, the overall rate capability improved considerably, as shown in Figure 5 for a static-argon environment.

Organic Additives

The results of tests at 1.6 W of heating using flowing nitrogen saturated with various organic materials are summarized in Table IV. The organic additives all increased the first-cycle reversible capacities and efficiencies over the control, but only the presence of

2-vinylyridine or furfuryl alcohol reduced the first-cycle irreversible losses. Of these, only the sample treated with 2-vinylpyridine showed a reduction in fade and had a higher capacity after the 20th cycle. Treatment with ethylene gas severely degraded the performance of the PMAN carbon, reducing the reversible capacity and efficiencies, even after 20 cycles. While some reduction in the first-cycle irreversible losses did occur, it was at the expense of the reversible capacity. The benefits reported by Buiel and Dahn (3) with ethylene treatment were not realized with our disordered PMAN carbons.

The effects of the organic additives on the rate capabilities of the 700°C PMAN carbon are summarized in Figure 6 for intercalation/deintercalation at the same rate. The beneficial effects of 2-vinylpryidine were maintained only up to a 0.6C rate, while those for pyrrole persisted up to the highest C rate studied (1.6C). The performance suffered in the presence of furfuryl alcohol but not to the extremes demonstrated in the presence of ethylene. When the intercalation rate was fixed at C/10, the relative performance levels changed somewhat, with the sample treated with 2-vinylpyridine now showing a slightly better performance than the control up to 1.5 C. As seen in Figure 7, all of the other samples showed inferior performance to the control over the entire rate range studied. As before, the performance of the sample heated under ethylene was very poor.

CONCLUSIONS

Pulsed laser heating can be used to induce surface reconstruction of a disordered PMAN carbon. The effects on the electrochemical performance is improved coulombic efficiencies, higher reversible capacities and rate capabilities, and, in once case (at 2.7 W), a reduction in the first-cycle irreversible capacity. The best overall results are obtained at the highest power level examined, 1.5 W, in a static argon environment. The use of a helium environment reduces the effectiveness of this process by increasing heat losses to the surrounding environment and producing new disordered, condensed phases at the surface. The goal of substantially reducing the first-cycle irreversible capacity in a consistent manner was not realized using laser surface reconstruction.

Laser heating of the PMAN carbon surfaces in the presence of pyrolyzable organic compound such as 2-vinyl pyridine, furfuryl alcohol, pyrrole, and ethylene produced mixed results. Beneficial results are obtained only with the use of pyrrole and 2-vinylpyridine, which increases the rate capability for intercalation and deintercalation when tested at the same rate. Severe degradation occurs in the presence of ethylene, however, with reduced reversible capacities seen under all the discharge regimes examined.

While surface reconstruction can be used to improve the performance of disordered carbons under certain conditions, the electrochemical behavior of these materials remains complex and not well understood. There are still bulk-chemistry effects that impact performance in an ill-defined manner. The high first-cycle irreversible losses and fade characteristics of PMAN carbons are too high to make them a viable choice for use in Li-ion cells, when compared to a number of available commercial graphites. However, PMAN carbons still serve as a good model material for pursuing physical understanding of highly disordered carbon systems.

ACKNOWLEDGMENTS

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

REFERENCES

1. W. R. Even, L. W. Peng, N. Yang, and T. Headley, *Mater. Res. Soc. Symp. Proc.*, **496**. 619 (1998).
2. W. R. Even and D. P. Gregory, *MRS Bull.* **19**(4), 29 (1994).
3. E. Buiel and J. R. Dahn, *J. Electrochem. Soc.*, **145** (6), 1977 (1998).

Table I. Testing Protocol for 32-Cycle Galvanostatic Cycling between 2 V and 0.01 V.

Number of Cycles	Intercalation Rate	Deintercalation Rate
20	C/5	C/5
3	C/10	C/10
3	C/2.5	C/2.5
3	C/1.25	C/1.25
3	C/0.625	C/0.625

Table II. Testing Protocol for 18-Cycle Galvanostatic Cycling between 2 V and 0.01 V.

Number of Cycles	Intercalation Rate	Deintercalation Rate
3	C/10	C/10
3	C/10	C/5
3	C/10	C/2.5
3	C/10	C/1.25
3	C/10	C/0.625
3	C/10	C/0.313

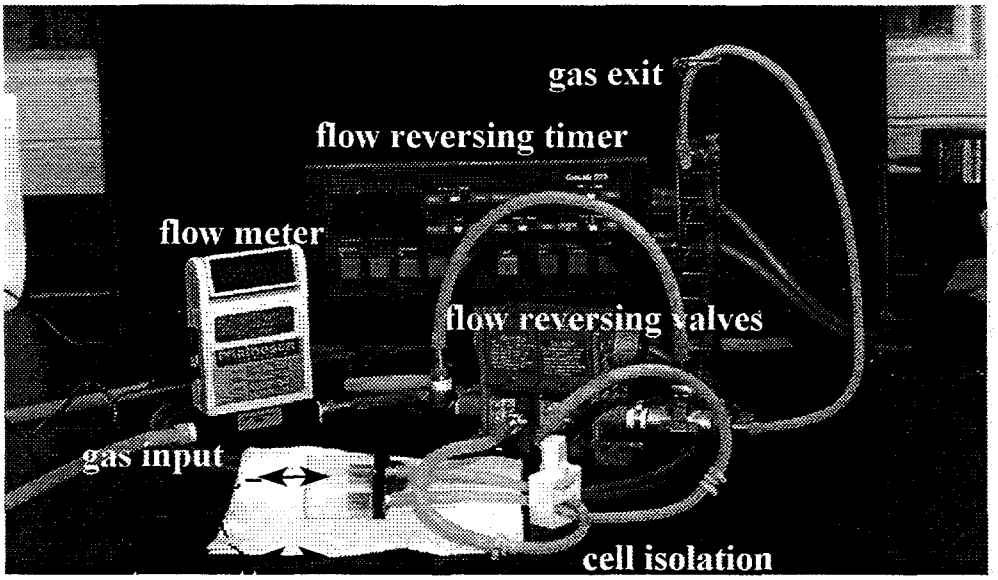
Table IIII. Effect of Laser Power and Atmosphere on Electrochemical Performance of 700°C PMAN Carbons.

Laser Power, W	Atmos.	1st Cycle Qrev, mAh/g	1st Cycle Qirrev, mAh/g	1st Cycle Effic., %	20th Cycle Qrev, mAh/g	Fade, mAh/g-cycle*
0	Static Ar	337.3	409.0	45.2	225.3	-1.94
1.60	Static Ar	354.9	425.0	45.5	245.6	-1.97
2.70	Static Ar	326.5	315.1	50.9	227.4	-1.94
3.25	Static Ar	541.8	407.1	57.1	316.4	-1.39
3.25	Static He	543.8	453.2	54.6	295.0	-1.77
3.25	Flow He	501.1	393.3	56.0	275.3	-1.70

* Fade = (Qrev for cycle 20-Qrev for cycle 11)/10

Table IV. First-Cycle Results of Heating 700°C PMAN Carbon at 1.6 W in Flowing Nitrogen Saturated with Various Organic Compounds.

Organic	1st Cycle Qrev, mAh/g	1st Cycle Qirrev, mAh/g	1st Cycle Effic., %	20th Cycle Qrev, mAh/g	Fade, mAh/g-cycle*
None	366.2	513.8	41.6	237.8	-1.54
2-Vinylpyridine	414.9	496.3	45.5	266.7	-1.60
Pyrrole	433.8	516.8	45.6	251.8	-3.00
Furfuryl alcohol	376.5	475.1	44.2	225.3	-2.02
100% Ethylene	296.3	429.9	40.9	139.0	-2.40



Fresh supply gas enters the cuvette regardless of flow direction; check valves insure exit gas does not re-enter cell

Figure 1. Experimental Setup Used for Laser Heating of Carbons.

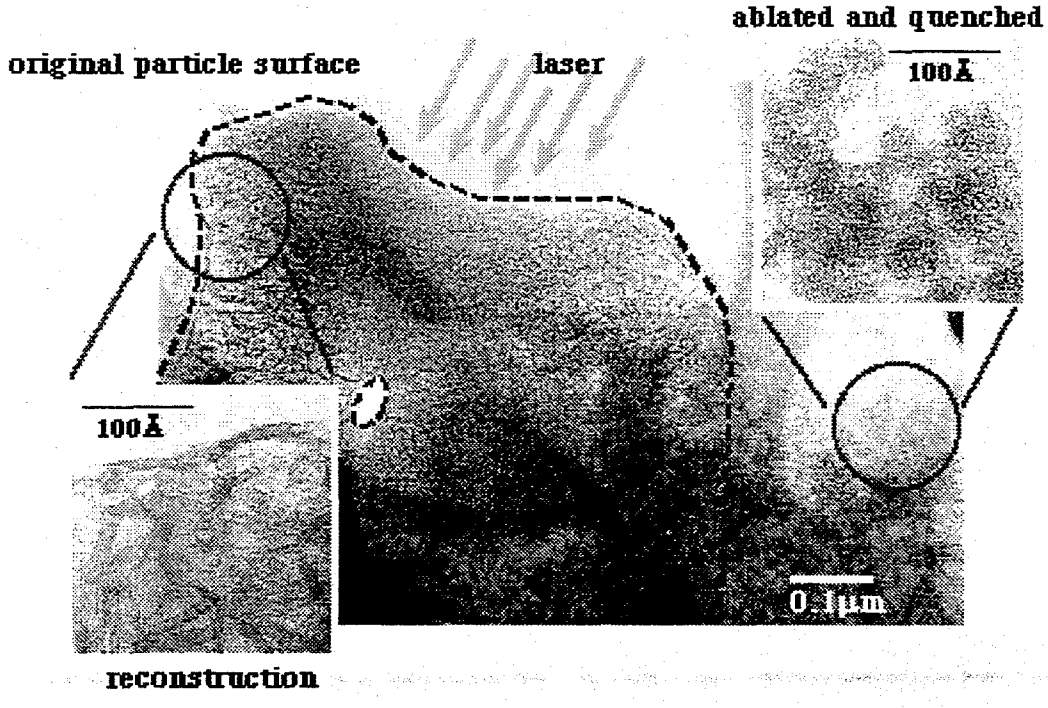


Figure 2. TEM Photomicrograph Showing Surface Reconstruction for 700°C PMAN Carbon after Laser Heating at 3.5 W under Static Helium and the Disordered Surface Condensate.

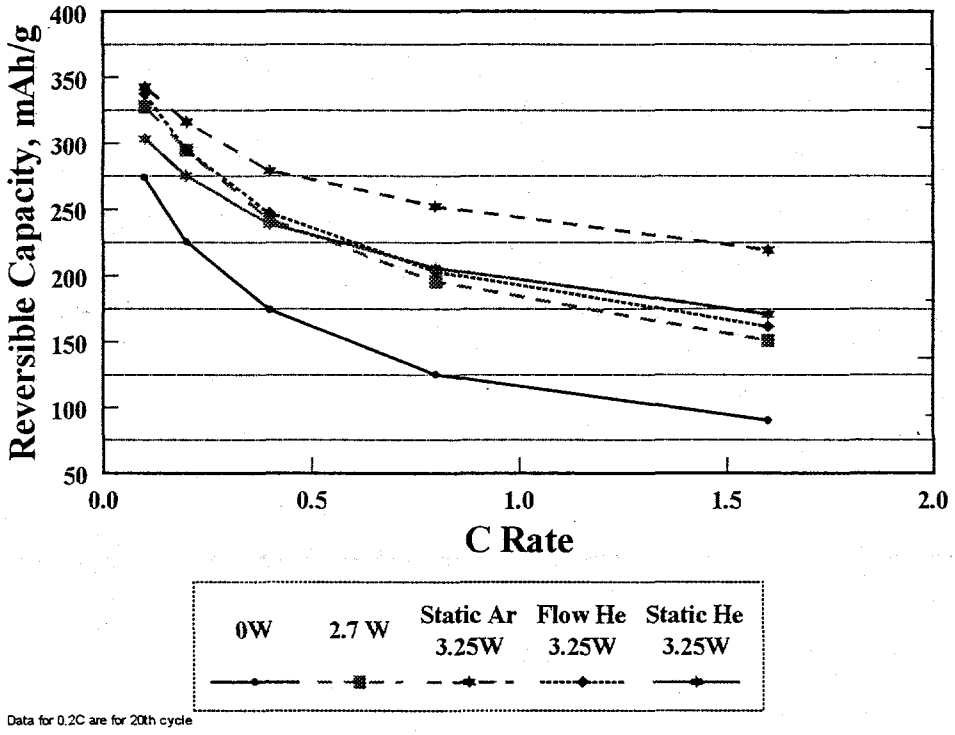


Figure 3. Effect of Laser Power and Atmosphere on the Rate Capabilities of 700C PMAN Carbon for the Same Intercalation/Deintercalation Rate.

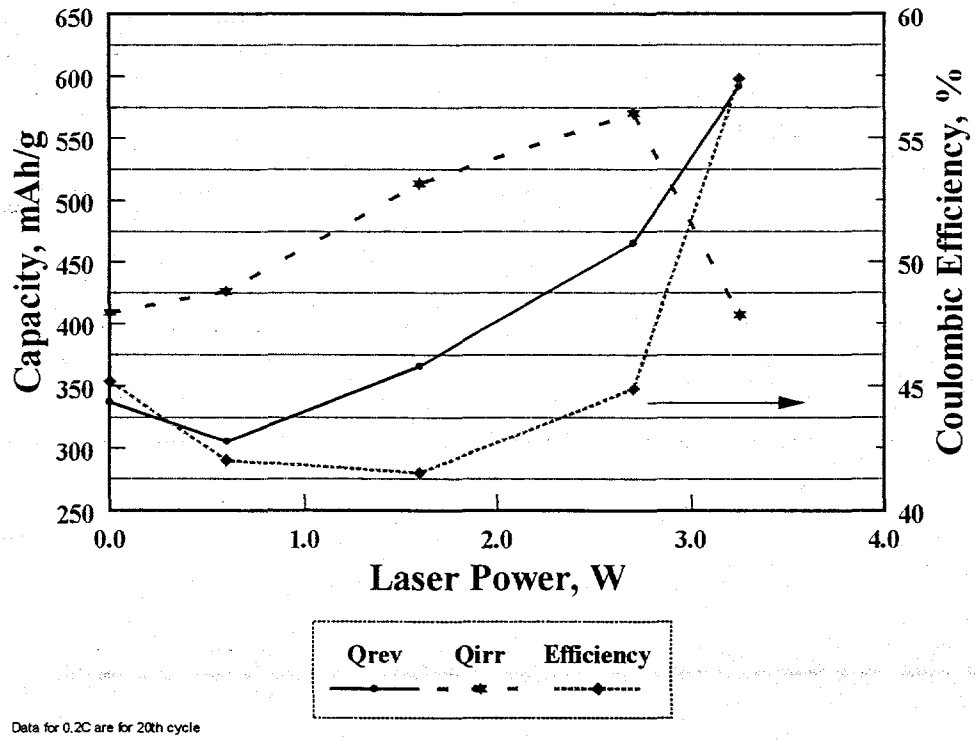


Figure 4. Capacities and Coulombic Efficiencies for 700°C PMAN Carbon as a Function of Laser Power for Static Argon.

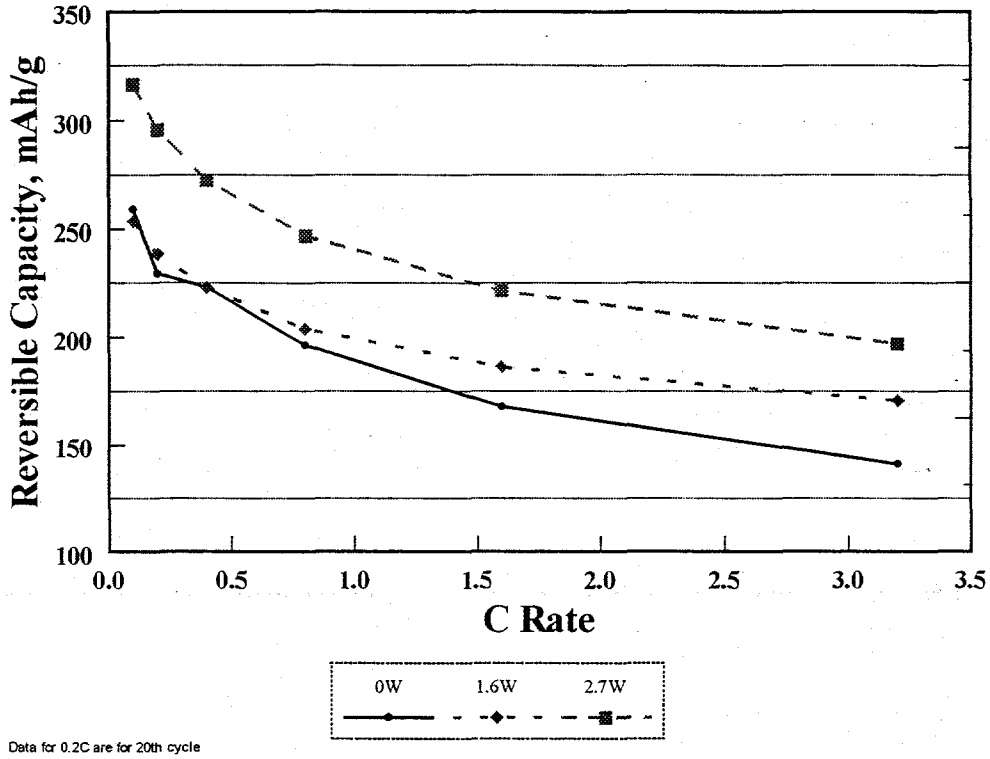


Figure 5. Effect of Laser Power on the Rate Capabilities of 700°C PMAN Carbon for the Intercalation Fixed at C/10 Rate for Static Argon.

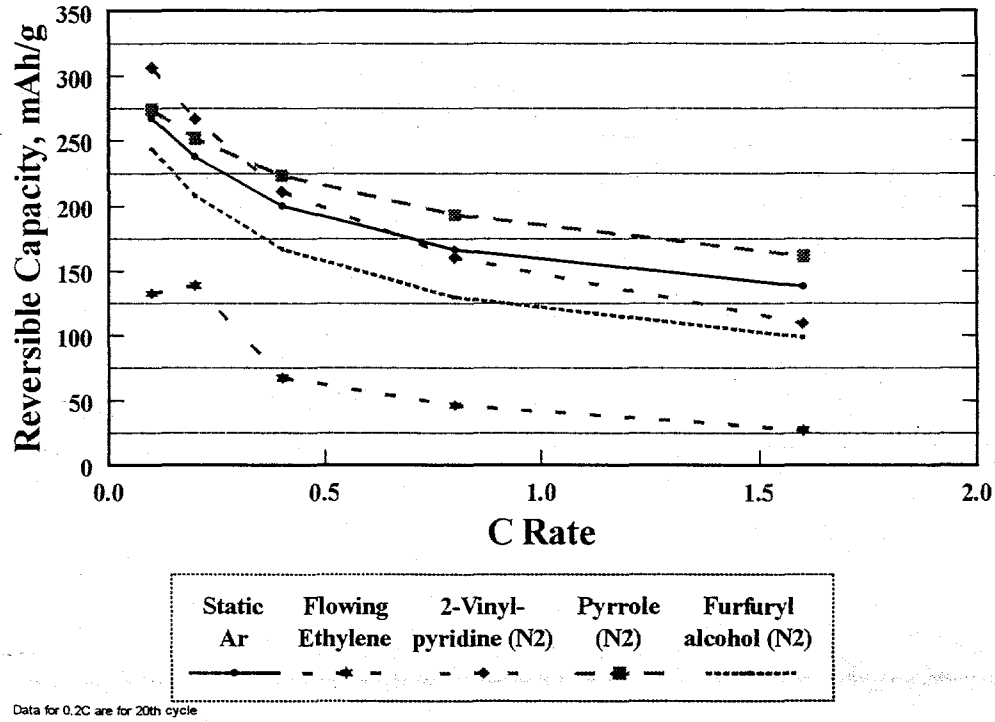


Figure 6. Effect of Organic Additive during Laser Heating under Nitrogen on Rate Capabilities of 700°C PMAN Carbon for Same Intercalation/Deintercalation Rate.

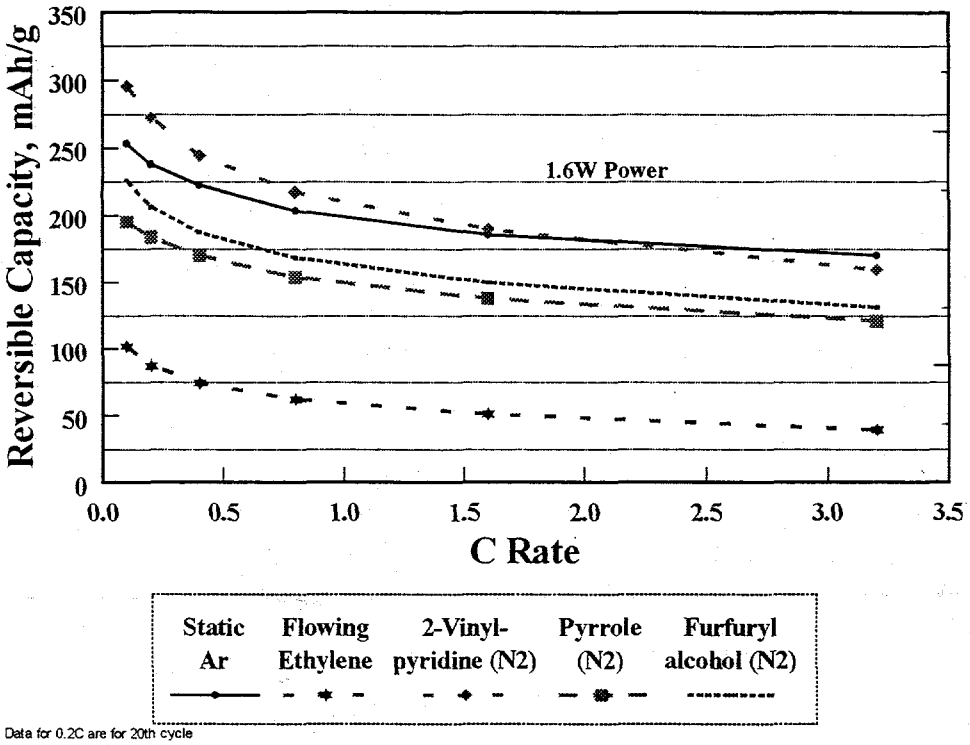


Figure 7. Effect of Organic Additive during Laser Heating under Nitrogen on Rate Capabilities of 700 C PMAN Carbon for Intercalation at C/10 Rate.