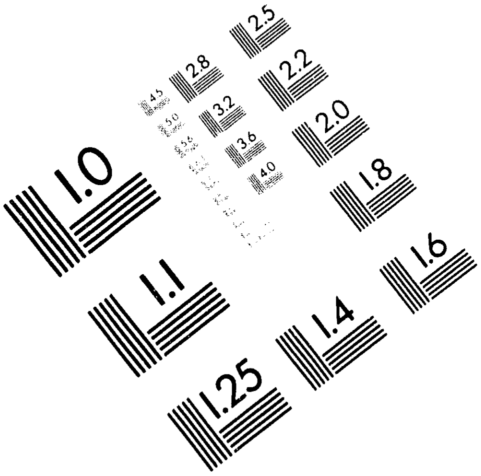
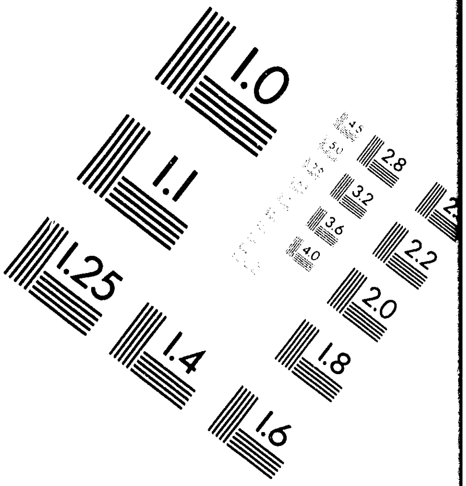


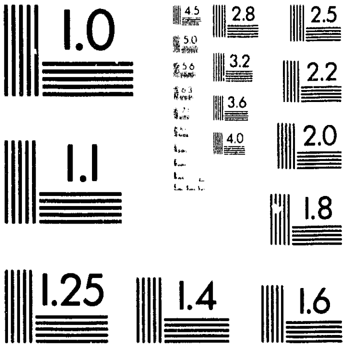
AIIM

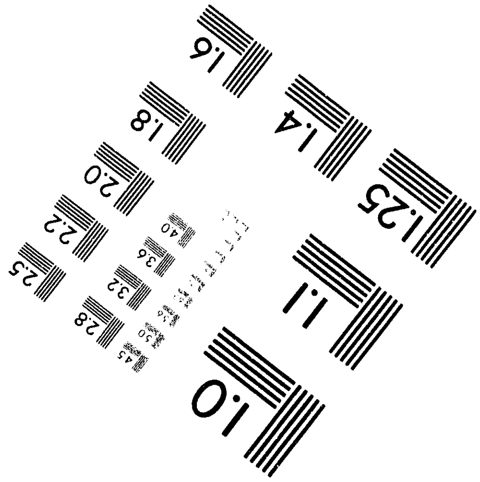
Association for Information and Image Management

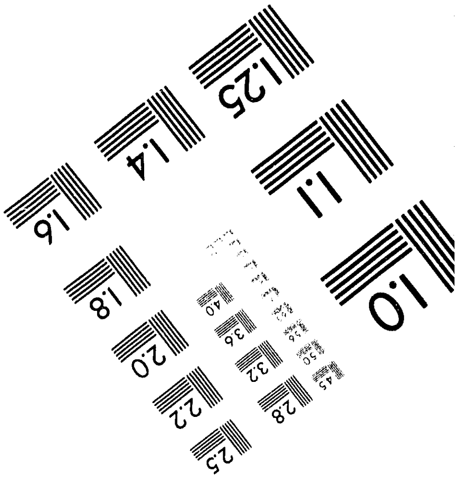
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Conf-940568--3

Proceedings, 7th International Meeting on Lithium Batteries, Boston, MA, May 15-20, 1994.

NOVEL FORMS OF CARBON AS POTENTIAL ANODES FOR LITHIUM BATTERIES*

Randall E. Winans and K. A. Carrado
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

---

*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

MASTER

RECEIVED
JUN 10 1994
OSTI

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOVEL FORMS OF CARBON AS POTENTIAL ANODES FOR LITHIUM BATTERIES

Randall E. Winans and K. A. Carrado
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

Abstract

The objective of this study is to design and synthesize novel carbons as potential electrode materials for lithium rechargeable batteries. A synthetic approach which utilizes inorganic templates is described and initial characterization results are discussed. The templates also act as a catalyst enabling carbon formation at low temperatures. This synthetic approach should make it easier to control the surface and bulk characteristics of these carbons.

Introduction

Electrode materials and their interfaces with electrolytes are critical areas that need to be addressed for the improvement of lithium secondary batteries. This paper will examine recent research in the development of materials for the negative electrode and will explore new approaches for preparing electrode materials.

Carbon is the material of choice for the negative electrode of these batteries [1,2,3]. Originally lithium metal was used for this electrode, but some severe problems ended its commercial application. First, dendrite growth on the electrode reduced its cycle life. Second, and more important, was the safety issue. These batteries tended to self-heat and sometimes ignite. Consequently, the more recent work has centered on several lithium insertion compounds that maintain a lithium activity close to unity [2], a value that is ideally suitable for a negative electrode. Graphite and other forms of carbon readily intercalate lithium metal. The exact composition of these Li_xC_6 compounds depends on the form of the carbon; for graphite, $x = 1.0$ and in some petroleum cokes, x is nearly 1.0 at room temperature. An important advantage of carbon over other host insertion compounds is that the potential is very close to that of lithium metal. A disadvantage is that the potential changes by as much as 1.5 V as the transfer of the lithium occurs [2].

The specific capacity for the negative electrode is smaller for lithium insertion compounds than for lithium metal. However, carbon electrodes appear superior in this respect to the metal oxide alternatives that have been examined [2]. Another important consideration is the diffusion of lithium into the electrode and its influence on the rates of charge and discharge. This matter is not well understood, and needs to be studied to define the limiting processes and provide information that can be used to guide synthetic approaches. The micro-texture [2,4,5] and the surface area of the electrode material are also significant. These properties make petroleum coke a better electrode than graphite.

The changing nature of the carbon electrode surface during the first charging cycle is another important factor in overall performance. Apparently, a film is formed on the electrode surface [6]. This film protects the cathode and prevents electrolyte from being carried into the electrode, and it contains the lithium metal that is lost in the first cycle. As expected, the amount of passivating film that forms is proportional to the surface area [6].

However, only a limited range of surface areas was explored, from 1.5 to 22.5 m^2/g, and very high surface area carbons were not examined. We conclude that controlling the nature of the surface of the negative electrode is a critical factor, and that a potential path toward this goal is the synthesis-by-design approach.

Other types of carbon besides graphite and petroleum coke have been examined as well. Dahn and co-workers have incorporated boron into carbon materials [7]. Some success was obtained with boron, but they found that nitrogen had detrimental effects. On the other hand, BC_2N material has been formed by chemical vapor deposition and claimed as potentially useful [8]. Disordered carbons such as carbon black and glassy carbons have been studied by Sleigh and von Sachen [9], who observed increased capacity while cycling above room temperature. Fullerenes (C_{60}) have been electrochemically intercalated with lithium in a step-wise process to yield Li_xC_{60} where x= 0.5,2,3,4 and 12 [10,11]. It is interesting to note that C_{60} contains 12 five-member rings which match the maximum number of Li intercalated. The maximum is six (M_6C_{60}) for other metals M = K, Rb, and Cs with a body-centered cubic structure [10]. However, the high cost of fullerenes prohibits their application in consumer batteries. Graphite fluorides that have been prepared at high temperature $(C_2F)_n$ and $(CF)_n$ or at room temperature $(CF_xX_y)_n$ (X= I, Br, Cl, and B) are claimed to be good electrode materials, but there is little documentation in the literature to support this claim [12,13]. Carbon fibers have been examined but they are inferior to petroleum coke [14]. Recently, petroleum coke has been incorporated into a PVC film to form an electrode, but there were problems with this configuration [15].

One of our goals is to design carbon electrodes with predictable porosity and surface area. We propose a new strategy that uses inorganic templates to direct the synthesis of carbons from polymeric precursors. Tomita and co-workers [16-19] have shown that layered carbons can be produced by heating polyfurfuryl alcohol or polyacrylonitrile that have been intercalated within clays such as montmorillonite. After removal of the inorganic template by acid hydrolysis, a highly-oriented graphite thin film remains. More recently they used two faujasites, a Y-zeolite and an HY-zeolite, as templates to produce three-dimensional graphitic materials with high surface areas and relatively narrow pore diameters [20]. The surface area of these materials can be controlled by subsequent high temperature treatments. Recently, a one-dimensional array of C_{60} has been prepared in a zeolite-related aluminophosphate VDI-5 [21].

A class of templates that we are studying is the synthetic pillared clays which have been designed and prepared in our laboratory [22-24]. Natural clays have a layered structure with the galleries between the layers filled with water and exchangeable ions. Clays that have been pillared have inorganic props between the layers. This prevents the collapse of the layers upon heat treatment. In the electrode-by-design synthesis, the organic polymer precursor is dispersed between the layers and then polymerized. Recently a method of incorporating polymers into an inorganic layered material without using a solvent has been reported [25]. Schwarz and co-workers have polymerized furfuryl alcohol within a pillared bentonite clay followed by carbonization [26]. However, their objective was to prepare an inorganic composite material and they did not remove the inorganic matrix. The resulting carbon will, therefore, have layers with holes due to the pillars as is depicted in Figure 1.

The extent of interlayer diffusion can be controlled by the concentration of pillars in the modified synthetic clays. Thus, the objective of our program to directly control the molecular nature of the carbons can be realized.

Experimental

Materials. A natural montmorillonite, Bentolite L, was used for these experiments. Detailed characterization of this clay has been published elsewhere [27]. The synthesis of pillared clays with Chlorhydrol has been previously described in detail [28]. During the preparation, the pH was kept near 5.5 by adding dilute NH_4OH. The pillared clays were calcined at 400 °C in air for 4 hrs.

Organic-loaded clays were made in the following manner. Naphthalene-montmorillonites were made by two different methods. The "melt" technique heated a mixture of 1:5 naphthalene:clay at 85 °C in a closed container for two days. The "solvent" method involved stirring the clay in a 0.5M solution of naphthalene in benzene. The former method results in about three times more incorporation of organic by the clay. A sample of polystyrene-clay was made according the procedure of Vaia, et al. [29]. The surfactant used to render the hydrophilic clay surface organophilic was a dimethyl dialkyl quaternary ammonium chloride. Pyrene-loaded pillared clays were made by the solvent method. Typically, 6.2 gms pyrene were dissolved in 300 ml benzene to which 3 gms pillared clay are added, and the slurry stirred at room temperature overnight. These samples were dark green to black in color, but this color change does not occur in benzene alone or in the presence of naphthalene or polystyrene.

Pyrolysis. Most samples were pyrolzed as reported by Sonobe, et al. for polyacrylonitrile-montmorillonites [30]. In this method, the organic-clays are heated at 700 °C for 3 hrs under N_2 flow in quartz boats.

Demineralization. The resultant carbon from the clays was liberated by standard demineralization methods, treatment by HF followed by HCl.

Characterization. Results from microanalysis are given in Table 1. X-ray powder diffraction (XRD) analyses were carried out on a Scintag PAD-V instrument using Cu K_a radiation and a hyperpure germanium solid-state detector, at a scan rate of 0.25 - 0.5° 2Θ/min. The instrument was calibrated to the (101) reflection of low-quartz at 3.34 Å. Powders were loosely packed in horizontally held trays or spread out on glass slides. Nitrogen BET surface areas were measured on a Quantasorb Junior sorption analyzer from Quantachrome Corp. Before measurements the samples were fully outgassed in a stream of nitrogen gas; correlation of fit was 99-100%. Thermal gravimetric analysis was performed on a Cahn 121 electrobalance from 25-800 °C at a rate of 10 °C/min under a N_2 atmosphere. Laser desorption mass spectra were taken on a Kratos Maldi III using 337 nm light.

Discussion and Results

In the XRD analysis all samples after pyrolysis and before demineralization show a peak at 3.14 - 3.20 Å that is not attributable to clay, and therefore must be due to an intercalated organic species, for example, see Figure 2. After demineralization, the carbons all show a broad peak at 3.5 Å, which is about where Sonobe et al. observe their peak.

However, Sonobe attributes this peak to the (002) reflection, but its possible that it is the (103) hkl reflection (many of the JCPDS graphite files show the (103) reflection from 3.45 - 3.67 Å). The carbon is not highly oriented, otherwise many (00l) reflections would be seen. You will notice that in some cases there is clear indication of peaks at 10.6 Å and 7.4 Å as well, both before and after demineralization. The 10.6 Å could be the collapsed basal spacing, indicating that minerals may still be present after demineralization. Neither peak is indicative of fluorosilicates due to incomplete HCl treatment.

Samples of pyrene/benzene-PILC and pyrene/benzene-montmorillonite were analyzed by TGA to examine thermal effects as the samples were heated in situ under nitrogen flow. The results are shown in Figure 3. The weight loss from room temperature to about 150 °C is due to water and possibly benzene. Nothing else is lost from a pure clay until about 700 °C when dehydroxylation occurs. Note that this peak is shifted in the case of the organic-loaded pillared clay, to just 566 °C. Thus pyrolyzing at 700 °C might be too high a temperature for the PILC. The weight loss regions from about 400-500 °C are due to intercalated organic. Note that less than half as much is incorporated by the unpillared natural clay (on the order of 2 wt%). The TGA value of about 5.8 wt% liberated organic compares well with the 5.35 wt% value obtained by microanalysis. The m.p. of pyrene is 156 °C and the b.p. is 393 °C.

The surface area of the carbon from pyrene-PILC is 23 m^2/gm, which compares to only 2 m^2/gm for that obtained by Sonobe. It is important to note that a fairly high surface area was produced under rather mild heating. Normally, these materials need to be heated a second time at >1000 °C to obtain this large an area.

The LDMS spectra shown in Figure 4 suggest that this material is highly carbonized. Even at m/z >1000, the major fragments are separated by C_2. At low mass, the fragments correspond to C_xH_y, $y = 0\text{-}3$, where the major peaks are at $y = 0$. There is no evidence for oxygen continuing species which would be detrimental to the behavior of these carbons in a lithium battery. The missing material in the elemental analysis is probably not oxygen, but could be residual inorganics.

Conclusions

In summary, these approaches to carbon synthesis should yield materials with properties which can be more easily controlled than those of traditional carbons, and may, therefore, be more applicable as anodes of secondary lithium batteries. Electrochemical testing of the carbons described in this paper is being planned. In addition, milder pyrolysis conditions will be explored.

Acknowledgments

Microanalyses were carried out by the Analytical Chemistry Division of ANL by Ms. Irene Fox. The contributions of Mr. J. Malinsky in obtaining TGA data and Dr. J. Hunt for acquiring LDMS data is acknowledged. This work was performed under the auspices of the U.S. Department of Energy, under contract number W-31-109-ENG-38.

References

1. J. R. Dahn, U. von Sachen, M. W. Juzkow; and H. Al-Janaby, *J. Electrochem. Soc., 138* (1991) 2207.

2. B. Scrosati, *J. Electrochem. Soc., 139* (1992) 2776.

3. R. Dagani, *C&EN, January 4th Issue* (1993) 34.

4. K. West, B. Zachau-Christiansen, M. J. L. Ostergard, and T. Jacobsen, *J. Power Sources, 20* (1987) 165.

5. R. Yazami and D. Guerard, *J. Power Sources, 39*, (1993) 43-44.

6. R. Fong, U. von Sachen, and J. R. Dahn, *J. Electrochem. Soc., 137* (1990) 2009.

7. J. R. Dahn, A. K. Sleigh, H. Shi, J. N. Reimers, Q. Zhong, B. M. Way, *Electrochimica Acta* (In press, 1993).

8. M. Morita, T. Hanada, H. Tsutsumi, Y. Matsuda, and M. Kawaguchi, *J. Electrochem. Soc., 139* (1992) 1227.

9. A. K. Sleigh, and U. von Sachen, *Solid State Ionics, 57* (1992) 99.

10. O. Zhou, and D. E. Cox, *J. Phys. Chem. Solids, 53* (1992) 1373.

11. Y. Chabre, D. Djurado, M. Armand, W. R. Romanow, N. Coustel, J. P. McCauley, Jr., J. E. Fischer, and A. B. Smith, III., *J. Am. Chem. Soc., 114* (1992) 764.

12. A. Hamwi, M. Daoud, D. Djurado, J. C. Cousseins, Z. Fawal, and J. Dupuis, *Synth. Met., 44* (1991) 75.

13. A. Hamwi, M. Daoud, and J. C. Cousseins, *J. Power Sources, 26* (1989) 525.

14. N. Imanishi, S. Ohashi, T. Ichikawa, Y. Takeda, O. Yamamoto, and R. Kanno, *J. Power Sources, 39* (1992) 185.

15. S. Passerini, J. M. Rosolen, and B. Scrosati, *J. Power Sources, 45* (1993) 333.

16. N. Sonobe, T. Kyotani, Y. Hishiyama, M. Shiraishi, and A. Tomita, *J. Phys. Chem., 92* (1988) 7029.

17. T. Kyotani, N. Sonobe, and A. Tomita, *Nature, 331* (1988) 331.

18. N. Sonobe, T. Kyotani, and A. Tomita, *Carbon, 28* (1990) 483.

19. N. Sonobe, T. Kyotani, and A. Tomita, *Carbon, 29* (1991) 61.

20. T. Kyotani, T. Nagai, and A. Tomita, *Proc. Carbon '92*, June 22-26, 1992, Essen, pp. 437-439.

21. M. W. Anderson, J. Shi, D. A. Leigh, A. E. Moody, F. A. Wade, B. Hamilton, and S. W. Carr, *J. Chem. Soc., Chem. Commun.* (1993) 533.

22. K. A. Carrado, P. Thiyagarajan, R. E. Winans, and R. E. Botto, *Inorg. Chem.*, *30* (1991) 794.

23. K. A. Carrado, *I&EC Research, 31* (1992)1654.

24. K. A. Carrado, J. E. Forman, R. E. Botto, and R. E. Winans, *Chem. Mater.*, *5* (1993) 472.

25. R. A. Vaia, H. Ishii, and E. P. Giannelis, *Chem. Mater.,5* (1993) 1694.

26. T. J. Bandosz, J. Jagiello, K. A. G. Amankwah, and J. A. Schwarz, *Clay Minerals, 27* (1992) 435.

27. K. A. Carrado, A. Kostapapas, S. L. Suib, and R. W. Coughlin, *Solid State Ionics, 22* (1986) 117.

28. K. A. Carrado, S. L. Suib, N. D. Skoularikis, and R. W. Coughlin, *Inorg. Chem., 25* (1986) 4217.

29. R. A. Vaia, H. Ishii, and E. P. Giannelis, *Chem. Mater., 5* (1993) 1694.

30. N. Sonobe, T. Kyotani,and A. Tomita, *Carbon, 26* (1988) 573.

Table 1. Microanalysis of organic intercalated clay, pyrolyzed organic clay, and demineralized carbon.

Sample	**%C**	**%H**
Naphthalene-mont, melt method	12.8	1.98
Naphthalene-mont, melt method - pyrolyzed and demineralized	84.0	2.98
Naphthalene-mont, solvent method	3.9	1.43
Naphthalene-mont, solvent method - pyrolyzed	0.4	0.26
Naphthalene-mont, solvent method - pyrolyzed and demineralized	78.5	2.72
Polystyrene-mont	38.7	5.24
Polystyrene-mont - pyrolyzed	1.0	0.32
Polystyrene-mont - pyrolyzed and demineralized	80.7	2.93
Pyrene-pillared clay	5.4	1.47
Pyrene-pillared clay - pyrolyzed	1.2	0.84
Pyrene-pillared clay - pyrolyzed and demineralized	84.2	2.67
References		
Benzene-pillared clay	0.7	1.50
pure graphite	100.8	0.14

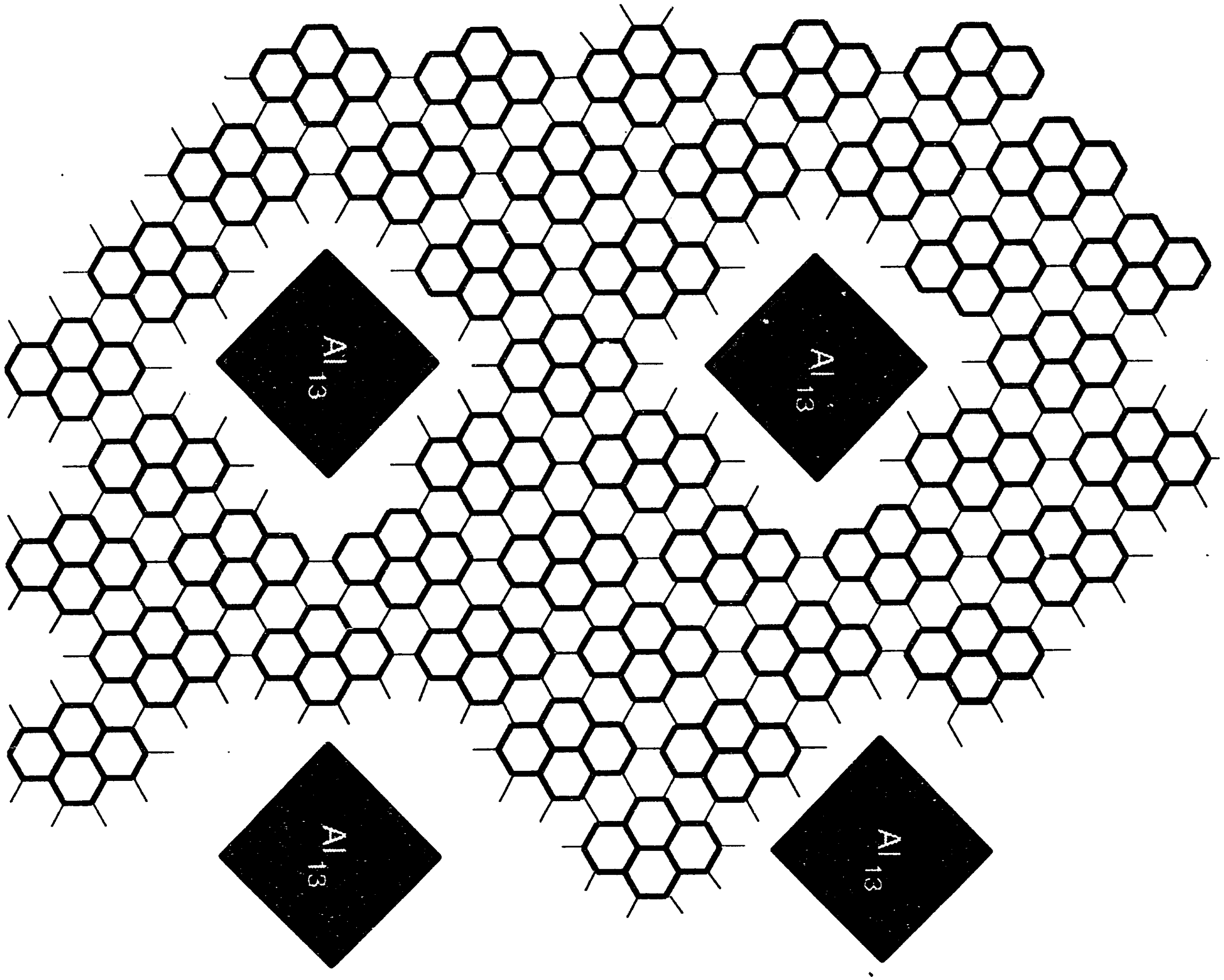
Figure Captions

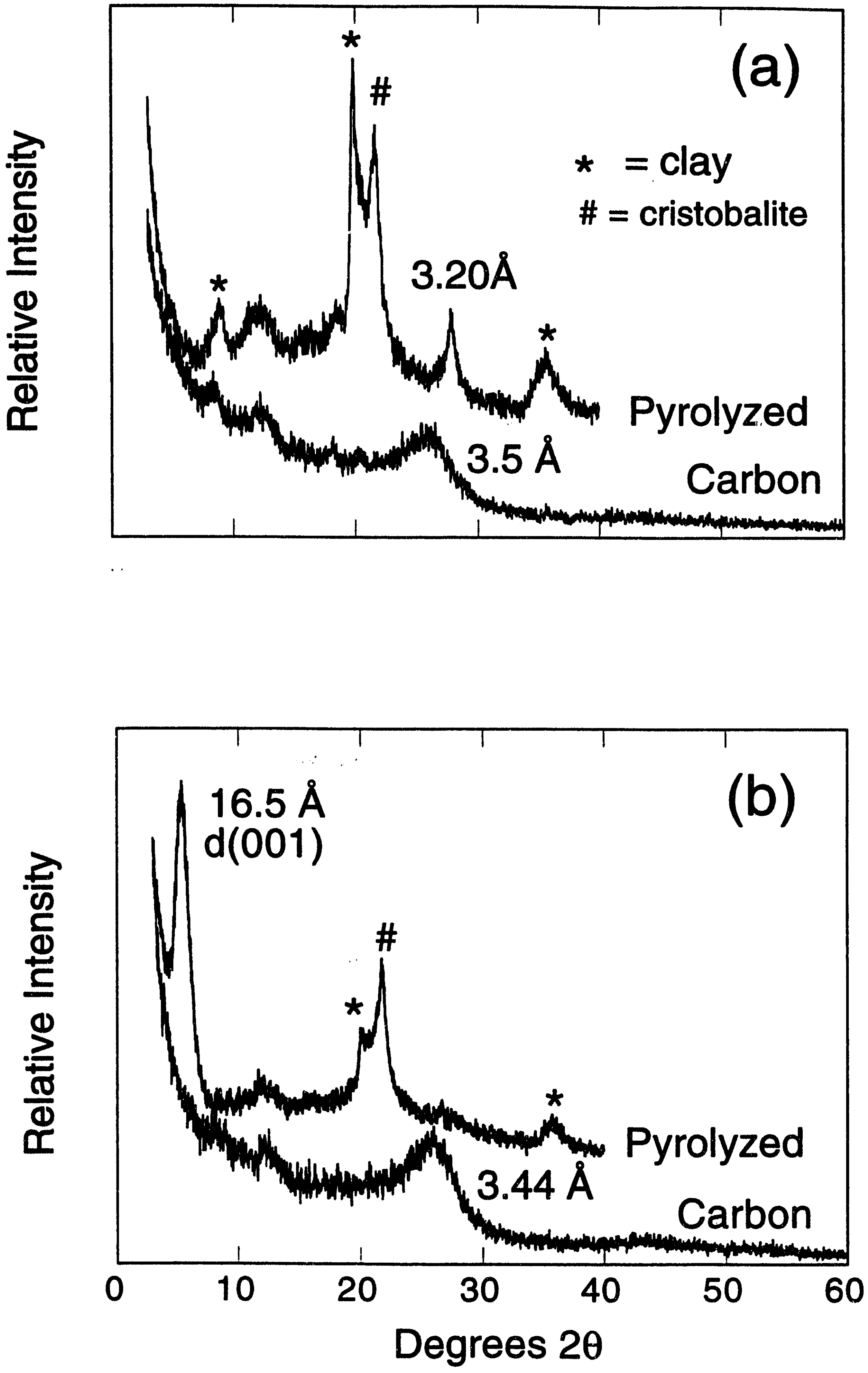
Figure 1. A depiction of the growth of carbon sheets from pyrolysis of pyrene. The Al_{13} pillars are approximately 8 Å square and separated on average by 14 Å.

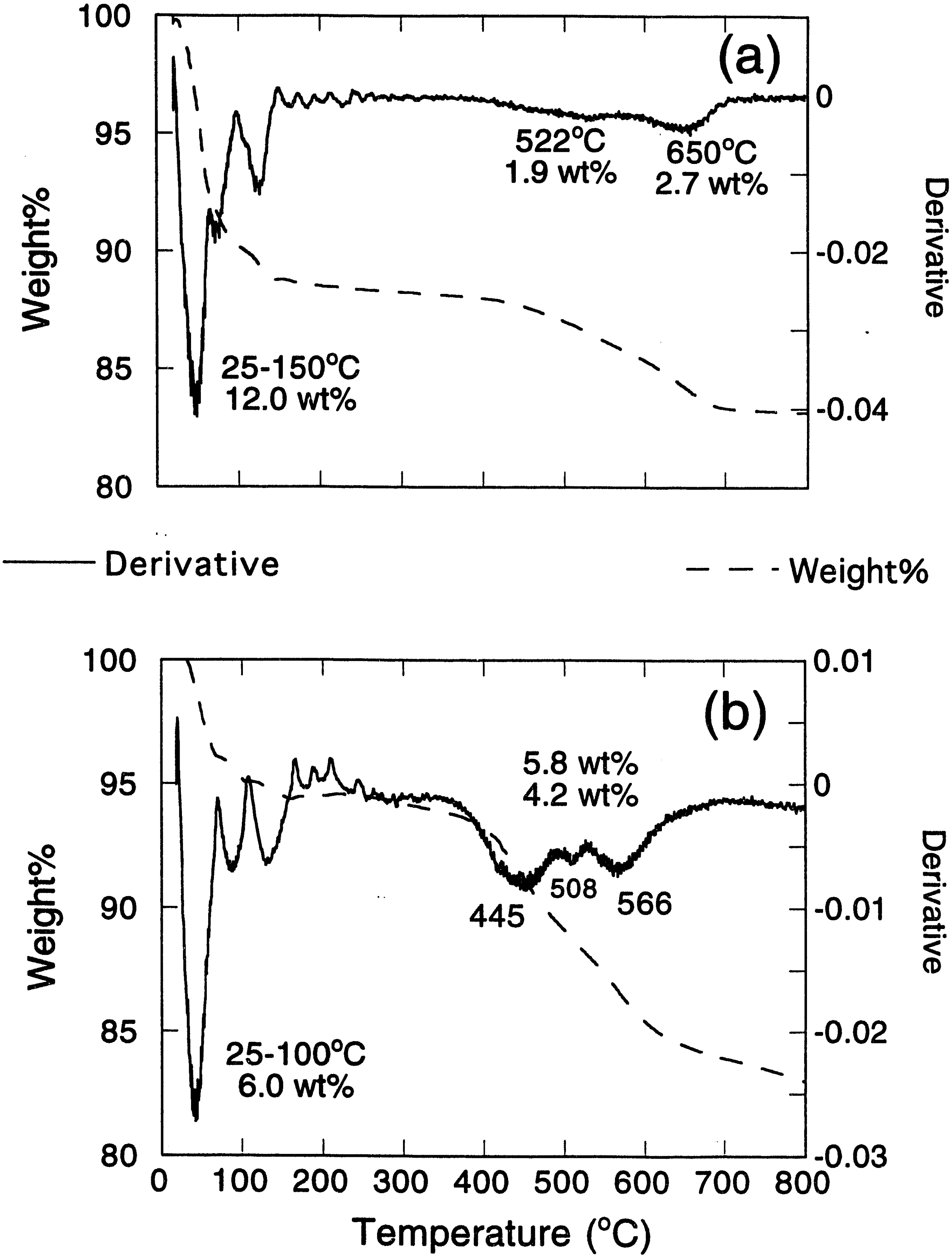
Figure 2. XRD of (a) polystyrene-montmorillonite and (b) pyrene-pillared montomorillonite systems, showing both the pyrolyzed organic-clay complex and the carbon liberated after demineralization.

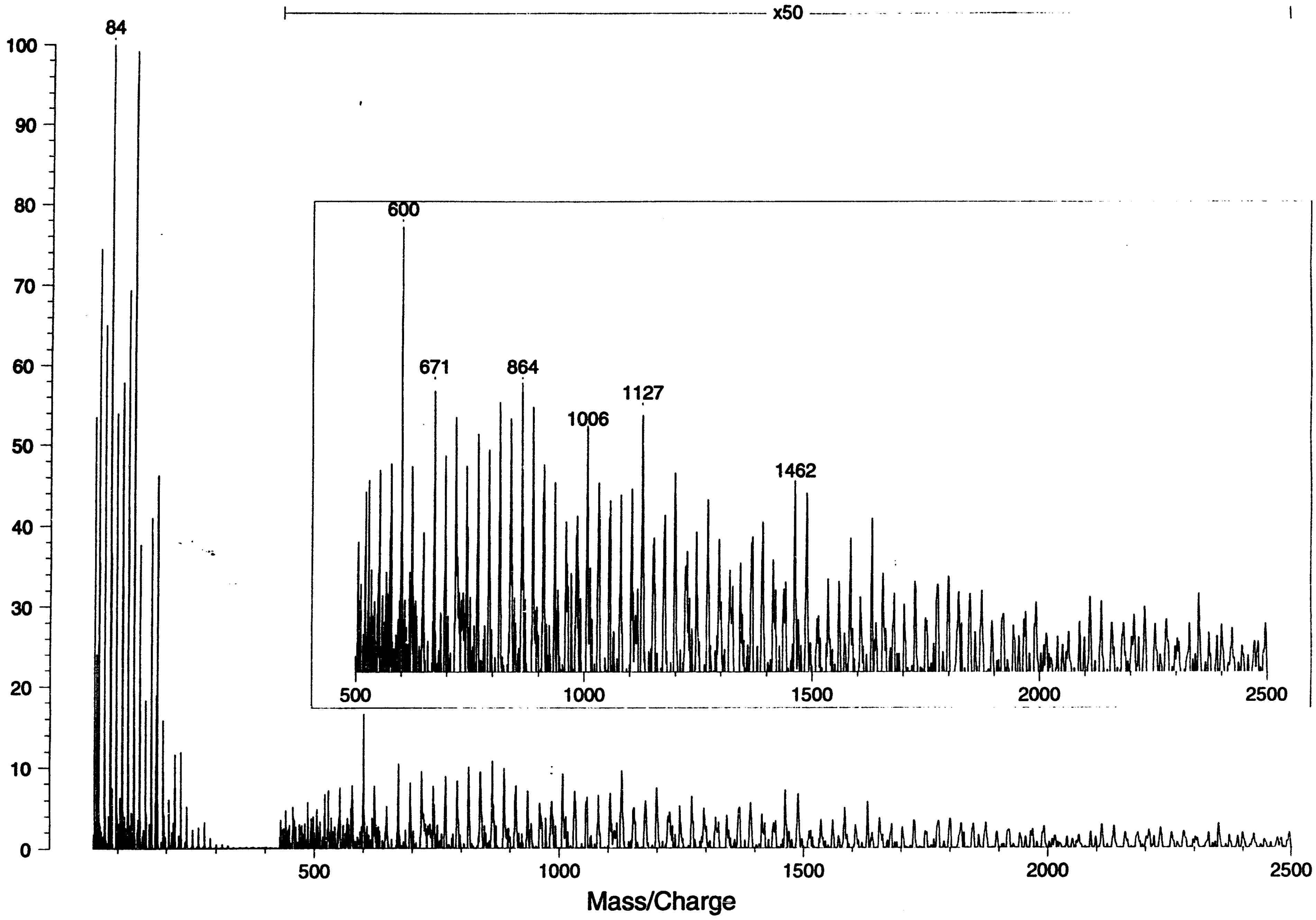
Figure 3. TGA under a N_2 atmosphere of (a) pyrene-montmorillonite and (b) pyrene-pillared montmorillonite; dashed curves are weight % and solid curve is the derivative.

Figure 4. Laser desorption mass spectra of demineralized pyrene-PILC (700 °C) sample at low laser power.


Al_{13}
Al_{13}
Al_{13}
Al_{13}


(a)
* = clay
# = cristobalite
Relative Intensity
*
#
*
3.20Å
*
Pyrolyzed
3.5 Å
Carbon
(b)
16.5 Å
d(001)
Relative Intensity
#
*
*
Pyrolyzed
3.44 Å
Carbon
0
10
20
30
40
50
60
Degrees 2θ


(a)
Weight%
Derivative
100
95
90
85
80
0
-0.02
-0.04
522°C
1.9 wt%
650°C
2.7 wt%
25-150°C
12.0 wt%
Derivative
Weight%
(b)
Weight%
Derivative
100
95
90
85
80
0.01
0
-0.01
-0.02
-0.03
5.8 wt%
4.2 wt%
445
508
566
25-100°C
6.0 wt%
0
100
200
300
400
500
600
700
800
Temperature (°C)


x50
84
600
671
864
1006
1127
1462
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
Mass/Charge

DATE

FILMED

7/14/94

END