LITHIUM INTERCALATION INTO CARBONS MADE FROM COMMERCIAL PRECURSORS

Rod S. McMillan Z.X. Shu, J.J. Murray and I. Davidson

National Research Council
Ottawa, Ontario, Canada

Introduction

Lithium ion rechargeable cells are commercially available from a number of companies.[1,2] Research and development of this technology is centered on the improvement and understanding of electrolytes and cathode and anode materials. At the NRC we have been contributing to the understanding of these components. We have reported on electrolytes that give higher lithium capacity carbons.[3,4] We have reported on heat treated soft carbons for use as carbon anodes with capacities greater than that of commercial pet. coke.[5] Recently, there has been reports of carbons with capacities greater than 372 mahr/g.[6] One example of these is mesophase microspheres heat treated to temperatures less than 1100 °C. This result caused us to initiate a study of hard carbons, in particular phenol-formaldehyde resins, and soft carbons heat treated to temperatures less than 800 °C. Our research approach, as in the past, was to use commercially available carbon processors along with in-house prepared model compounds. During the course of our investigation a report of lithium intercalation into low temperature heat treated phenol-formaldehyde resins was published.[7] The authors found, as we have, lithium capacity to be a function of H/C ratio for these materials.

We have expanded our investigation of phenol-formaldehyde resins to try to answer some basic questions. Is the variation of lithium capacity with H/C ratio due to structural or electronic properties? Is the large capacity due to irregular graphene layer stacking brought on by tetrahedral carbon, as has been suggested by Dahn?[8] High capacity carbons tend to have large irreversible lithium capacities, larger than can be explained by simple apparent surface passivation reactions. What is the nature of this large irreversible capacity? The experimental approach chosen to answer these questions was to try to influence the structural and electronic properties of resoles using different heat treating profiles. The resultant materials would be characterized by their density, XRD spectrum, surface area and hydrogen content, and by their lithium intercalation capacities. Here we report some of our initial findings.

Experimental

This study employed a commercial phenol-formaldehyde resole resin from Durez, Plyophen 43290 and model one-step resoles made from phenol and formaldehyde. Both the commercial resole and the NRC resoles were cured and heat treated in the same manner. Samples were cured with heat in air in Teflon boats at 80, 120, and 180 °C. The hard set materials were ground up in a coffee grinder, placed in Alumina crucibles in graphite boats and heat treated to 330, 440, and 700 °C in a tube furnace under Argon atmosphere in three ways. Samples were heated at 2 and 15 °C/min., and 15 °C/min. with a temperature soak of 140 min. at the final heat treatment temperature. At the end of heating the samples were cooled in the furnace at 10 °C/min. Densities were measured with a Micromeretics Accupyc 1330 He pycnometer and XRD spectra were obtained with a Scintag XDS 2000 spectrophotometer equipped with a Cu tube. Hydrogen and carbon analyses were obtained by combustion and detection of CO_2 and H_2O. Lithium intercalation capacities were obtained in duplicate by fabricating the carbons as cathodes in galvanic cells with lithium metal anodes. The carbon electrodes were prepared by milling the carbon powder to less than 10 μm particle size with 5 wt % Super S carbon black and 5 wt % Kynar PVDF with N-methyl pyrrolidinone as the slurrying agent. The mix was spread on Cu foil, dried at ca. 100 °C, hot pressed at 1000 psi and punched to give 0.5" dia. electrode disks. Typical electrode disks were 0.005" thick and had a carbon weight of 16 mg. In an inert atmosphere chamber, a carbon electrode disk, a Celgard 3501 polypropylene separator, a lithium metal disk electrode and electrolyte, 1M $LiPF_6$ in EC/DEC 30/70 , ethylene carbonate/ diethyl-carbonate, water content < 10 ppm., were placed in 2325 coin cell hardware of NRC design and the closure effected. The coin cells were then discharged and charged at constant current at room temperature at 30, 50, 100, and 200 hr rates. The first cell discharge employed a cutoff voltage of 0.001v and was done repetitively until additional capacity gained was < 1% of the first discharge capacity. This typically took three discharges. Cell charging was to a cutoff voltage of 2.0 v.

Results and Discussion

TGA results of resole samples heated at various heating rates to 1000 °C indicated that weight loss due to dehydration and dehydrogenation was a complex function of temperature and heating rate. The TGA spectra indicated two regions of rapid weight loss, one from 200 to 330 °C and one from 330 to 440 °C. From 440 to 700 °C the weight loss was less than 10% of total sample weight loss. The heating profiles of 2 and 15 °C/min., and heat treatment temperatures of 330, 440 and 700 °C were chosen using this information . The heating profile i.e. heating rate, had an effect on the yield, density, and H/C ratio of the sample. The cure temperature of the NRC and commercial resoles also affected these same properties. These results for the NRC resoles can be summarized in part by figure 1. Here is seen how the H/C ratio for sample #1, cured at 80 °C, sample #2, cured at 120 °C, and sample #3, cured at 180 °C are affected by heating profiles and resole cure temperature. Lithium intercalation for two heating profiles is shown in figure 2. For sample #1, reversible lithium capacity is larger with the smaller H/C while for irreversible capacity the effect is reversed. In addition the shape of the voltage curves, i.e., capacity distribution is different with the different H/C ratio.

Conclusions

Cure temperature and heating profiles have an effect on the H/C ratio of heat treated carbon precursors. They also affect the reversible and irreversible lithium capacities.

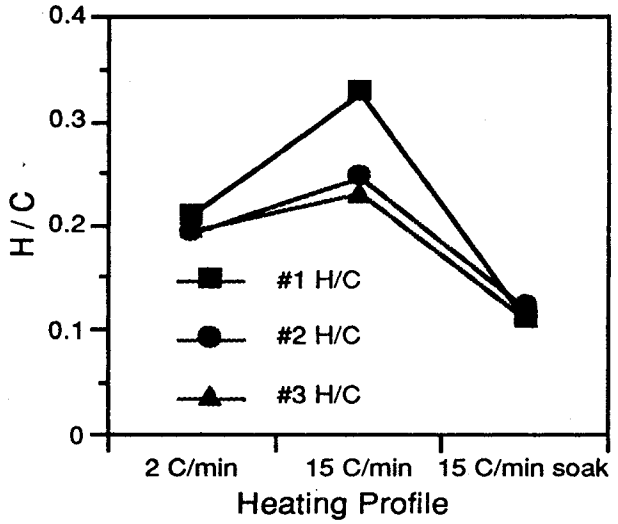

Figure 1. H/C atomic ratio of resoles heated as Indicated. #1 NRC model resole cured at 80 °C, #2 at 120 °C and #3 at 180 ° C.

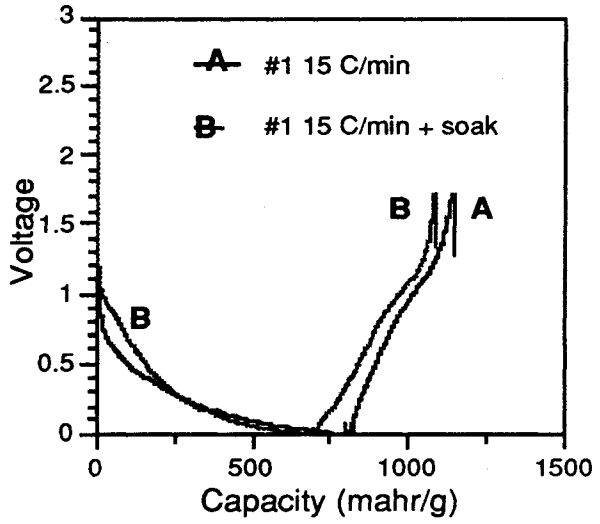

Figure 2. Voltage vs. Capacity Curves for Sample #1 heat treated as indicated. The first cycles are shown for a 30 hr. rate discharge and charge.

Acknowledgment

Thank you to Ms. Ann Webb for performing the C and H analyses and to Occidental Chemical Corp., Durez Engineering Materials Division, for the samples of Phenolic Resoles.

References

[1]T.Nagaura and K. Tozawa, Progress in Batteries and Solar Cells 9 209 (1990).

[2] I. Kuribayashi, J. Electron. Eng. 30, 51 (1993).

[3]Z.X. Shu, R.S. McMillan, and J.J. Murray, J. Electrochem. Soc., 140 922 (1993).

[4]Z.X. Shu, R.S. McMillan, and J.J. Murray, J. Electrochem. Soc., 140 L101 (1993)

[5]R.S. McMillan, Z.X. Shu, J.J. Murray, and I. Davidson, "Carbons for Use as Anodes....." Proceedings Carbon '93, Buffalo, USA, 1(993).

[6]A. Mabuchi, K. Tokumitsu, H. Fujimoto and T. Kasuh, 7th International Meeting on Lithium Batteries, May 15-20, (1994) Boston, USA., paper I-A-10, p 207.

[7]S. Yata, H.Kinoshita, M. Komori, N. Ando, T. Kashiwamura, T. Harada, K. Tanaka, and T. Yamabe, Synthetic Metals, 62 152 (1994).

[8]J. R. Dahn, private communication, (1995).