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INTRODUCTION

The use of lithium intercalated graphite as a negative electrode has been known since 1983 [1] when Yazami and Touzain investigated highly oriented pyrolytic graphite (HOPG) in a cell with a polymer electrolyte and elevated temperature cycling. Subsequent work led to the development of liquid electrolyte lithium ion cells which utilized a high voltage lithiated metal oxide as a positive electrode and a low temperature coke as a negative electrode. The solvent utilized in the early cells was based on propylene carbonate, which was known for many years to be reactive with lithiated graphite [2]. More recent work has focused on the use of electrolytes based on ethylene carbonate which has a very limited reactivity with lithiated graphite [3]. The recent electrolytes are sufficiently stable, that it seemed useful to look again at HOPG to try to determine fundamental properties of the electrochemical intercalation on a very well defined material. The properties and structure of HOPG and its intercalation compounds are reviewed by Moore [4].

Other electrochemical studies of lithium intercalation in graphite using liquid electrolytes include those on prelithiated HOPG graphite [5], natural graphite [6-7] and synthetic graphite [8].

EXPERIMENTAL

Large pieces of HOPG were obtained from Advanced Ceramics Co., Cleveland, OH. These were cut into smaller sections and cleaved with adhesive tape to obtain samples with a basal plane orientation and a thickness of about 2 microns. Samples with a transverse orientation were obtained by mounting roughly cut samples in a microtome and cleaving with an orientation of 0° with respect to the blade, after several preliminary passes to clean the surface, to obtain a thickness of about 25 microns. Some smearing and elongation of the sample resulted from the cuts, although they were mostly transverse. The samples were then mounted on a stainless steel disc of 1 cm^2 area using an Acheson Electrodog compound to provide good physical and electrical contact to the substrate. The basal plane sample was placed in a three necked electrochemical cell in a Vacuum Atmospheres dry box with a 1 cm^2 lithium counter electrode and a similar reference electrode. The electrodes were connected to feed throughs in the dry box and then to the potentiostat. In order to shorten the spacing between electrodes and minimize the electrical resistance of the cell, the transverse samples were placed in a demountable electrochemical cell with a counter electrode of lithium and a lithium reference electrode. Prior to final assembly, the cells were filled with a 1M solution of LiPF_6 in 66 weight % ethylene carbonate (EC)

and 33 weight % dimethylcarbonate (DMC) [3]. The demountable cell was placed in a hermetically sealed jar so that the cell could be removed from the dry box for easier testing.

Cyclic voltammetry measurements were carried out using a 263A potentiostat from EG&G Instruments and their 352/252 Corrosion Software package and a desktop computer for control and analysis. Galvanostatic measurements were made with a constant current supply, controlled with a desktop computer and a Hewlett Packard 3852A Data Acquisition/Control Unit.

RESULTS

The sample with the basal plane exposed to the electrolyte did not show activity. The cyclic voltammetry results gave currents too small to measure.

The transverse sample, however, showed considerable electrochemical activity, although the reaction did not go to completion with regard to the C_6Li compound (stage 1). Figure 1 shows the cyclic voltammetry results at a scan rate of 1 mV/s. No staging is apparent because the sweep rate is too high to permit the formation of equilibrium structures. Figure 2 shows the cyclic voltammetry for 0.01 mV/s scan rate. The stages of the reaction are apparent from the resolution of the peaks at 56 and 175 mV on the anodic sweep and 289, 184 and 117 mV on the cathodic sweep. The total anodic area was 3.6 mAh in the anodic direction and 3.9 mAh in the cathodic direction. The cell was then subjected to galvanostatic tests with cut-off voltages of 0.05 V in the cathodic (carbon charging) direction and 1.2 V in the anodic (carbon discharging) direction. The second charge and discharge curves are shown in Figure 3. Steps are apparent in these curves which correspond to the peaks in the cyclic voltammetry curves at 0.01 mV/s scan rate. Differentiation of the galvanostatic curves and plotting as dQ/dV versus V, showed a weak peak at about 100 mV, and peaks at 150 and 220 mV in the cathodic direction and 200, 120 and less than 100 mV in the anodic direction. The capacity of this cycle in the cathodic direction was 3.6 mAh and 4.0 mAh in the anodic direction in good agreement with the cyclic voltammetry experiments. The capacity faded rapidly following the second cycle, probably because of the difficulty in maintaining electrical contact with the sample. Based on the weight of the sample, we expected a capacity of 21 mAh.

DISCUSSION

Previous workers have seen similar results to the above. The careful studies of Ohzuku et al. [7], on a natural graphite powder and using a combination of ex situ XRD structural studies with galvanostatic studies found equilibrium values for the lowest voltage reaction at 85 mV, and the next at about 120 mV. A third region gave a sloping curve between 120 and 210 mV and a fourth region gave a plateau at about 210 mV. In order for the cathodic reaction to go to completion, the lithium and carbon electrodes were shorted out for 48 hours at 30°C following galvanostatic current at 0.17 mA/cm² to 0 V. We did not carry out this kind of exhaustive oxidation. Ohzuku found that the lowest voltage region corresponds to a heterogeneous process between stages 1 and 2 with stoichiometries C₆Li and C₁₂Li in agreement with Yazami et al. [3,6]. The second peak, however, did not give any indication of third stage graphite and Ohzuku concluded that the 120 mV peak was due to a reordering of the second stage graphite, C₁₂Li, to a diffuse second stage graphite lattice with the stoichiometry C₁₈Li. The third region was poorly defined by the XRD studies since no two phases were observed together. At 210 mV, the simultaneous presence of stage 4 and 8 were found by XRD (region 4). These assignments differ from those of Yazami and indicate the need for further structural studies. We believe that our somewhat low efficiencies of oxidation and reduction are due in part to the difficulty of attaching the entire sample to the electrode and to the use of relatively thick layers compared to the currents applied.

CONCLUSIONS

Our electrochemical studies on HOPG are in substantial agreement with those of other workers on various forms of graphite. Further structural studies would be desirable to enable better assignments of the different electrochemical regions.

ACKNOWLEDGMENT

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REFERENCES

1. R. Yazami and Ph. Touzain, *J. Power Sources*, **9**, 365 (1983)
2. A. N. Dey and B. P. Sullivan, *J. Electrochem. Soc.*, **117**, 222 (1970)
3. D. Guyomard and J-M. Tarascon, U.S. Patent 5,192,629, March 9, 1993
4. A. W. Moore, in *Chem. and Phys. of Carbon*, Vol. 17, P. L. Walker, Jr. and P. A. Throver, eds., Marcel Dekker, Inc., New York, 1981, p.233
5. R. Yazami, A. Cherigui, V.A. Nalimova and D. Guerard in *Proc. Vol. 93-24*, The Electrochemical Society, Pennington, N.J., S. Surampudi and V. Koch, eds., 1993, p.1
6. R. Yazami, K. Zaghbi and M. Deschamps, *J. Power Sources*, **52**, 55 (1994)
7. T. Ohzuku, Y. Iwakoshi and K. Sawai, *J. Electrochem. Soc.*, **140**, 2490, (1993)
8. R. Fong, U. vonSacken and J. R. Dahn, *J. Electrochem. Soc.*, **137**, 2009 (1990)

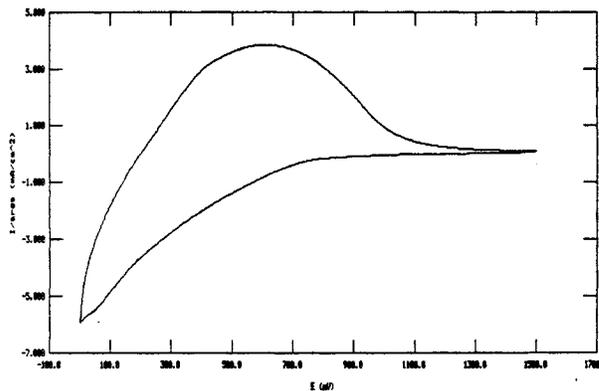


Fig. 1. Cyclic Voltammetry of transverse section of HOPG at 1 mV/s scan rate.

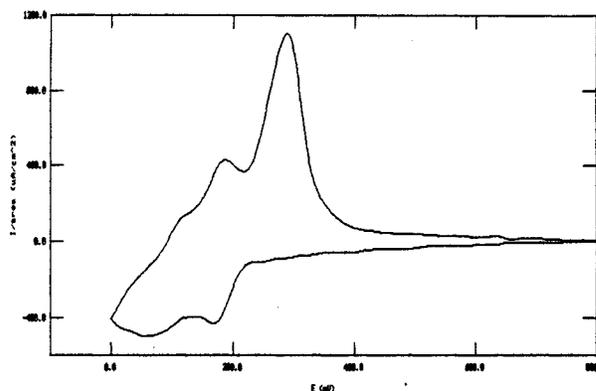


Fig. 2. Cyclic Voltammetry of transverse section of HOPG at 0.01 mV/s scan rate.

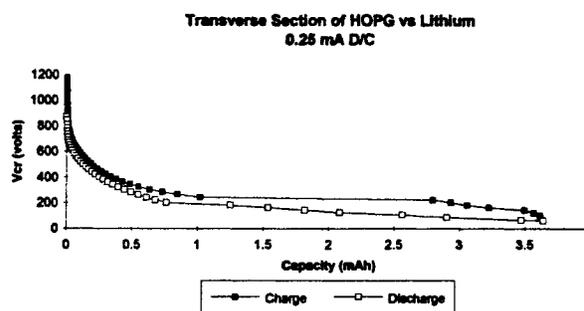


Fig. 3. 0.25mA constant current charge and discharge of transverse section of HOPG.