

Electrochemical performance of natural Brazilian graphite as anode material for lithium-ion rechargeable cells

V. Manev^{a,*}, I. Naidenov^a, B. Puresheva^a, P. Zlatilova^a, G. Pistoia^b

^a Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

^b Centro di Studio per la Elettrochimica e la Chimica Fisica delle Interfasi, Consiglio Nazionale delle Ricerche, 00161 Rome, Italy

Received 4 January 1995; accepted 30 January 1995

Abstract

The properties of natural Brazilian graphite have been investigated in a three-electrode laboratory button cell containing 1 M LiPF₆ dissolved in ethylene carbonate–dimethyl carbonate (EC–DMC) as the electrolyte. The charge/discharge behaviour of the graphite is greatly affected by the preliminary treatments and techniques used for the preparation of the electrode. By optimizing these procedures, a specific capacity very close to the theoretical value can be obtained. When using LiPF₆/EC–DMC electrolyte, a high charge/discharge coulombic efficiency is observed.

Keywords: Graphite; Anodes; Rechargeable lithium-ion cells

1. Introduction

In the last few years a number of carbon materials have been intensively investigated with the aim of exploring the possibilities of using them as the alternative negative electrodes for secondary lithium cells [1–14]. It was shown that some of them, mostly synthetically obtained products [3–12], can reversibly intercalate significant amounts of lithium ions. It was assumed that the maximum amount of lithium that can be intercalated reversibly into the carbon corresponds to the LiC₆ stoichiometry [3–5,12,13].

The goal of the present work was to investigate the possibility of using natural Brazilian graphite as the negative electrode in rechargeable lithium cells. Our main objective was to elucidate the factors affecting the reversibility of the intercalation process of lithium ions and, thus, to seek ways of its enhancement.

2. Experimental

All studies were performed on natural Brazilian graphite supplied as a common sample by the International Battery Materials Association (IBA). After a series of comparative tests with polytetrafluoroethylene

(PTFE) and ethylene/propylene/diene polymer (EPDM), PTFE was selected as the electrode binder due to the more reproducible results obtained in comparison with EPDM. The graphite was treated for several hours with an aqueous PTFE emulsion and then dried for 48 h at 120 °C. The electrodes were prepared by pressing the graphite–PTFE blend on a copper foil disk (15 mm in diameter). Typical cathodes weighed about 10 mg cm⁻² and, depending on the compacting pressure, had a thickness in the range 50–100 μm.

Preliminary experiments displayed a rather significant impact of the compacting time on the electrochemical performance of the electrode. The porosity measurements exhibited that, because of its softness, graphite behaves as a highly viscous Newtonian liquid, this decreasing the electrode porosity with increase in compacting time. This phenomenon deserves a separate investigation which we intend to publish in a forthcoming paper. However, in this study, a standard pressing method was used in which the compacting pressure was increased linearly to reach its maximum value in about 0.5 s and then abruptly switched to zero.

The electrochemical measurements were conducted in a three-electrode laboratory button cell containing a lithium reference electrode. Before the cell assembly, the test electrode was additionally dried at 120 °C for 3 h under vacuum.

* Corresponding author.

The electrolyte used was 1 M LiPF_6 dissolved in EC-DMC (1:1 ratio). The water content in the solution was lower than 20 ppm.

During some of the experiments, irreproducibility of the specific capacity was observed. In these cases, the average discharge (charge) capacity from five identical experiments is given.

3. Results and discussion

The preliminary results obtained with natural Brazilian graphite as supplied by IBA, without any additional treatment, were rather discouraging. Such results are illustrated in Fig. 1, where the charge and discharge curves obtained at the first cycle for current densities of 0.1, 0.2 and 0.4 mA/cm^2 are shown. The Figure reveals two essential disadvantages of these electrodes. First, the reversible capacity has a value of 0.14–0.21 Ah/g, which is about 35–55% of the theoretical LiC_6 capacity reported for natural graphite by others. Second, the coulombic efficiency of the first cycle defined as the ratio of discharge and charge capacity, $K_{\text{eff}} = Q_{\text{dsc}}/Q_{\text{ch}}$ is lower than 70%. The same conclusions can be drawn from Fig. 2 which presents the charge and discharge capacities at 0.2 mA/cm^2 , obtained during the first twelve cycles. From the data presented in Fig. 2, it can be also calculated that the coulombic efficiency in the second cycle is lower than 90%, and

it is only after the fifth cycle that a nearly steady value of ~98% is reached. However, the coulombic efficiency calculated from Fig. 2 for the first five cycles (${}^5E_{\text{eff}} = {}^1K_{\text{eff}} \cdot {}^2K_{\text{eff}} \cdot \dots \cdot {}^5K_{\text{eff}}$) is only 50%, which is too low for practical use.

The scanning electron microscope (SEM) photographs of Brazilian graphite supplied by IBA (Fig. 3(a)) showed that some of its particles reach 100 μm . It was observed at a higher magnification (Fig. 3(b)) that the particles have a dense structure, obviously lacking inner pores. It is evident that lithium-ion intercalation into these large and compact particles is strongly inhibited, especially at higher charge/discharge rates. For this reason, we subjected the material to additional grinding in a ball mill, whereby its specific surface area increased from 3.3 to 5.4 m^2/g .

A comparison of the discharge curves of untreated graphite with those of additionally ground samples, presented in Fig. 4 for two current densities, showed a remarkable improvement due to the grinding procedure. The SEM photographs of the additionally ground material at small magnifications (Fig. 3(c)) do not differ substantially from those of the untreated samples (Fig. 3(a)), but at greater magnifications of the large particles (Fig. 3(d)) it is observed that they consist of graphite slabs densely packed one over the other. In order to separate them, thus facilitating the free penetration of electrolyte, after the extra grinding the material was dispersed in water for 3 h in a high-speed mixer, in the presence of small amounts of surfactants. It can be seen in the SEM photograph of Fig. 5(a) that in this case the graphite slabs are better separated. Fig. 6 compares the discharge curves of electrodes made with additionally dispersed and undispersed Brazilian graphite after grinding in a ball mill. The Figure demonstrates that this procedure leads to a remarkable increase in the specific capacity and its value at 0.2 mA/cm^2 reaches 280 mAh/g , which is 75% of the theoretical capacity of LiC_6 , 372 mAh/g [3–5,12,13].

The influence of the PTFE content on the electrode specific capacity is demonstrated in Fig. 7. It reveals that electrodes with a lower PTFE content should be preferably used, since the reduction of the binder content to 2.5% leads to some increase in the specific capacity. It can be seen in the SEM pictures of the electrodes with 10% PTFE that a significant amount of PTFE is situated as inert material within the graphite particles (Fig. 5(a)) and that the PTFE particles block considerably the graphite surface (Fig. 5(b)). This clarifies the negative effect of the greater amounts of binder on the electrode specific capacity. The reduction of the specific capacity with the decrease of the binder content below 2% can be explained with the isolation of graphite particles taking place during the formation of a passivating film.

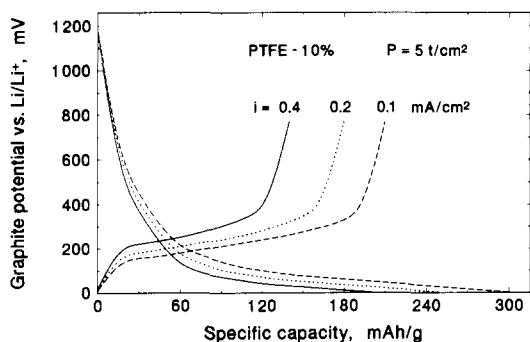


Fig. 1. First charge and first discharge curves obtained with electrodes from natural Brazilian graphite at 0.1, 0.2 and 0.4 mA/cm^2 , respectively.

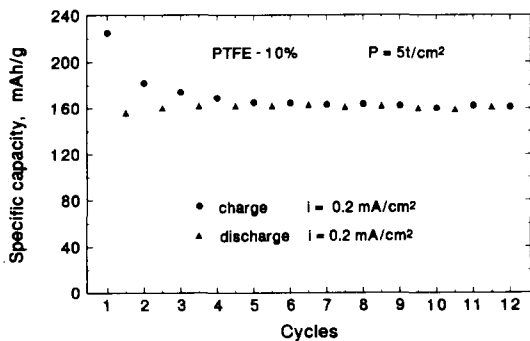


Fig. 2. Specific capacity vs. cycle number for a natural Brazilian graphite electrode without additional treatment.

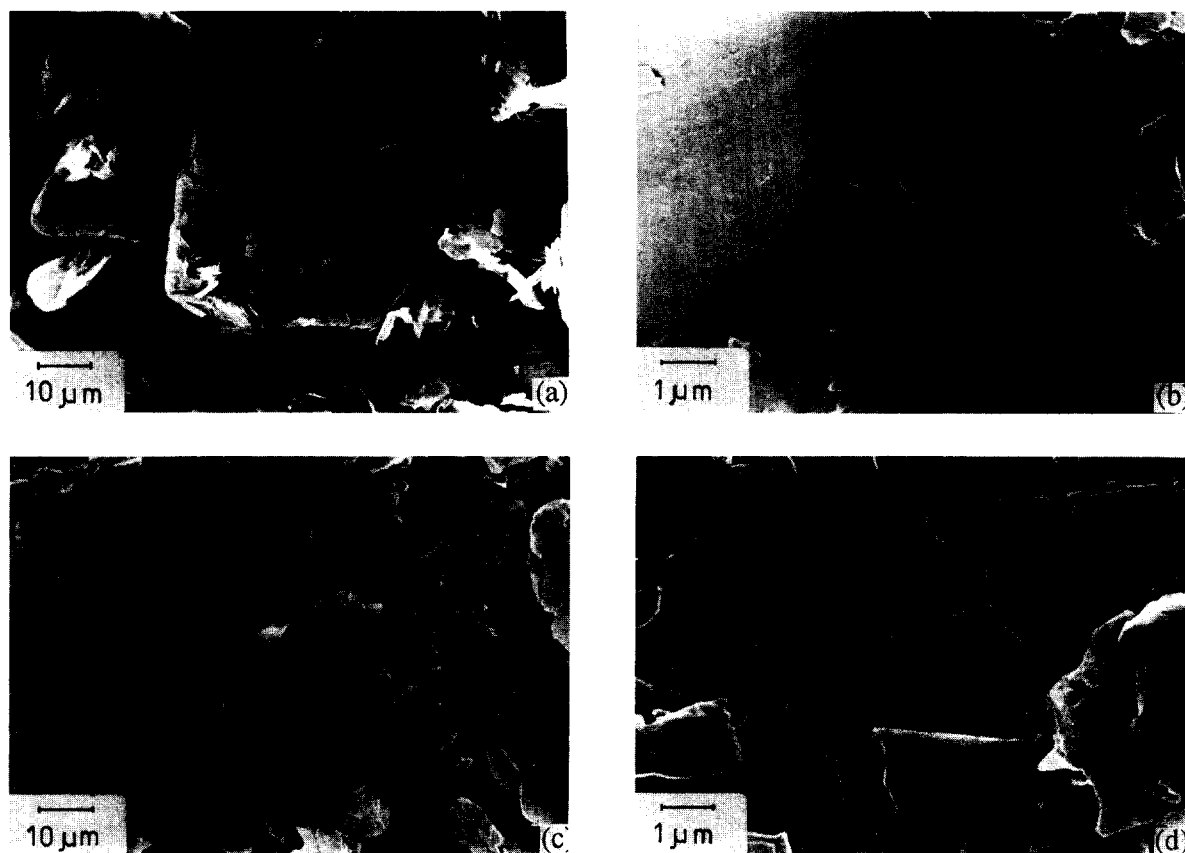


Fig. 3. Scanning electron micrographs of Brazilian graphite as received from the International Battery Materials Association: (a) $\times 500$; (b) $\times 10\,000$, and after extra grinding (c) $\times 500$, and (d) $\times 10\,000$.

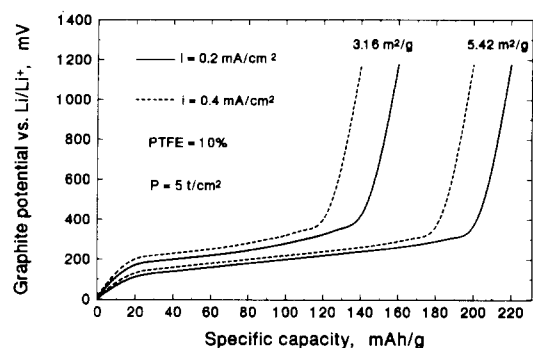


Fig. 4. Discharge curves at the fifth cycle of graphite electrodes before and after extra grinding at a current density of 0.2 and 0.4 mA/cm².

Since graphite is a soft material and can undergo plastic deformations, so forming layered slabs even at comparatively low pressures, it should be expected that this particular feature may result in a strong dependence of the electrode specific capacity on the compacting pressure. Such dependence is shown in Fig. 8, leading to the conclusion that the most appropriate compacting pressure of Brazilian graphite electrodes is about 1.5–2.0 t/cm². Presumably, at lower pressures the contact resistance between the particles rises due to the for-

mation of the passivating film, while under higher compacting pressures the electrodes become too dense to operate efficiently.

Fig. 9 presents the charge/discharge curves at the first cycle of electrodes made of Brazilian graphite, additionally ground and dispersed in water. The electrodes were prepared under the optimum conditions discussed above: 2.5% PTFE content and a compacting pressure of 2 t/cm². As it can be seen, the graphite shows a high specific capacity after these treatments, and at a current density of 0.1 mA/cm² its specific capacity (350 mAh/g) is very close to the theoretical LiC₆ value (372 mAh/g). At a current density of 0.4 mA/cm² (Fig. 10) the reversible specific capacity is still very high and this makes it a promising anode material for commercial lithium cells.

The behaviour of the Brazilian graphite electrodes, processed as described above and subjected to short cycling tests between 0 and 1200 mV in coin cells, is shown in Fig. 10. In addition to the good electrode reversibility, there is a substantial improvement in the first cycle coulombic efficiency (80%) in comparison with the data shown in Fig. 2. Fortunately, all the factors that have been shown to increase remarkably the specific capacity of the graphite affect positively

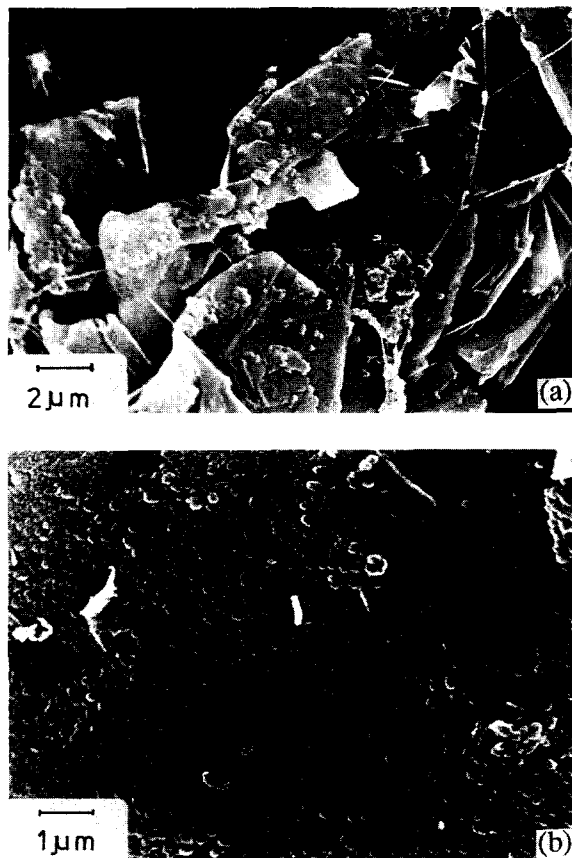


Fig. 5. Scanning electron micrographs of the Brazilian graphite electrode blend with 10% PTFE binder: (a) $\times 5000$, and (b) $\times 10\,000$.

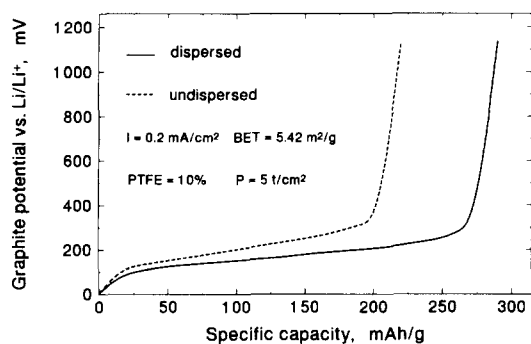


Fig. 6. Comparison of discharge curves at the fifth cycle of dispersed and undispersed graphite.

the coulombic efficiency calculated from the first five cycles. The value estimated from Fig. 10 is higher than 70% at a current density of 0.4 mA/cm^2 and higher than 75% at a current density of 0.1 mA/cm^2 .

From the data presented in Fig. 10 it can also be seen that the nearly steady value of the coulombic efficiency reached after several cycles, is $\sim 99\%$ at a current density of 0.1 mA/cm^2 and 98% at a current density of 0.4 mA/cm^2 . The lower steady value of the coulombic efficiency at higher current densities can be attributed to the formation of a defective passivating

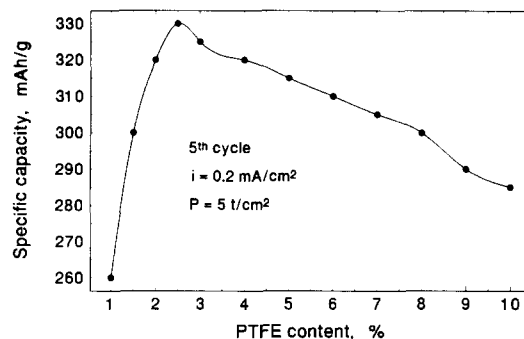


Fig. 7. Influence of the binder content in the electrode blend from Brazilian graphite and PTFE on the specific capacity at a current density of 0.2 mA/cm^2 .

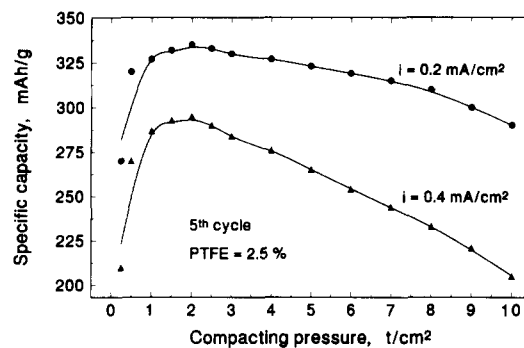


Fig. 8. Effect of the compacting pressure on the specific capacity of the electrode.

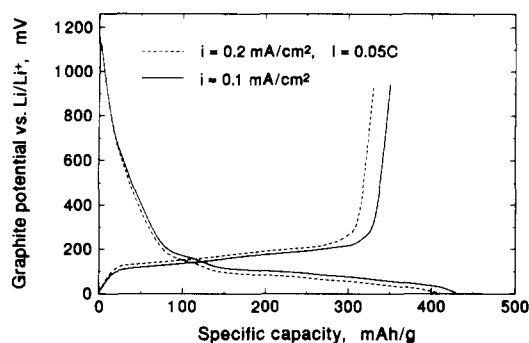


Fig. 9. First charge/discharge curves at a current density of 0.1 and 0.2 mA/cm^2 of Brazilian graphite electrodes prepared under optimum conditions.

film, which intensifies the decomposition of the electrolyte.

4. Conclusions

Applying appropriate preliminary treatments to natural Brazilian graphite and proper techniques for the electrode preparation, it is possible to obtain electrodes with specific capacity very close to the theoretical value of 372 mAh/g for LiC_6 , which makes this graphite a promising material for rechargeable lithium-ion cells. When using $\text{LiPF}_6/\text{EC}-\text{DMC}$ electrolyte and comparatively low current density (0.1 mA/cm^2), a high initial

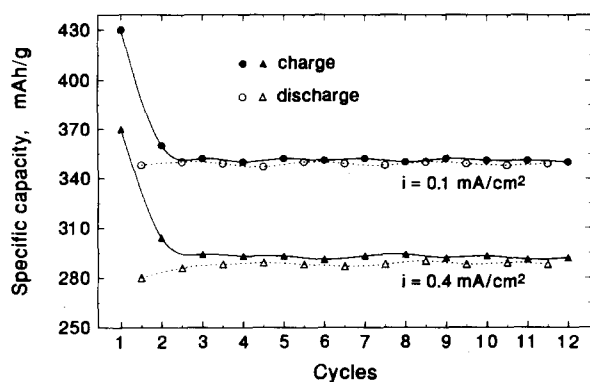


Fig. 10. Specific capacity vs. cycles number for electrodes prepared under optimum conditions, cycled at a current density of 0.1 and 0.4 mA/cm², respectively.

charge/discharge coulombic efficiency is observed that, after several cycles, reaches an almost steady value of ~99%.

Acknowledgement

One of us (G.P.) gratefully acknowledges the financial support of Valence Technology Inc., San Jose, CA, USA.

References

- [1] J.O. Besenhard and H.P. Fritz, *Angew. Chem.*, 22 (1983) 950.
- [2] R. Yazami and P. Touzain, *J. Power Sources*, 9 (1983) 365.
- [3] M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitate, S. Nakajima, M. Yoshida, Y. Yoshimoto, T. Suzuki and H. Wada, *J. Power Sources*, 26 (1989) 545.
- [4] R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi and O. Yamamoto, *J. Power Sources*, 26 (1989) 535.
- [5] J. Dahn, R. Fong and M. Spoon, *Phys. Rev.*, 42 (1990) 6424.
- [6] R. Fong, U. von Sacken and J. Dahn, *J. Electrochem. Soc.*, 137 (1990) 2009.
- [7] R. Kanno, K. Kawamoto, Y. Takeda, S. Ohashi, N. Imanishi and O. Yamamoto, *J. Electrochem. Soc.*, 139 (1992) 3397.
- [8] T. Mitate, H. Tanaka, A. Umemoto, H. Kitayama and M. Yoshikawa, *Prog. Batteries Battery Mater.*, 10 (1991) 134.
- [9] T. Nagaura, *Prog. Batteries Battery Mater.*, 10 (1991) 218.
- [10] D. Guyomard and J. Tarascon, *J. Electrochem. Soc.*, 139 (1992) 937.
- [11] B. Simon, J. Boeueve and M. Broussely, *J. Power Sources*, 43/44 (1993) 65.
- [12] R. Yazami and D. Guerard, *J. Power Sources*, 43/44 (1993) 39.
- [13] T. Ohzuku, Y. Iwakoshi and K. Sawai, *Ext. Abstr.*, 33rd Battery Symp. Japan, Tokyo, Japan, 1992, p. 123.
- [14] S. Miura, H. Nakamura and M. Yoshio, *Ext. Abstr.*, Tianjin Power Sources Symp., Tianjin, China, Sept. 1993, p. 141.