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Effect of electrode porosity on the performance of natural Brazilian graphite electrodes

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Abstract

Natural Brazilian graphite has been investigated as a reversible Li^+ -intercalating electrode for lithium-ion cells. Its performance is greatly influenced by the electrode preparation technique. A short compacting time (1 s or less), when pressing the powders, increases the specific capacity because the porosity remains sufficiently high. Low pressures ($< 200 \text{ kg/cm}^2$), which create higher porosities, give limited capacities due to poor inter-particle electrical contact. Excellent results have been obtained by substituting pressed powders with slurry-derived electrodes. In this case, an electrode porosity of 25–30% can be measured from compacting pressures between 20 and 200 kg/cm^2 . With this technique, it is possible to obtain: (i) an efficiency of 85% in the first cycle; (ii) a high rate capability, and (iii) a high and constant capacity upon cycling, i.e. 340 mAh/g at 0.4 mA/cm^2 . Cycling produces an increase in graphite surface area, a phenomenon which deserves a closer attention in view of possible safety problems.

Keywords: Graphite; Electric porosity; Electrodes

1. Introduction

Carbon-based intercalation compounds are considered as the most promising anode materials for rechargeable lithium-ion batteries [1–3]. Recently, using electrodes prepared by pressing graphite–polytetrafluoroethylene (PTFE) powders on a copper foil current collector, we have shown that an appropriate preliminary treatment of the natural Brazilian graphite and proper techniques for electrode preparation make it possible to obtain electrodes with specific capacities very close to the theoretical value of 372 mAh/g (LiC_6) [4]. This makes natural Brazilian graphite a suitable material for lithium-ion rechargeable cells. However, a good electrochemical performance was displayed only at the comparatively low current density of 0.1 mA/cm^2 . This work is aimed at elucidating the influence of electrode porosity and pore size distribution on the electrochemical behavior of this graphite. As the electrode characteristics depend on the method of electrode preparation, this factor should also be taken into consideration.

2. Experimental

Natural Brazilian graphite was supplied as a common sample by the International Battery Materials Association (IBA). Prior to electrode preparation, the graphite was ground for several hours in a ball mill and then dispersed in a water solution as described in Ref. [4]. The electrodes were prepared by pressing the graphite–PTFE (2.5 mass%) blend on a copper foil (diameter: 15 mm) or, alternatively, by spreading on the same support a paste of these components in alcohol. The electrochemical measurements were carried out in a three-electrode laboratory button cell (with $\text{LiPF}_6\text{-EC/DMC}$ as electrolyte) containing a lithium reference electrode.

The graphite surface areas were measured both with the BET method (on the powders) and with the mercury porosimeter (on the pellets). The porosity and the integral pore size distribution were obtained with a mercury porosimeter. A check of the porosity of pellets was also made with propanol. In this case, the pellets were filled under vacuum with propanol and the porosity was calculated from the weight difference before and after filling.

3. Results and discussion

The effect of the compacting pressure and its duration on the specific capacity and the reproducibility for pressed-pow-

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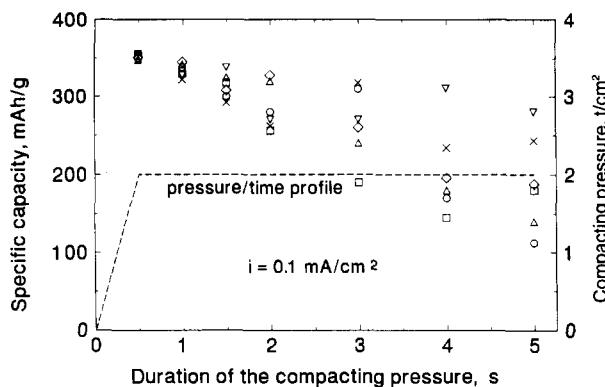


Fig. 1. Effect of compacting pressure duration on the specific capacity dispersion of the Brazilian graphite electrodes.

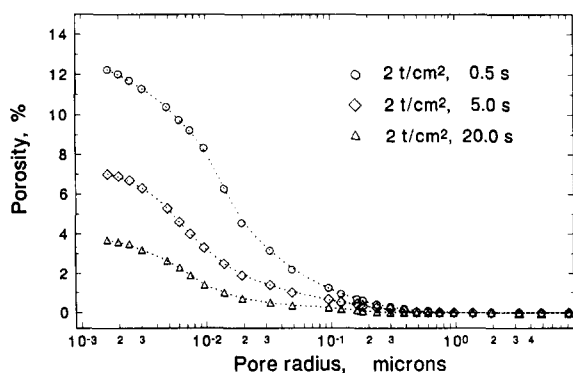


Fig. 2. Integral pore distribution curves of pressed-powder electrodes as a function of time.

der electrodes is shown in Fig. 1. In the same figure, the pressure–time profile is displayed, which indicates that the pressure was raised during the first 0.5 s to its maximum value, 2000 kg/cm², and then maintained constant. The device used for such experiments allowed us to apply this pressure for selected times of a few seconds. At each time, six different samples were tested to evaluate the reproducibility.

It is evident that the increase in pressing time does not only reduce the specific capacity of the graphite electrode, but also decreases its reproducibility. We suggest that, because of its softness, graphite behaves as a highly viscous Newtonian liquid, whereby the electrode porosity is reduced with the increase in compacting time. This suggestion is supported by the data presented in Fig. 2, where the integral pore-distribution curves of electrodes pressed at 2000 kg/cm² for 0.5, 5.0 and 20.0 s respectively, are compared. One may observe that for the longest time, the porosity decreases by a factor of three and the mean pore radius is reduced from 150 to 50 Å.

Fig. 3 presents the integral pore-distribution curves of pressed-powder electrodes, compacted for 0.5 s at different pressures. It is clear that the appropriate porosity of about 30% can be obtained at a compacting pressure of 200 kg/cm². Unfortunately, according to the data presented in Fig. 4, the electrodes pressed at 200 kg/cm² display significantly lower specific capacities than those pressed at 2000 kg/cm².

This result leads to postulate that in the case of pressed-power electrodes the reduction of the specific capacity for compaction pressures below 2000 kg/cm² is associated with contact losses between the graphite particles and/or between graphite particles and the current collector. This supposition prompted us to develop a slurry method for electrode preparation, where much better contacts can be obtained at extremely low compacting pressures. From the data presented in Fig. 4, it can be seen that using an alcohol-based slurry technique for electrode preparation a wide and flat maximum of the specific capacity exists for compacting pressures between 20 and 200 kg/cm². Fig. 4 also shows that the maximum specific capacity at 0.2 mA/cm² of the electrodes prepared by the slurry technique is greater than that of those manufactured by the powder method.

The effect of compacting pressure on the porosity of slurry- and powder-prepared Brazilian graphite electrodes is shown in Fig. 5. It is evident that by decreasing the compacting pressure the porosity of the slurry-prepared electrodes tends to a constant value of about 30%. This porosity allows a satisfactory electrolyte penetration, while keeping the electrode volume sufficiently low.

The use of our slurry method for electrode preparation does not clog part of the electrode pores, this being a typical disadvantage of the classical slurry methods. This is evident in the data displayed in Table 1, where the specific surface area

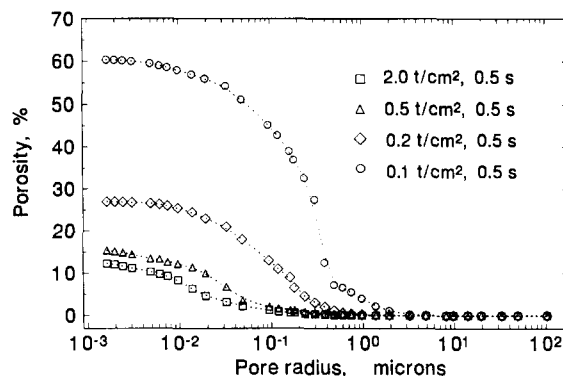


Fig. 3. Integral pore distribution curves of pressed-powder electrodes as a function of pressure.

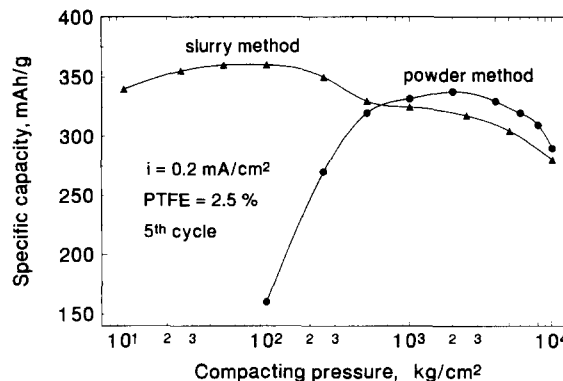


Fig. 4. Influence of compacting pressure and method of preparation on the electrode capacity.

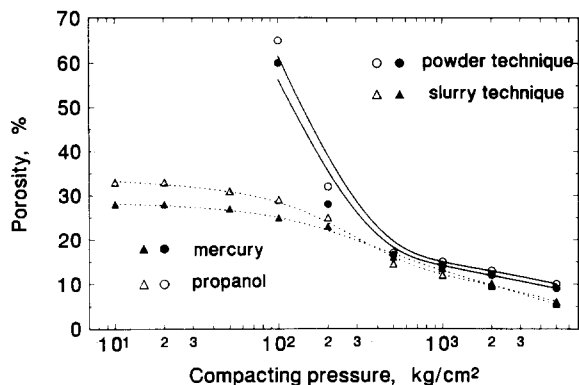


Fig. 5. Effect of compacting pressure on the porosity of powder- and slurry-prepared electrodes.

Table 1
Surface area of natural Brazilian graphite (powder and pellets)

Method of preparation	Method of measurement			
	BET	Mercury porosimeter		
		100 kg/cm² pellets (m²/g)	500 kg/cm² pellets (m²/g)	2000 kg/cm² pellets (m²/g)
Powder technique	9.8	9.83	10.70	10.87
Slurry technique	9.8	9.74	10.42	11.12

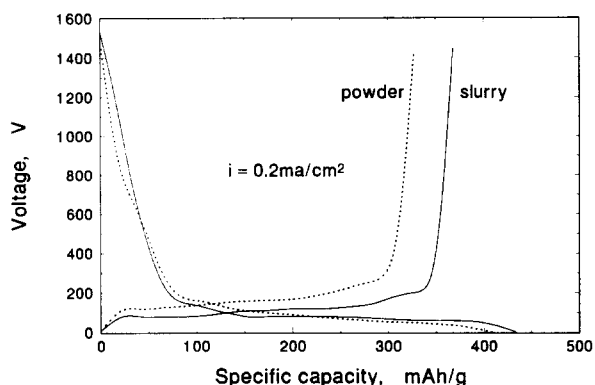


Fig. 6. First charge/discharge curves of electrodes prepared with the powder or slurry method.

of electrodes prepared by powder and slurry techniques is compared. The areas of the electrodes prepared by the two methods are practically the same and do not differ much from the initial surface area of the starting graphite powder.

The first charge/discharge curves of the electrodes prepared by powder and slurry methods are compared in Fig. 6. It can be calculated that the coulombic discharge/charge efficiency of the pressed-powder electrodes is about 80%, whilst that of the slurry-prepared electrodes is about 85%. This is one of the highest efficiencies reported thus far [5].

The discharge curves at different current densities of the electrodes prepared by the slurry method are compared in

Fig. 7. From these data it can be concluded that graphite electrode prepared by this technique can withstand very high discharge rates without substantial decrease in their capacity.

A comparison of the long cycling tests of graphite electrodes prepared by powder and slurry methods, presented in Fig. 8, shows that the use of the latter improves not only the specific capacity but the cycleability as well. This is especially evident at the higher current density (0.4 mA/cm²).

One of the reasons for the good electrochemical performance of electrodes prepared by the slurry method, is that, during the first several cycles, the morphology of the electrode is changed substantially. This is shown in Fig. 9, where the scanning electron microscopy pictures of the electrodes before cycling and after five cycles are compared. It is evident that, after cycling, the electrode structure is transformed from well-ordered slabs, stacked one up another, into 'chain' structures of particles with a diameter of about 0.2 μm.

We have measured the surface area after five cycles and found a rather surprising increase, i.e. from 9.7 to 48.6 m²/g. Such a high value might create concern in terms of safety, should metallic lithium be present at the electrode surface [6,7]. More tests would be necessary on other natural and synthetic graphites to see if the same extent of 'electrochemical grinding' occurs. Thus far, this aspect has not been discussed by people working in this field, as it has often

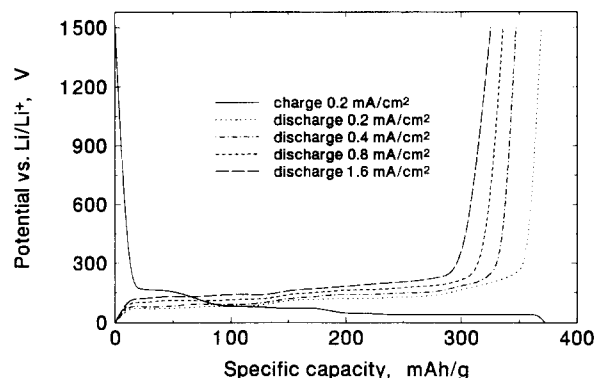


Fig. 7. Discharge curves at different current densities of electrodes charged at $I_c = 0.2 \text{ mA/cm}^2$.

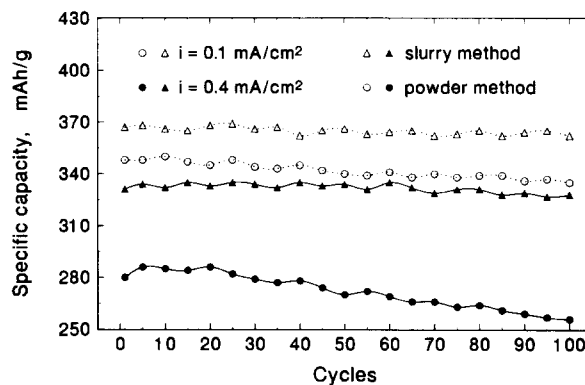


Fig. 8. Comparison of cycling tests of electrodes prepared with the powder or slurry method.

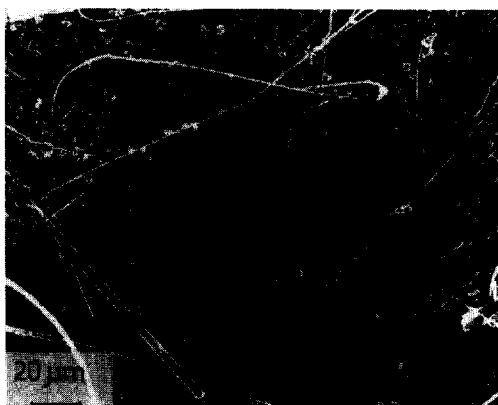
Before cycling:**After 5 cycles:**

Fig. 9. Scanning electron microscopy pictures of electrodes (before cycling and after five cycles) at two magnifications.

been assumed that the surface area remains constant upon cycling [7].

4. Conclusions

Properly treated natural Brazilian graphite can be used as an effective Li^+ -intercalating compound. In particular, electrodes having a porosity of $\sim 30\%$, prepared by the slurry technique, give high capacities which remain constant upon cycling. These electrodes also exhibit a good rate capability and a satisfactory first-cycle efficiency ($\sim 85\%$). Cycling breaks up the graphite slabs into small pieces, thus increasing the surface area. High-surface lithiated carbons have self-heating rates rapidly increasing with temperature, this resulting in the risk of thermal runaway [7]. This aspect requires a deeper investigation on this and other graphite electrodes.

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