

Plasticized carbon electrodes of interest for lithium rocking chair batteries

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Abstract

The electrochemical properties of a carbon-coke electrode, fabricated in the form of a thin-film, flexible membrane by a procedure which involves the immobilization of carbon into a poly(vinyl chloride) (PVC) matrix, have been examined. The thermodynamics and the kinetics of the lithium insertion/deinsertion process in these Li_xC_6 carbon-coke membrane electrodes have been investigated by voltage–composition and galvanostatic curves, by cyclic voltammetry, and by impedance spectroscopy. The expectation is that the data obtained in this work may serve as a basis for the evaluation of the applicability of the carbon membrane as anode in rocking chair batteries of the most common liquid-electrolyte type and, in prospective, of the polymer-electrolyte type.

Introduction

The original investigation of lithium rocking chair batteries, where the 'conventional' lithium metal anode is replaced by a nonmetal material capable of storing and exchanging large quantities of lithium ions, dates back to early 1980s [1–3]. However, in more recent years, the rocking chair concept has gained a renewed interest [4] and many university and industrial laboratories are presently involved in the investigation and development of related battery systems where, most commonly, the anode is lithiated carbon coke and the cathode is a compound of the LiMO_2 family (with $M = \text{Co}$, Ni or Mn).

So far, the majority of the studies have been directed to rocking chair batteries using liquid electrolytes, namely solutions of lithium salts in organic, aprotic solvents. However, on prolonged cycling, these batteries may be affected by instability due to electrolyte decomposition [2] and, thus, the development of a truly stable and safe rocking chair battery would require the replacement of the 'conventional' liquid solutions with alternative electrolytes having a wider electrochemical stability window. A promising choice is the polymer-electrolyte family, namely the class of lithium ion-conducting membranes formed by the combination of poly(ethylene oxide) (PEO) with lithium salts [5] or by gelification of lithium solvates in a polymer matrix [6].

The idea is ultimately to realize thin-layer, flexible-shaped, lithium polymer rocking chair batteries which could combine the already established favourable performance of the lithium polymer batteries [7] with the safe and reproducible performance expected

by the rocking chair concept. However, to maintain the plasticity and flexibility, which are among the most appealing features of the lithium polymer battery, a lithium-source, nonmetal electrode, having ductile properties matching those of the electrolyte and of the cathode membranes, would be greatly welcome.

With this in mind, we have prepared the carbon-coke anode in the form of a thin, flexible membrane by a procedure which involves the immobilization of carbon into a poly(vinyl chloride) (PVC) matrix. In this work we report the electrochemical characterization of this carbon thin-film electrode in conventional liquid electrolytes. The expectation is that the data obtained in this work may serve as a basis for the evaluation of the applicability of the carbon membrane as anode in rocking chair batteries of the general type and, in prospective, of the polymer electrolyte type.

Experimental

As the main source of carbon we have used petroleum coke (200 mesh, 95%) powder samples, kindly provided by Conoco Inc., USA. PVC, a Fluka high molecular weight product, was used as received. The carbon electrodes were prepared in the form of membranes by dissolving 0.2 g PVC in 10 cm³ tetrahydrofuran (THF) and then by slowly adding 0.8 g of carbon-coke powder. No plasticizers were used. The slurry was first homogenized for 5 min (by ultrasonic stirring) and then mechanically stirred for 1 h. Finally, films of about 50 to 100 μm thickness were obtained using a 'Doctor Blade'-type casting technique by slowly evaporating the solvent in air. The membrane samples were then aged in an argon-filled dry box for 2 to 3 weeks in order to eliminate residual solvent or water traces. The films had an average composition of 80 wt.% coke-20 wt.% PVC corresponding to a total capacity of 0.29 Ah g⁻¹. In preparation for the electrochemical tests, the films were generally backed on a nickel foil current collector. However, free-standing carbon membranes could also be obtained with the above-described casting procedure. Figure 1 shows a photograph of a typical example of these membranes.

For comparison purpose, pellet-like electrodes also were prepared by mixing 84 wt.% of carbon coke with 16 wt.% of Teflon binder in dry methanol (7.5 cm³ methanol/g of coke), with a total capacity of 0.31 Ah g⁻¹. Again, the slurry was homogenized by ultrasonic stirring before mechanically stirring. After a slow, spontaneous solvent evaporation, a paste mixture was obtained which was then compressed up to 8 t cm⁻² to form pellets with a surface of 1.13 cm² and a thickness of 1 mm. The pellets were finally dried at 250 °C for 30 min and stored in an argon-filled dry box for the electrochemical tests.

All the electrochemical measurements were carried out by means of three-electrode cells, where the working electrode was alternatively the carbon membrane or the carbon pellet, and the reference electrode a lithium wire, while the counter electrode was a lithium foil. The electrolyte was generally a 1 M LiClO₄ solution in propylene carbonate (thereafter briefly indicated as LiClO₄/PC). For the voltammetric tests, a 1 M LiClO₄ solution in a 50/50 propylene carbonate-ethylene carbonate mixture (thereafter briefly indicated as LiClO₄/PC-EC) was used. PC, an anhydrous (HPLC grade) product, was used as received. EC, a reagent-grade product, was further purified by reflux on molecular sieves followed by distillation under vacuum. The cells were assembled and stored in an argon-filled dry box (less than 5 ppm r.h).

The voltage-composition curves of the coke electrodes (of Li_xC₆ general formula) were obtained by promoting lithiation of carbon by progressive coulombic steps run

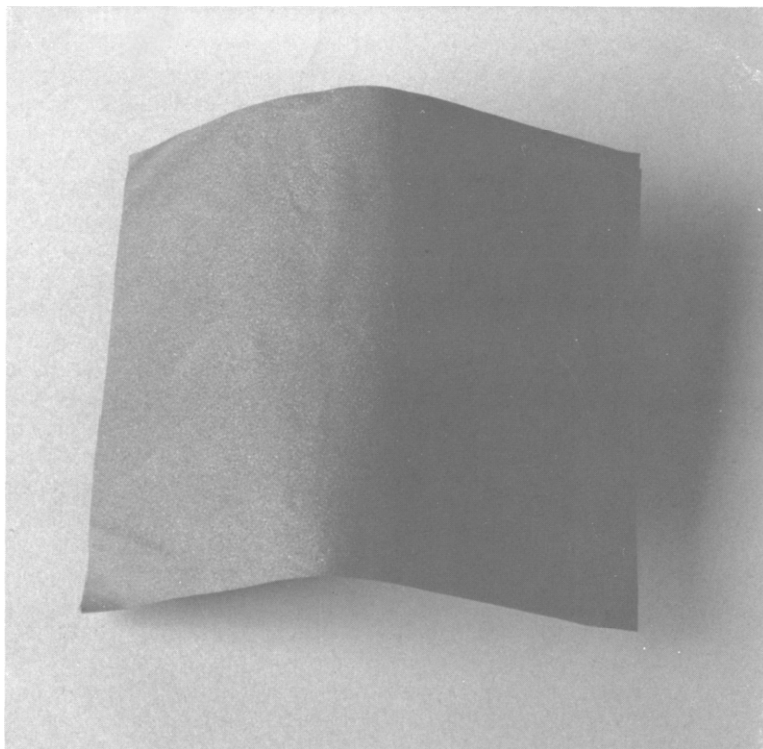


Fig. 1. Photograph of a dimensionally-stable PVC-carbon membrane.

at constant current ($I=0.05 \text{ mA cm}^{-2}$) for fixed amount of time, and following the consequent open-circuit voltage (OCV) relaxation until constant values (less than 0.1 mV change per hour) was reached. The OCV- Li_xC_6 curves were developed by subsequent $x=0.1$ steps for the pellet electrodes and by $x=0.25$ steps for the film electrodes. The cyclic voltammetry curves were run at various scan rates using a PAR model 362 scanning potentiostat. Lithium insertion/deinsertion galvanostatic ($I=0.13 \text{ mA cm}^{-2}$) cycles were run and controlled by an AMEL model 545 galvanostat.

The impedance analysis was carried out by means of a Solartron model 1255 frequency response analyser coupled with a Solartron model 1286 electrochemical interface, both instruments controlled by an IBM computer.

The electronic conductivity of the carbon membrane electrodes was measured by a four-point method and found to be 0.03 S cm at room temperature.

Results and discussion

The basic electrochemical characteristics of lithiated carbon electrodes have been studied by several authors [8–15] and it is now well recognized that in the most

common cases the composition is of the Li_xC_6 type, with a maximum uptake of one lithium equivalent ($x=1$) per six carbon atoms [16]. It has been reported [8, 9] that the voltage of the Li_xC_6 electrode varies about 1.5 V as the value of x varies from 0 to 1 during lithiation. This, however, has been generally evaluated under non-equilibrium conditions, namely by following the voltage assumed by the Li_xC_6 electrode under current flowing either during charge (lithium uptake) and discharge (lithium release) processes.

In this work we have attempted to determine the quasi-thermodynamic voltage-composition curve by imposing progressive, short charge steps on the Li_xC_6 carbon electrode and then monitoring its voltage under open-circuit condition until the value remained unchanged within 0.1 mV. Figure 2 illustrates the results for both the membrane and the pellet electrode configurations. As expected, following progressive lithium loading, the voltage of the Li_xC_6 electrode constantly decreases to reach a value of about 0.5 V versus lithium for $x=1$, this giving a thermodynamic range for this electrode of the order of 1.5 V for the exchange of 1300 C g^{-1} of charge. In summary, the data obtained in this work confirm other workers' previous observations and outline that the voltage of the Li_xC_6 electrode varies significantly with the state-of-charge. This is a major drawback: in fact, a wide voltage variation is an undesired feature which may reflect into poor voltage regulations upon charge and discharge and, ultimately, may rule out this electrode from applications in multi-purpose, rocking chair batteries.

Another aspect of concern is associated with the value reached by the Li_xC_6 electrode at its high loading limit ($x \rightarrow 1$) which falls into the range where most of the liquid aprotic solvents decompose. This circumstance may ultimately pose some questions on the overall stability (upon prolonged cycling) of Li_xC_6 -based rocking chair cells.

To control this aspect and to further characterize the electrochemical behaviour of the Li_xC_6 electrode, we have examined its cycling response by following the trend of charge/discharge curves. Figure 3 shows the profile of the initial galvanostatic ($I=0.13 \text{ mA cm}^{-2}$) charge (Li^+ insertion)/discharge (Li^+ extraction) cycles of the

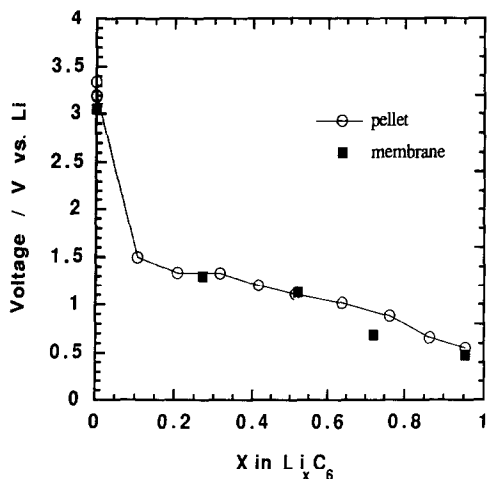


Fig. 2. Voltage-composition curve for the Li_xC_6 electrode at room temperature; lithium reference electrode; LiClO_4/PC electrolyte.

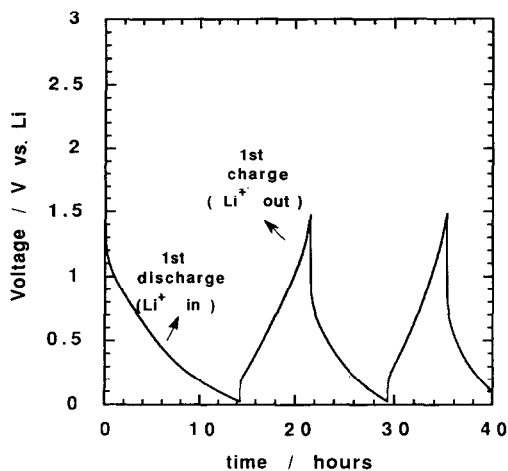


Fig. 3. Initial charge (lithium insertion)/discharge (lithium extraction) galvanostatic cycles for a Li_xC_6 (PVC membrane) electrode at room temperature; $I=0.13 \text{ mA cm}^{-2}$; lithium counter and lithium reference electrode; LiClO_4/PC electrolyte.

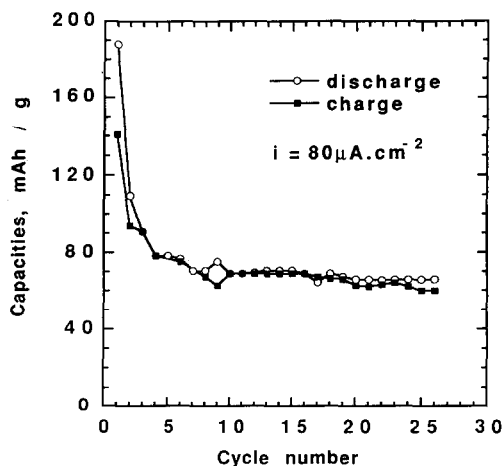


Fig. 4. Capacity exchanged during progressive charge/discharge galvanostatic cycles of a Li_xC_6 (PVC membrane) electrode at room temperature; $I=0.08 \text{ mA cm}^{-2}$; lithium counter and lithium reference electrode; LiClO_4/PC electrolyte; voltage limits: charge 0.02 V, discharge 1.9 V.

Li_xC_6 electrode in the preferred membrane configuration. One can clearly notice that only a fraction of the charge consumed in the first charging (Li^+ insertion) cycle is released and exchanged in the following cycles. This is confirmed, and even more clearly shown, by Fig. 4 which illustrates the trend of the capacity exchanged in charge and in discharge over a more prolonged cycling regime. It may be easily seen that the Li_xC_6 electrode, after a progressive loss, reaches a steady behaviour with a highly reversible capacity exchange, which, however, is limited to about 50% of the initial content.

This capacity loss is again a well-established phenomenon which has been observed by many authors [8, 9, 11] and generally explained assuming that the lost fraction of charge is due to the decomposition of the solvent (here PC) at the carbon electrode with the consequent formation of a passivation film on its surface. It has also been assumed that the passivation film, being electronically insulating but ionically conducting, prevents further solvent decomposition while it allows ionic transfer with the electrolyte [8]. In summary, such a film formation would be essential in assuring the stability and the cycleability of the Li_xC_6 electrode since it would allow its operation, even at those voltage levels which fall below the stability window of the electrolyte solution.

This is obviously a very crucial aspect which appears of prior importance to the evaluation of the effective role of the Li_xC_6 electrode in the development of practical rocking chair batteries. Therefore, it seemed of interest to devote further attention to the characteristics of the lithiation process of the Li_xC_6 membrane electrode with the prime objective of gaining more information on its cycleability in the liquid organic solutions and, hopefully, in the majority of suitable electrolyte media.

Figure 5 illustrates a slow scan (0.1 mV s^{-1}) cyclic voltammetry of a Li_xC_6 membrane electrode in the LiClO_4/PC electrolyte. The results clearly show that the amount of cycleable charge decreases consistently passing from the first initial cycle to the second and third following cycles, after which a steady-state condition is reached. Therefore, these cyclic voltammetry curves seem to confirm the galvanostatic results and to support the generally-accepted conclusion that after the initial charge losses, the Li_xC_6 electrode reaches a stable and reproducible behaviour [8, 9].

On the other hand, some questions are still left on the effective mechanism of the initial loss of charge. As already pointed out, this loss is generally attributed to the reduction of the electrolyte with the consequent passivation of the electrode by the deposition on its surface of an electronically blocking layer. However, the charge/discharge test as well as the cyclic voltammetry test reported in this work, support only in part this theory. In fact, to be effective, the passivation layer should uniformly grow in the course of the very few initial cycles and, accordingly, the electrode should quickly assume a steady response. On the contrary, the cycling results of Fig. 4 point

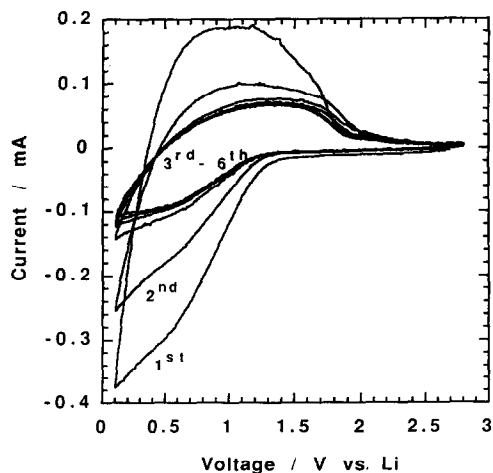


Fig. 5. Low scan (0.1 mV s^{-1}) cyclic voltammetry of a pristine Li_xC_6 (PVC membrane) electrode at room temperature; lithium reference electrode; LiClO_4/PC electrolyte.

out that full reversible exchange is reached only after ten or more cycles. Furthermore, by examining closely the trend of the first cycle of Fig. 5, one may detect a shoulder in the cathodic scan (at about 0.7 V versus Li) with no corresponding effect in the following anodic scan. Since this is an interesting event, which undoubtedly deserves further attention, we have repeated the test by running the cyclic voltammetry of a pristine Li_xC_6 electrode in $\text{LiClO}_4/\text{PC-EC}$, namely in one of the electrolyte media considered to be the most suitable for rocking chair operation [9]. The results, illustrated in Fig. 6, clearly confirm the occurrence of the irreversible cathodic peak in the initial cycle.

Both the cycling and the voltammetric effects cannot be explained simply on the basis of passivation phenomena but it seems reasonable to assume that other irreversible electrochemical processes, more directly related to the feature of the intercalation process of the lithium ions into the carbon structure, may be involved as well. For instance, it is possible to presume that the carbon structure, which is essentially described as a combination of distorted graphite stages [15], may offer different sites having different binding energy for accommodating the incoming inserted lithium ions. Accordingly, the initial loss of charge could also be in part associated to a fraction of lithium ions which in the course of the first charging cycles are inserted and stored in strongly bounded lattice positions from where they cannot be removed during the following discharges. Indeed, an initial irreversible uptake of guest ions is not an uncommon phenomenon in insertion electrochemical processes and its occurrence also in graphite-like Li_xC_6 compounds has been postulated by other authors [16].

With the hope of gaining more information on this aspect, we have carried out an impedance analysis of the Li_xC_6 electrode at various composition levels. Figure 7 illustrates the responses in the impedance plane for $x=0$, $x=0.3$ and $x=0.5$. One can clearly notice that the middle-frequency semicircle, which may be associated with interfacial effects, increases upon lithiation. However, this result is not conclusive since there is no clear evidence that the expansion of the semicircle can definitely be attributed to the formation of a passivation layer at the interface.

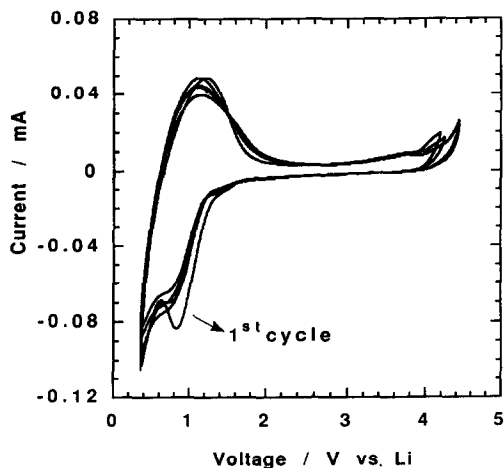


Fig. 6. Low scan (0.1 mV s^{-1}) cyclic voltammetry of a pristine Li_xC_6 (PVC membrane) electrode at room temperature; lithium reference electrode; $\text{LiClO}_4/\text{PC-EC}$ electrolyte.

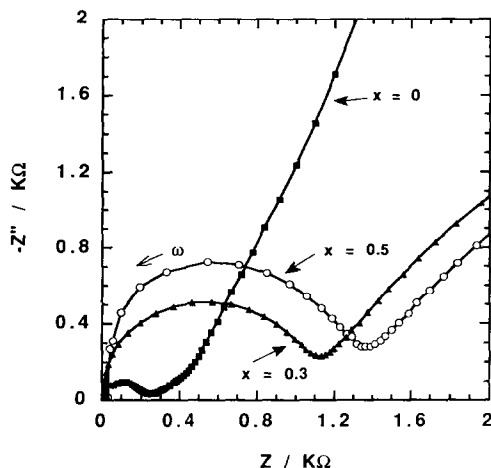


Fig. 7. Impedance response of Li_xC_6 (PVC membrane) electrode at various compositions at room temperature; lithium reference electrode; LiClO_4/PC electrolyte; high frequency limit: 30 kHz.

One may then conclude that carbon electrodes of the Li_xC_6 type are certainly of interest for the development of lithium rocking chair batteries, especially due to the low cost and the reasonably high-specific capacity. However, some basic aspects of the behaviour of this electrode still remain to be investigated, such as, in particular, the initial loss of charge, a phenomenon not yet fully understood. Finally, consideration should also be given to the fact that uncontrolled operating conditions may drive the voltage of the Li_xC_6 electrode to values at which lithium plating, rather than lithium inserting, may become the predominant process, with a consequent serious hazard. The conditions which control these aspects will be the future object of investigation.

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