

Stability of lithiated carbon electrodes in organic electrolytes

R. Bittihn, R. Herr* and D. Hoge

VARTA R & D Centre, Gundelhardtstraße 72, 6233 Kelkheim/Taunus (Germany)

Abstract

Lithiated carbon electrodes have been tested for applications in secondary cells. The stability of these electrodes at elevated temperatures (60 °C) and the loss of lithium during the first cycle have been investigated.

Introduction

Carbon seems to be the ideal material for 'rocking chair' lithium cells [1, 2]. It is cheap, nontoxic and air stable in the discharged state. Early attempts to use pure graphite as host material for Li failed [3].

Recent results show that only disordered turbostratic carbon [4] is the appropriate material for secondary Li cells. Two main problems, the loss of Li in the first cycle and the high temperature stability are investigated.

Experimental

All experiments were carried out in an argon glove box. If not stated otherwise, potentials refer to the Li/Li⁺ electrode. Solvents and salts used for the electrolytes were dried prior to use by conventional means and kept under argon. Specific capacities were determined in coin-type cells of size 2025 with a 1 M LiClO₄/propylene carbonate (PC) electrolyte if not stated otherwise by using an in-house built computer-controlled current supply and data logger.

Results and discussion

A special feature of lithiated carbon electrodes is, that only a certain amount of the Li reacted during the first charge, that is first Li insertion, can be discharged again. Figure 1 shows the first cycle of a needle-coke electrode against Li metal; 309 A h/kg are charged but the discharge up to 1.0 V yields only 179 A h/kg. Even a discharge up to 4.0 V cannot recover all the Li. There is still a loss of 23%. It is generally accepted that this effect is due to a film formation on the carbon electrode

*Author to whom correspondence should be addressed.

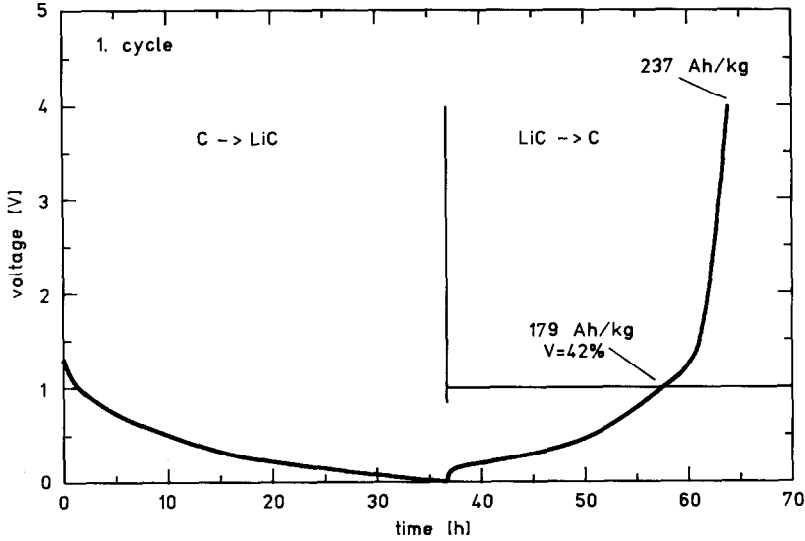


Fig. 1. Loss of lithium during the first lithiation of a carbon electrode.

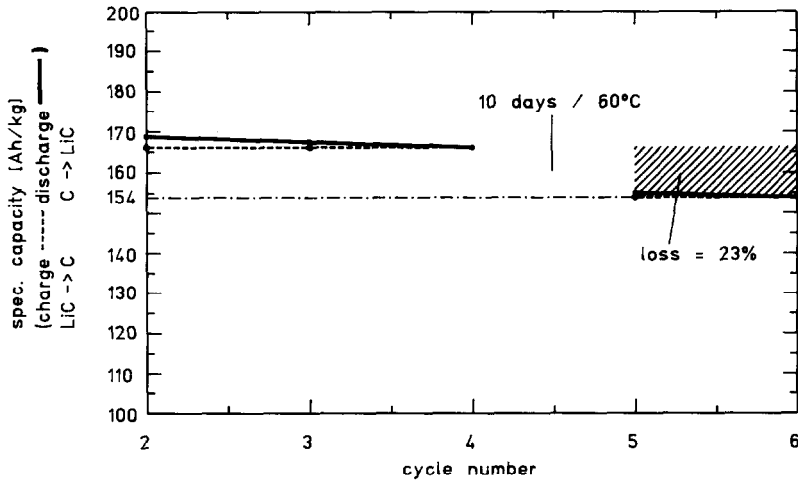


Fig. 2. Irreversible loss of specific capacity of carbon material after high temperature storage in the charged state.

surface [5, 6]. After the first cycle, the carbon electrode has a coulombic efficiency of more than 99% when cycled between 1.0 and 0.0 V versus Li/Li^+ .

Self-discharge at room temperature is moderate (5% per month) and reversible. It becomes critical at elevated temperatures.

Figure 2 shows the irreversible loss of specific capacity of a lithiated carbon electrode after 10 days storage at 60 °C. The high temperature storage behaviour depends strongly on the electrolyte composition.

Figure 3 shows the results with several electrolytes. Coke samples cycled in 1.0 M LiClO_4/PC electrolyte have a specific room temperature capacity of 153 A h/kg.

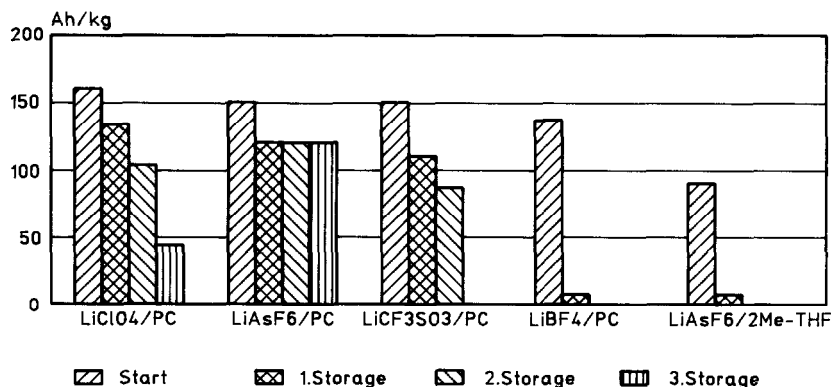


Fig. 3. Specific capacity of carbon material after several high temperature storage periods in the charged state.

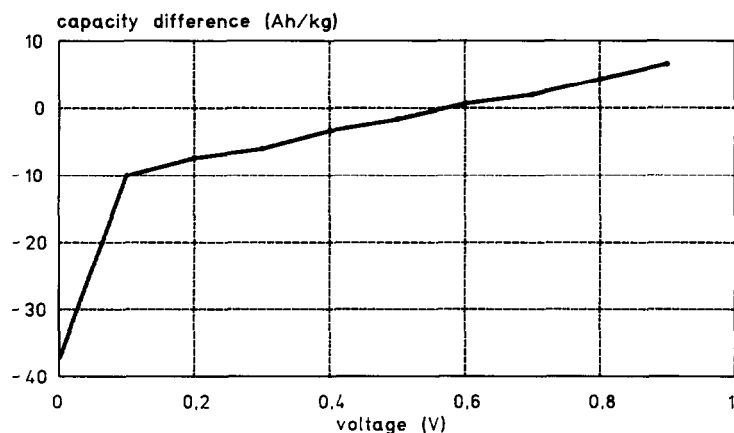


Fig. 4. Difference in the specific capacity of carbon material after high temperature storage (10 days, 60 °C) at different potentials which were adjusted potentiostatically.

Successive periods of high temperature storage (13 days 60 °C) cause a severe loss of capacity. Cells with 1.0 M LiCF₃SO₃/PC electrolyte have nearly the same behaviour. Samples in 1.0 M LiBF₄/PC and 1.0 M LiAsF₆/2-MeTHF electrolytes are already destroyed by one high temperature storage period. Only the sample with the 1.0 M LiAsF₆/PC electrolyte showed a stable capacity after a 20% loss at the first storage. It has probably the most flexible surface film.

In order to evaluate the influence of the potential of the electrode on the amount of irreversible loss of capacity at high temperature storage, another series of experiments was carried out. Button cells with coke electrodes were cycled three times galvanostatically with 0.25 mA/cm². They were then held at a certain potential (0.1–0.9 V versus Li/Li⁺) until the current dropped below 1×10^{-5} A. The cells were then stored for 10 days at 60 °C. In order to measure the loss of Li during the high temperature storage, the cells were held at the same potential as before until the current dropped below 1×10^{-5} A (Fig. 4). The greatest loss of capacity occurred at 0.0 V (38 mA h/g). From 0.1 to 0.6 V there is a linear decrease in capacity loss. At 0.6 V the electrode

is stable and has no self-discharge. At higher potentials, a decrease in voltage was observed during storage. This is rather surprising. The open-circuit voltage of fresh coke versus Li/Li^+ is 3.0 V. There is no reason why the potential of Li/carbon cathode should drop after it was maintained potentiostatically at 0.8 V.

The experiments indicate, that the loss of Li in the first cycle cannot be attributed solely to a film formation. There is some Li stored in the coke material which is kinetically strongly hindered and cannot be discharged potentiostatically at room temperature. However, this feature affects the potential after high temperature storage and may be comparable to the phenomenon of residue compounds in graphite intercalation compounds.

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