Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 147 (2005) 269–281
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Ageing mechanisms in lithium-ion batteries☆

J. Vetter[a,*], P. Novák[a], M.R. Wagner[b], C. Veit[b], K.-C. Möller[b], J.O. Besenhard[b], M. Winter[b], M. Wohlfahrt-Mehrens[c], C. Vogler[c,1], A. Hammouche[d]

[a] *Electrochemistry Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[b] *Institute for Chemical Technology of Inorganic Materials, Graz University of Technology, A-8010 Graz, Austria*
[c] *ZSW Center for Solar Energy and Hydrogen Research Baden Wuerttemberg-Division 3, Electrochemical Energy Storage and Conversion, Helmholtzstrasse 8, D-89081 Ulm, Germany*
[d] *Institute for Power Electronics and Electrical Drives, Aachen University of Technology, Jaegerstrasse 17–19, D-52066 Aachen, Germany*

Received 17 July 2004; received in revised form 20 December 2004; accepted 7 January 2005
Available online 14 March 2005

Abstract

The rechargeable lithium-ion battery has been extensively used in mobile communication and portable instruments due to its many advantages, such as high volumetric and gravimetric energy density and low self-discharge rate. In addition, it is the most promising candidate as the power source for (hybrid) electric vehicles and stationary energy storage. For these applications in durable equipment, the long-term cycling and storage behaviour becomes of increasing interest. In this paper, the mechanisms of lithium-ion battery ageing are reviewed and evaluated.

Keywords: Lithium-ion battery; Ageing; Power fade; Capacity fade; Impedance; Life-time

1. Introduction

Lithium-ion batteries have been commercially used for a number of years in small portable devices like cell phones, laptop computers, camcorders, and similar electronic devices. Due to short innovation cycles in this field, battery life-time beyond a limited period of time played only a minor role for this kind of applications. But the commencing penetration of lithium-ion batteries in the market of durable consumer and investment goods, like (hybrid) electrical vehicles, temporary storage systems for renewable energy sources, and also in the market of batteries for conventional vehicles, requires a more sophisticated evaluation of battery life-time. The goals of the United States Advanced Battery Council (USABC) in the FreedomCAR research initiative (2002; www.uscar.com), e.g., demand a calendar life-time of 15 years for 42 V battery systems and hybrid electrical vehicles (HEV's), and 10 years for electrical vehicles (EV's). In terms of cycle life, a life-time of up to 1000 cycles at 80% depth-of-discharge (DOD) is demanded.

Unfortunately, lithium-ion batteries are complex systems to understand, and the processes of their ageing are even more complicated. Capacity decrease and power fading do not originate from one single cause, but from a number of various processes and their interactions. Moreover, most of these processes cannot be studied independently and occur at similar timescales, complicating the investigation of ageing mechanisms.

In this paper, we will give a review on today's knowledge on the mechanisms of ageing in lithium-ion batteries. We will try to identify and evaluate different processes, as far as they are known from the literature, in order to establish a solid basis for further investigations.

Ageing mechanisms occurring at anodes and cathodes differ significantly and are therefore discussed in two separate chapters. The influence of the electrolyte and the ageing of

☆ Prepared within the framework of the European project LIBERAL.
* Corresponding author. Tel.: +41 56 310 2165; fax: +41 56 310 4415.
E-mail address: jens.vetter@psi.ch (J. Vetter).
[1] Present address: Sued-Chemie AG, Ostenriederstrasse 15, D-85368 Moosburg, Germany.

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.01.006

the electrolyte itself (and the separator as well) mainly take place at the electrodes and in interaction with them, so they are covered in the corresponding chapters. The article closes with a review on electrochemical impedance spectroscopy as the tool of choice for non-destructively studying ageing processes and determining the state of health of lithium-ion batteries.

2. Ageing of carbonaceous anodes

2.1. General aspects

Carbon, in particular graphite, is the most important anode material in lithium-ion batteries, and thus, the greatest understanding of anode ageing has been accomplished with graphite-based cells [1–3]. Although alternative anode materials like lithium storage metals and alloys have recently found increased attention among researchers, emphasis was mostly laid on the active materials itself and related problems (e.g., nanostructured materials, control of volume changes), whereas ageing effects have found considerably less attention [4–6]. Hardly any literature data exists on ageing mechanisms of hard carbons [7]. Thus, unsurprisingly, the vast majority of references in the literature related to anode ageing concentrates on graphitic carbons. In general, the situation reported in the literature is difficult to analyze as each lithium-ion cell system has its own chemistry and many ageing effects are influenced by the nature of the cell components (e.g., active material and electrode design, electrolyte composition, impurities, etc.). Furthermore, most available literature data concentrates on complete cells without the attribution of certain effects to either anode or cathode. In view of these limitations, this part of the study can summarise and discuss only the dominant ageing mechanisms of graphite anodes.

As for the cathode, ageing effects at the graphite anode lead to a modification of the electrode properties with time and use. Ageing effects that may occur during storage (e.g., self-discharge, impedance rise) will affect the calendar life of the battery, whereas the cycle life is in addition influenced by ageing effects that may occur during use (e.g., mechanical degradation, lithium metal plating) [8]. Ageing during storage can be monitored by electrochemical "values" such as capacity loss, impedance rise, potential change, state of charge (SOC) and state of health (SOH) [9]. However, it is important to point out that anode materials such as graphite may exhibit discharge plateaus, i.e., the electrode potential does not significantly vary with the state of charge [10–12]. During cycling, one can measure the capacity fade, the impedance rise which is closely related to power fade, and overpotentials that influence the potential profile of the charge/discharge curves. For a concise discussion, it should be pointed out that ageing with time and use can lead to—and may be caused by—changes (i) of the electrode/at the electrolyte interface and in the electrolyte, (ii) of the active material, and (iii) of the composite electrode (current collector, active materials, conductive additives, binder, porosity, etc.). Most literature data account changes at the electrode/electrolyte interface for being responsible for the ageing of/at carbon electrodes, and hence, this influence on anode ageing will be discussed in more detail here [13,14]. Changes of the active material and the composite electrode are seldom discussed, but they may have an influence on the ageing process, which will be regarded by short summaries in the corresponding chapters.

2.2. Changes at the electrode/electrolyte interface

Changes at the electrode/electrolyte interface (Fig. 1) due to reactions of the anode with the electrolyte are considered by many researchers to be the major source for ageing of/at the anode [15]. It is well known that lithium-ion

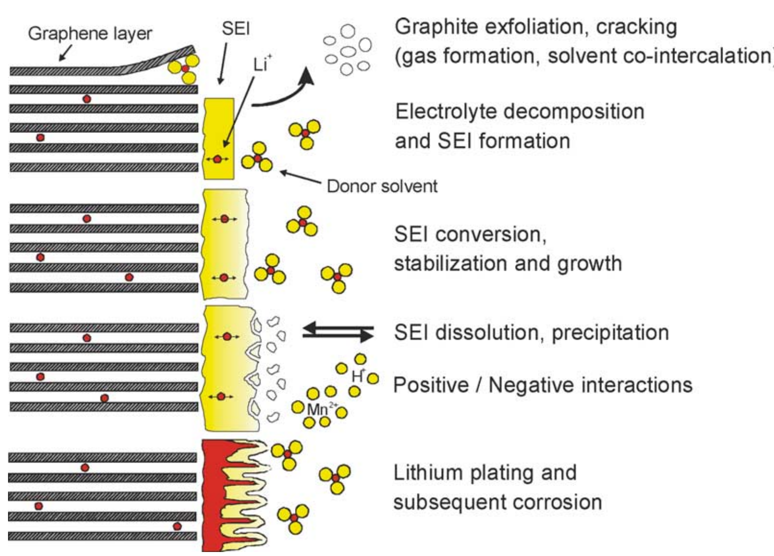

Fig. 1. Changes at the anode/electrolyte interface.