



Altered electrode degradation with temperature in LiFePO₄/mesocarbon microbead graphite cells diagnosed with impedance spectroscopy



Matilda Klett*, Tommy Georgios Zavalis, Maria H. Kjell, Rakel Wreland Lindström, Mårten Behm, Göran Lindbergh

School of Chemical Science and Engineering, Department of Chemical Engineering and Technology, Applied Electrochemistry, KTH Royal Institute of Technology, SE-10044 Stockholm

ARTICLE INFO

Article history:

Received 11 April 2014
Received in revised form 10 June 2014
Accepted 12 June 2014
Available online 18 July 2014

Keywords:

battery aging
temperature
electrode impedance
EIS modeling
LiFePO₄/MCMB graphite

ABSTRACT

Electrode degradation in LiFePO₄/mesocarbon microbead graphite (MCMB) pouch cells aged at 55 °C by a synthetic hybrid drive cycle or storage is diagnosed and put into context with previous results of aging at 22 °C. The electrode degradation is evaluated by means of electrochemical impedance spectroscopy (EIS), measured separately on electrodes harvested from the cells, and by using a physics-based impedance model for aging evaluation. Additional capacity measurements, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) are used in the evaluation. At 55 °C the LiFePO₄ electrode shows increased particle/electronic conductor resistance, for both stored and cycled electrodes. This differs from results obtained at 22 °C, where the electrode suffered lowered porosity, particle fracture, and loss of active material. For graphite, only cycling gave a sustained effect on electrode performance at 55 °C due to lowered porosity and changes of surface properties, and to greater extent than at low temperature. Furthermore, increased current collector resistance also contributes to a large part of the pouch cell impedance when aged at increased temperatures. The result shows that increased temperature promotes different degradation on the electrode level, and is an important implication for high temperature accelerated aging. In light of the electrode observations, the correlation between full-cell and electrode impedances is discussed.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Li-ion batteries are becoming the preferred energy storage for hybrid electric (HEV) and battery electric (BEV) vehicles due to their high energy and power densities. Among the different technologies, the LiFePO₄/graphite chemistry is a common commercial material choice due to low cost and high stability. Still, a remaining issue of using Li-ion batteries in vehicles is the aging of the battery, affecting the production and economy of HEVs and EVs. For this reason, aging of Li-ion batteries is widely studied. Furthermore, the design and material variations, and complexity of different battery systems call for studies with varying aging scenarios and materials to help expand our understanding of degradation mechanisms. For use in HEVs, the degradation effects on batteries from high-power cycling are of particular interest.

The capacity fade and impedance increase, which are the two general symptoms of aging in a battery cell, are affected by the manner of which the cell is used. Especially temperature is known to be heavily influential on cell aging both at storage and cycling. For the LiFePO₄/graphite battery chemistry several authors report the loss of cyclable lithium as the main contributor to the observed capacity loss [1–7] and overall cell aging when cycling at both low and high temperatures, and therefore an important issue for battery aging. However, degradation of the electrodes themselves and also the separator, affecting capacity and impedance, have been observed during different aging conditions. Safari *et al.* [2] observed a slight loss of graphite active material in a full cell cycled at 45 °C related to the build-up of solid electrolyte interface (SEI) and cyclable lithium loss while assuming negligible degradation of the LiFePO₄ electrode. Liu *et al.* [1] reported similar results when also including separate electrode measurements in their methodology. A much larger degradation was reported by Amine *et al.* [8], observing a substantial increase in graphite impedance at 55 °C compared to both a fresh cell and a cell aged at 37 °C. Iron was in that case found

* Corresponding author.

E-mail address: [mklett@kth.se](mailto:mklet@kth.se) (M. Klett).

Nomenclature

a	specific material surface area [m ⁻¹]
$a_{cs} C_{dl,cs}$	the double-layer capacitance per unit volume electronically conductive additive (specific electronically conductive additive surface area double-layer capacitance per electronically conductive additive area) [F m ⁻³]
c	concentration [mol m ⁻³]
$C_{dl,cc}$	double-layer capacitance at current collector per geometric area [F m ⁻²]
$C_{dl,S}$	double-layer capacitance per active electrode material area [F m ⁻²]
D_L	diffusion coefficient with respect to the thermodynamic driving force in the electrolyte [m ² s ⁻¹]
D_S	diffusion coefficient in active electrode material [m ² s ⁻¹]
E_{OCP}	open-circuit potential at active material surface [V]
i	current per active material surface area [A m ⁻²]
i_0	exchange current per active material surface area [A m ⁻²]
i_{cell}	total current in the three-electrode cell per geometric area [A m ⁻²]
$i_{dl,cc}$	double-layer current at the current collector per geometric area, $\tilde{i}_{dl,cc} = j\omega C_{dl,cc} (\tilde{\varphi}_{WE} - \tilde{\varphi}_L)$ [A m ⁻²]
i_F	faradaic current per active material surface area [A m ⁻²]
j	imaginary unit, $j^2 = -1$
L	length (domain thickness) [m]
N	anion (PF ₆ ⁻) flux [mol m ⁻² s ⁻¹]
r	radial distance in spherical active material particle [m]
r_p	active material particle radius [m]
R_{cc}	resistance between the current collector and the porous electrode per geometric area [Ω m ²]
R_{loc}	local resistance; resistance per active electrode material area due to resistive film on the surface of the active material and poor contact between active material and electronically conductive additive [Ω m ²]
$t_{solv}^{Li^+}$	transport number of Li ⁺ with solvent as reference [-]
$V_m^{LiPF_6}$	molar volume lithium hexafluorophosphate salt [m ³ mol ⁻¹]
x	1D spatial coordinate [m]
$1 + \ln f_{\pm} / \ln c_L$	thermodynamic enhancement factor
α	transfer coefficient [-]
β	Bruggeman constant [-]
ε	volume fraction [-]
κ	ionic conductivity of the liquid (electrolyte) phase [S m ⁻¹]
σ	electronic conductivity [S m ⁻¹]
φ	electric potential [V]
ω	angular frequency [rad s ⁻¹]

Subscripts

a	anodic
c	cathodic
cc	current collector
cS	electronically conductive additive
dl	double layer
L	liquid (electrolyte) phase

RE	reference electrode
S	active electrode material phase
$solv$	solvent
tot	total
WE	working electrode
l_0	at equilibrium (i.e. not perturbed)
-	at the electrode surface ($\tilde{\varphi}_s$)

to dissolve from the LiFePO₄ electrode and was detected on the graphite surface. Enhanced iron dissolution from LiFePO₄ in LiPF₆ at elevated temperatures has also been reported [9,10]. The degradation of the separator is more rarely studied, but can, if distorted, affect power capabilities [11].

The effect of temperature on electrode degradation at cycling and storage conditions is an important consideration from several aspects. Firstly, in the case of accelerated aging. Increased temperature is sometimes used as a stress factor in aging studies, however, different degradation processes do not necessarily have the same temperature dependence [12]. Secondly, in large batteries used in vehicles, above room-temperature conditions can be reached during cycling, especially for high power cycling in HEVs, and need to be taken into consideration [13,14]. Thirdly, temperature variations within the cell [15,16] can lead to different degradation in different parts of the cell [13], and thereby complicate the interpretation of the aging on cell level. A better understanding of high temperature aging of electrodes from controlled experiments using high current to resemble hybrid vehicle conditions can help in the evaluation of aging in scaled-up systems.

Previously, we used electrochemical impedance spectroscopy (EIS) to study the degradation of electrodes harvested from LiFePO₄/mesocarbon microbead (MCMB) graphite pouch cells that had been calendar and cycle aged with a high-power standardized HEV cycle at 22 °C [4,17]. EIS on harvested electrodes has been shown to be a valuable technique to investigate aging [4,18–21]. It was found that calendar aging at this temperature had negligible effect on both positive and negative electrodes, though loss of cyclable lithium reduced the capacity of the full cell. Cycling, however, had a more detrimental effect on the full cell regarding both capacity and impedance. By EIS of harvested electrodes, it was found that the positive LiFePO₄ electrode had the largest contribution to the impedance increase seen for the pouch cell, even though some increase was also seen for the graphite impedance. A physics-based EIS model was, in resemblance to other studies [20,22–25], utilized to interpret the experimental spectra, and also used the input from scanning electron microscopy (SEM) and low-rate capacity measurements. With this method it was further possible to relate the graphite electrode impedance increase to an increased local resistance, and the LiFePO₄ electrode impedance to morphological degradations of the composite electrode structure, by lowered porosity, particle size reduction and loss of active material.

To study the effect of temperature, the LiFePO₄/MCMB graphite pouch cells have also been aged with the same procedure at 55 °C [17]. Large differences in cell performance were observed between the 22 °C and 55 °C cases. At 55 °C the full-cell 1 C discharge capacity dropped much quicker and the cells reached end-of-life (EOL) after 3000 cycles (25 days, 600 capacity throughputs based on initial capacity) while the cells aged at 22 °C reached EOL after 14 000 cycles (115 days, 2800 capacity throughputs based on initial capacity), at which time the high-power cycle could no longer be performed. At EOL, the cells aged at 55 °C had lost 49% (cycled) and 38% (stored) of their initial capacity while the cells at aged at 22 °C had lost 44% (cycled) and 11% (stored). It is hence clear from

Download English Version:

<https://daneshyari.com/en/article/185286>

Download Persian Version:

<https://daneshyari.com/article/185286>

[Daneshyari.com](https://daneshyari.com)