Journal of Power Sources 386 (2018) 85–95

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Practical high temperature (80 °C) storage study of industrially manufactured Li-ion batteries with varying electrolytes

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HIGHLIGHTS

- Different degradation for cells stored rather than cycled at 80 °C.
- In-situ volume changes during and after storage at elevated temperatures.
- Resistance decrease during cycling, after ageing with sulfur containing additives.

ARTICLE INFO

Keywords:
Li-ion battery
Elevated temperature
Storage
Electrolyte additive
Cell swelling
Gas consumption

ABSTRACT

A previous study is focused on high temperature cycling of industrially manufactured Li-ion pouch cells (NMC-111/Graphite) with different electrolytes at 80 °C [JPS 373 (2018) 172–183]. Within this article the same test set-up is used, with cells stored for 30 days at different open circuit potentials and various electrolytes instead of electrochemical cycling. The most pronounced cell degradation (capacity fade and resistance increase) happens at high potentials. However appropriate electrolyte formulations are able to suppress ageing conditions by forming passivating surface films on both electrodes. Compared with electrochemical cycling at 80 °C, cells with enhanced electrolytes only show a slight resistance increase during storage and the capacity fade is much lower. Additionally it is shown for the first time, that the resistance is decreasing and capacity is regained once these cells are cycled again at room temperature. This is not the case for electrolytes without additives or just vinylene carbonate (VC) as an additive. It is further shown that the resistance increase of cells with the other electrolytes is accompanied by a reduction of the cell volume during further cycling. This behaviour is likely related to the reduction of CO_2 at the anode to form additional SEI layer components.

1. Introduction

Presently Li-ion batteries are used in nearly all portable electronic devices. Some of them, such as mobile phones, could not work in their current form without this type of battery technology. However, the operational temperature limit for most of the secondary Li-ion chemistries is stated around 60 °C. At higher temperatures gas generation and additional cell degradation is observed and batteries can even undergo thermal runaway reactions as a worst case scenario [1–3]. Nevertheless, in several cases batteries can even reach temperatures up to 80 °C. These incidents can for example be induced by prolonged sunlight exposure [4], but there are also other applications in which high temperatures are experienced more frequently, including sensor technologies, military operations and subterranean high temperature environments [1]. In previous studies cells which are based on $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC-111) as the cathode material were cycled at temperatures around 80 °C [5]. The use of suitable electrolyte additives enabled cells to be operated at these temperatures without large amounts of solvent oxidation and gas generation [6]. However a cathode-related resistance increase leads to a great loss of power, based on the disintegration of secondary cathode particles with new decomposition layers along grain boundaries [6]. The fragmentation was also observed in other suitable cathode materials, such as $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ (NCA) [7,8]. However, for most of the batteries lifetime it is stored at an open circuit voltage (OCV) rather than being charged or discharged. During this time cells can undergo a self-discharge which is triggered by several mechanisms. These can include electron leakages, (internal electron transfer through insulating materials) or the reaction of the electrolyte with anode and cathode surfaces [9]. Such reactions can be differentiated into reversible (no capacity loss upon additional cycling) and irreversible reactions (permanent consumption of Li-ions or Li-ion storing materials) [9,10]. Generally the

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https://doi.org/10.1016/j.jpowsour.2018.03.050
Received 8 November 2017; Received in revised form 16 March 2018; Accepted 19 March 2018

kinetic of these reactions will accelerate with increasing temperature, which results in a faster rate of self-discharge and OCV drop [11]. However, additional new reaction paths will also be introduced. Chemical compounds of the Solid Electrolyte Interface (SEI) on the anode surface will start to decompose at temperatures around 80 °C [12,13]. These "holes" within the SEI enable a fresh electrolyte contact with the lithiated graphite surface to form additional decomposition products and consume Li-ions and solvent molecules. It was therefore reported that the anode morphology transforms towards a more crystalline composition at elevated temperatures [14]. Further reactions in the 80 °C environment are related to a lowered oxidation potential of the electrolyte with increasing temperature [15,16]. Solvents such as ethylene carbonate can be oxidized, which results in a cell swelling due to the generation of CO and CO_2 [17]. Many studies were aimed at the use of electrolyte additives to inhibit this gas generation and to improve the performance at elevated temperatures [18–22]. One very promising electrolyte mixture was recently introduced by Xia et al. which is based on a ternary additive system of PES (Prop-1-ene-1,3-sultone), DTD (1,5,2,4-Dioxa-dithiane 2,2,4,4-tetraoxide) and TTSPi (Tris-trimethylsilyl-phosphite) [19]. However, most of the additive related studies were either performed at temperatures ≤60 °C or used laboratory-scale electrodes, typically in half cells vs. lithium. Recent investigations show the importance of using full cells for a broader understanding of degradation effects, as it is believed that both electrodes can interact and influence each other during operation [23–26].

In this article we investigate the degradation of industrially manufactured pouch cells with different electrolytes during and post storage at 80 °C. A similar study was recently published but was aimed on the degradation observed during cycling rather than as a function of the storage conditions of NMC/Graphite based Li-ion batteries.

2. Experimental

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC111)/graphite pouch cells (ca. 1.2 Ah) without electrolyte were obtained from LiFun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). The electrode loading for the anode was 95 g/m^2 with 95% active material, 3.8% binder (CMC/SBR) and 1.2% conductive carbon. The cathode loading was 185 g/m^2 with 96.4% active material, 2% binder and 1.6% conductive carbon. The cells arrived vacuum sealed with extra pouch material for the degassing process still attached and filling/formation steps have been described in detail within an earlier publication [6]. The electrolyte compositions used for this work as well as the related supplier details can be found in Table 1.

Composition C was achieved by adding PES (Fluorochem, 95%), DTD (Fluorochem, 95%) and TTSPi (Sigma Aldrich, 95%) to Electrolyte A. Electrolytes A and B exhibited a water content of ca. 2 ppm, whilst the modified electrolyte C measured approximately 20 ppm (due to the water within the additives). Cells with electrolyte D were pre-filled by the manufacturer and so an analysis of the water content was not possible. Prior to the storage at elevated temperatures the cells also underwent two comparison cycles between 2.5 V and 4.2 V at 240 mA (C/5) to demonstrate reproducible capacity and resistance values (end voltage ≈ 3.5 V). For the elevated temperature storage cells of each electrolyte composition were placed in thermal chambers set at 80 °C (± 0.1 °C). They were charged/discharged to their initial storage voltage and during a time period of 30 days the OCV and volume expansion were continuously monitored. The experimental setup for the in-situ volume measurements has been described in detail by Aiken et al. [27]. Thin film load cells (0.2 N) were obtained from Strain Measurement Devices and the voltage reading was amplified using a self-built device. The signal was measured via the external VMP3 port to enable time resolved data acquisition of battery voltage and volume expansion. Fig. S1 shows photographs and a schematic of the volume change test apparatus. Every 24 h potentiostatic electrochemical impedance spectroscopy (PEIS) was performed with a scanning range between 100 kHz and 10 mHz and an amplitude of 10 mV. The data were fitted using ZView with the following circuit elements: inductor (L), series resistance (Rs), SEI resistance (Rsei), charge transfer resistance (Rct), constant phase elements (CPE) and Warburg element (W). Due to faster kinetics at elevated temperatures it is difficult to differentiate multiple semicircles, so for further comparisons of cell resistances the SEI related resistance and charge transfer resistance were combined (shown as Rct within the results). After 30 days of elevated temperature storage the climate chambers were set to 25 °C (± 0.1 °C). 24 h later the cells were cycled for 50 additional cycles between 2.5 V and 4.2 V in a CC-CV mode with 400 mA (C/3) constant current (CC) down to 60 mA (C/20) during the constant voltage step (CV) at 4.2 V. During the cycling PEIS measurements were performed every two cycles at 3.5 V, 30 min after the discharge, using the same settings as previously described. The cells were subsequently discharged to 3.5 V and opened in an argon filled glovebox (O_2 and H_2O below 0.1 ppm) where the electrodes were washed with DMC (di-methyl carbonate) for further investigation. SEM images were obtained using a Carl Zeiss Sigma Field Emission Scanning Electron Microscope (FE-SEM) at 5 kV accelerating voltage in combination with in-lens detection at working distances of approximately 2 mm. Cross-sections were obtained via an ion-milling process at 6 kV acceleration and 1.5 kV discharge voltage with a swing angle of ± 30° (HITACHI IM4000 plus). Coin-cell sized discs (15 mm diameter) of anodes and cathodes were cut from the aged electrodes to build symmetrical coin cells (two discs of the same electrode against each other) inside the glovebox. The procedure is similar to that described by Petibon et al. [28] and all cells were filled with fresh electrolyte of composition A (Table 1). The impedance for symmetrical coin cells was measured at 25 °C using the same settings as for the pouch cell measurements. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical Ltd.) with monochromatic Al-Kα source (hn = 1486.6 eV). High-resolution spectra were obtained using a 20 eV pass energy and an analysis area of approximately 300 × 700 μm. Samples were transferred under argon atmosphere and peak fitting was conducted by using the CasaXPS software. The oxidation potentials of electrolytes at 25 °C and 80 °C were measured from OCV after assembling to 7 V vs. Li/Li^+ with a sweep rate of 1 $mV\,s^{-1}$. Cells containing 100 μl electrolyte were assembled in a three-electrode Swagelok design with platinum as the working and lithium as the counter and reference electrode.

3. Results and discussion

3.1. Cell parameters during storage at 80 °C

Fig. 1a shows the voltage profiles of pouch cells filled with the

Table 1
Electrolyte compositions for cells cycled at 80 °C – the salt concentration was 1 M $LiPF_6$.

No.	Solvents (vol. ratio)	Additives (mass ratio)	Supplier	Synonym
A	EC:EMC (3:7)	none	BASF (LP57)	Standard
B	EC:EMC (3:7)	1% VC	Soulbrain	Standard + 1% VC
C	EC:EMC (3:7)	2% PES, 1% DTD, 1% TTSPi	Electrolyte A modified	Standard + PES 211
D	EC:PC:DEC (35:30:45)	1% VC, 1% PES + other	LiFun Technology	Industrial