The influence of cycling temperature and cycling rate on the phase specific degradation of a positive electrode in lithium ion batteries: A post mortem analysis

Mariyam Susana Dewi Darma [a, *], Michael Lang [a], Karin Kleiner [a], Liuda Mereacre [a], Verena Liebau [b], Francois Fauth [c], Thomas Bergfeldt [a], Helmut Ehrenberg [a]

[a] Karlsruhe Institute of Technology — Institute for Applied Materials (KIT — IAM), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany
[b] Bayerische Motoren Werke AG, Petuelring 130, 80788, München, Germany
[c] CELLS-ALBA Synchrotron, E-08290 Cerdanyola del Valles, Barcelona, Spain

HIGHLIGHTS

- Phase specific capacity loss of the blended cathode is quantified by in situ XRD.
- The NCM becomes partially inactive due to the extensive cycling.
- The LMO shows a good cycling stability at 25 °C.
- The overvoltage of the fatigued phases increases.
- Inhomogeneous lithium distribution during cycling is identified.

GRAPHICAL ABSTRACT
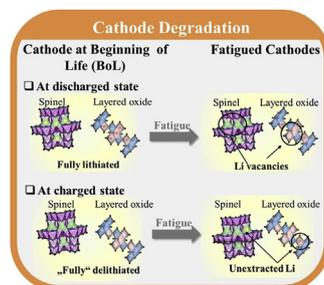
ABSTRACT

The influence of cycling temperatures and cycling rates on the cycling stability of the positive electrode (cathode) of commercial batteries are investigated. The cathode is a mixture of $LiMn_2O_4$ (LMO), $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). It is found that increasing the cycling temperature from 25 °C to 40 °C is detrimental to the long term cycling stability of the cathode. Contrastingly, the improved cycling stability is observed for the cathodes cycled at higher charge/discharge rate (2C/3C instead of 1C/2C).

The microstructure analysis by X-ray powder diffraction reveals that a significant capacity fading and an increased overvoltage is observed for NCM and NCA in all the fatigued cathodes. After high number of cycling (above 1500 cycles), NCM becomes partially inactive. In contrast to NCM and NCA, LMO shows a good cycling stability at 25 °C. A pronounced degradation of LMO is only observed for the fatigued cathodes cycled at 40 °C. The huge capacity losses of NCM and NCA are most likely because the blended cathodes were cycled up to 4.12 V vs. the graphite anode during the cycle-life test (corresponds to 4.16 V vs. Li^+/Li); which is beyond the stability limit of the layered oxides below 4.05 V vs. Li^+/Li.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

High specific capacity, good rate capability, good thermal

---

* Corresponding author.
E-mail addresses: mariyam.darma@kit.edu, msdd040877@yahoo.com (M.S.D. Darma).

stability and long cycle life are the requirements of the lithium ion batteries (LIBs) used for electro mobility applications [1—8]. For automotive applications, e.g. plug-in hybrid electric vehicles (PHEV), hybrid electric vehicles (HEV) or electric vehicles (EV), one of the greatest concerns is the cell lifetime [9]. The LIBs are supposed to show a good cycle life of at least 1000 cycles at 80% depth of discharge (DoD) [9]. They reach the end of life (EOL) when the discharge capacity drops to less than 80% of its initial capacity [10]. The cell performance deteriorates eventually after extensive cycling due to the degradation of its cell components, i.e. electrode (cathode and anode), separator, electrolyte and current collector. The cell degradation is greatly influenced by cell chemistry as well as by cycling conditions such as cycling temperature, cycling rate and voltage window [8,11,12]. Cell degradation becomes apparent through several parameters like increasing overvoltage, increasing impedance and decreasing capacity. Nevertheless, there is no single cathode material that exhibits all the desired properties at the same time. As an example, $LiMn_2O_4$ (LMO) shows good rate capability and a relatively high operating voltage (vs. Li^+/Li), which ensures a high power density of the battery, but it suffers from low specific capacity and shows fast capacity fading at elevated temperature [2—5]. In contrast to LMO, layered oxide based cathode materials such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) have a larger specific capacity than LMO (~50% larger), but their operating voltage is lower than that of LMO [2,5—8]. Moreover, this type of material shows inferior rate capability [5].

One of the strategies to fulfil the existing demands is to use blended cathodes, which consist of at least two different active materials. The laboratory scale research on blended cathodes emerged decades ago and today blended cathodes are commercially available [2,5,13—18]. The properties of the blended cathodes can be tailored depending on its constituent [5,13,14,17,18]. The LIBs requirements of high energy and power densities might be fulfilled by using a blended positive electrode consisting of materials which exhibit high specific capacity and good rate capability such as a blend of NCM and LMO. Besides, it is reported that the blending of NCM and LMO suppresses manganese dissolution, hence, it leads to better capacity retention during cycling [15,18]. However, by mixing materials which are active at significantly different voltage windows might lead to the situation that the materials which operate at a lower voltage window get overcharged during cycling and therefore they eventually degrade more rapidly.

The focus of the work reported here is to investigate the influence of cycling rate and cycling temperature on the degradation mechanism of a blended cathode. The cathode consists of a mixture of the good rate capability material $LiMn_2O_4$ (LMO) and the high specific capacity materials $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). The investigated blended cathodes are taken from positive electrodes of dedicated battery electric vehicle (BEV) LIBs. In the present report, a post mortem examination of fatigued cathodes was performed using combined methods: X-ray diffraction, electrochemical tests and elemental analysis. Based on the results, phase specific degradation and local variation of the state of charge (SoC) in the cathodes are discussed.

2. Experimental part

2.1. Sample preparation

For the cycle-life test, four dedicated BEV prismatic 60 Ah LIBs were cycled between 2.7 V and 4.12 V at two different cycling temperatures and cycling rates. The cycling conditions of the fatigued cathodes (LR25, HR25, LR40 and HR40) during the cycle-life tests are given in Table 1. The samples were labelled with LRTemp for the fatigued cells cycled at lower rate (1C/2C charge/

Table 1
The list of samples evaluated in this report. The cycling conditions of the fatigued cathodes (LR25, HR25, LR40 and HR40) during cycle-life test are given.

Sample name	BoL	LR25	HR25	LR40	HR40
Number of cycles	—	1600	2100	1900	2160
Charge/Discharge rate	—	1C/2C	2C/3C	1C/2C	2C/3C
Cycling temperature	—	25 °C	25 °C	40 °C	40 °C

discharge rate) and HRTemp for the fatigued cells cycled at higher rate (2C/3C charge/discharge rate). Temp refers to the cycling temperature. For the post mortem analysis of the fatigued cathodes, the LIBs were disassembled in a glove box with argon atmosphere.

As observed by Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), the blended cathode consists of three phases, i.e. $LiMn_2O_4$ (LMO), $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). SEM-EDS also detects C and F which are attributed to the binder and conductive agent.

The area density of the blended cathode is 12.94 mg cm^{-2}. It is observed by SEM that size of the primary particle of all phases is in the range of 300 nm—900 nm while the average size of the secondary particles is 9 μm for LMO and NCM and 6 μm for NCA.

The active material of the cathode was coated on both sides of the aluminium current collector. Because one side coated electrodes are needed for the in situ powder diffraction investigations, the active material on one side of the cathode was removed using *N*-Methyl-2-pyrrolidone (NMP). The remaining cathode was then immersed in dimethyl carbonate (DMC) to dissolve the residual salts. For the structural characterization, the cathode sheets were cut into discs with a diameter of 12 mm. To understand the influence of the cycling rate and the cycling temperature on the degradation of the cathodes, the microstructure of the fatigued cathodes was analysed and compared to that of the Beginning of Life (BoL) cathode.

2.2. In situ synchrotron powder diffraction measurements

In situ X-ray synchrotron powder diffraction experiments were performed during electrochemical cycling of the blended cathode vs. Li^+/Li (a half-cell setup). This cell consists of a blended cathode, two layers of Celgard separator, and lithium metal as the anode. The cells were assembled in a custom made coin cell with Kapton windows inside a glove box with argon atmosphere [19]. $LiPF_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC) 1:1 (w/w) (LP30 from Merck) was used as the electrolyte.

For in situ powder diffraction experiments, all cathodes were galvanostatically cycled at a constant current of 0.625 mAh (corresponding to C/3 rate) from 3.0 V to 4.20 V using a VMP3 multichannel potentiostat (Bio-Logic, France). The 1C rate was calculated by dividing the nominal capacity of the full cell by the total area of the cathode, which corresponds to a current density of 1.66 mA cm^{-2}.

In situ powder diffraction patterns were collected at the Material Science and Powder Diffraction beamline (MSPD) at the ALBA synchrotron in Barcelona/Spain in transmission mode at ambient temperature [20]. The acquisition time was 40 s per pattern. The two-dimensional powder patterns were recorded by a MYTHEN 6 K Position Sensitive Detector covering 2θ angles from 1° to 44° (for the BoL and the LR40) and from 4° to 40° (for the LR25, the HR25 and the HR40). In the diffraction patterns, the integrated intensity of the powder rings is plotted as a function of q, where q is the magnitude of the scattering vector, i.e. $q = 4\pi\lambda/\sin\theta$ (θ is a scattering angle). The diffraction pattern of an LaB_6 (NIST 660b) reference was measured, and it was used to refine the wavelength and to determine the instrumental resolution function. For the BoL and