Degradation mechanism of over-charged LiCoO₂/mesocarbon microbeads battery during shallow depth of discharge cycling

Lingling Zhang ^{a, †}, Yulin Ma ^{a, †}, Xinqun Cheng ^a, Yingzhi Cui ^a, Ting Guan ^a,

Yunzhi Gao ^a, Chunyu Du ^a, Geping Yin ^{a, *}, Feng Lin ^b, Dennis Nordlund ^c

^a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

^b Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

^c Stanford Synchrotron Radiation Lightsource at SLAC, Menlo Park, CA 94025, USA

*Corresponding author: Geping Yin (G. P. Yin)

E-mail: yingeping@hit.edu.cn (G. P. Yin)

Author contributions: Authors L. Z. and Y. M. contributed equally to this work.

Telephone number: 86-451-86413721

Fax number: 86-451-86403807

Postal address: P.O. BOX 1247, No.92, Xidazhi Street, Nan'gang District, Harbin

Institute of Technology, Harbin 150001, China.

ABSTRACT: LiCoO₂/mesocarbon microbeads (MCMB) batteries are over-charged to different voltage (4.4 V, 4.5 V, 4.6 V, and 4.7 V, respectively) for ten times, and then

are cycled 1000 times for shallow depth of discharge. The morphology, structure, and electrochemical performance of the electrode materials were studied in detail in order to identify the capacity fading mechanism of over-charged battery after long-term cycling. The cycling performances of LiCoO₂/MCMB batteries are gradually aggravated with the increase of over-charging voltage and the degradation mechanism is diverse upon the degree of over-charging. The capacity fading after long-term cycling of battery over-charged to 4.6 V or 4.7 V is mainly attributed to the cathodes. Soft X-ray absorption spectroscopy (XAS) demonstrates that the lower valence state of cobalt exists on the surface of the LiCoO₂ after serious over-charging (4.6 V or 4.7 V), and cobalt is dissolved then deposited on the anode according to the result of energy dispersive spectrometry (EDS). However, after shallow over-charging (4.4 V or 4.5 V), the capacity deterioration is proposed as the loss of active lithium, presented by the generation of the SEI film on the anode, which is verified by water washed tests.

Keywords: LiCoO₂/MCMB battery; Over-charging; Capacity fading mechanism; Long-term cycling; Lithium dendrites; Reduction and dissolution of cobalt

1. Introduction

Lithium-ion batteries (LIBs), a promising power sources, have long been pursued for application in mobile communication and portable instruments [1-5]. However, the safety problem of lithium-ion batteries prevented avenues of application [6-8]. Over-charging, one of the important safety issues, can lead to thermal runaway of batteries and ultimately to fire or explosion [9, 10].

The failure mechanisms of over-charged battery have been widely studied. When the battery is over-charged, the excessive lithium ions removed from cathode to deposit on the anode generating lithium dendrite [11, 12] and react with electrolyte causing destructive side reactions, which will deteriorate the electrochemical performance and finally lead to internal short circuiting during repeated charged/discharged cycles [13, 14]. For the over-charged cathode, the large volume changes induced by the drastic reduction in the c lattice parameter can cause loss of inter-particle contact, which may lead to capacity fading [15]. Especially in LiCoO_2 , over-charging can lead to a loss of crystallinity [16], structural transformations [17, 18] and the release of oxygen [19]. Meanwhile, the temperature and pressure of the battery rise due to these reactions, eventually causing thermal runaway with battery rupture [20].

Over-charging always happens and causes enormous damage in the single cell and the lithium-ion battery packs. Indeed, a lithium-ion battery pack is made of a large number of cells, in which the cell with the lowest capacity may undergo sustained over-charging while the pack is still charge/discharge repeatedly because of hard detecting of subtle trouble and cost. However, after over-charging, whether these batteries can work normally or not, and the effect of over-charging on the electrochemical performances of battery, these are issues needed to be answered.

Such a study is beneficial for the diagnosis of battery performance and the estimation of state-of-safety (SOS), which is helpful to refine the safety standard and facilitate more effectively resource utilization. In our previous works [21, 22], the

effect of over-discharge and short-time external short-circuit on the capacity fading have been reported, herein, the effect of over-charging on the capacity fading mechanism of $\text{LiCoO}_2/\text{MCMB}$ battery after long-term cycling is investigated.

In this study, $\text{LiCoO}_2/\text{MCMB}$ batteries were over-charged to different voltage (4.4 V, 4.5 V, 4.6 V, and 4.7 V, respectively) for ten times, and then cycled for shallow depth of discharge at 0.6C. The shallow discharge cycle system is often used by power supply for smart-grid electricity systems and satellites. The effect of over-charging on the capacity fading mechanism of battery after long-term cycling is investigated. To confirm the root of capacity fading after long-term cycling of over-charged battery, the battery over-charged for ten times (BO) and battery over-charged for ten times and then charged/discharged for 1000 cycles (BOC) were characterized by the electrochemical tests and postmortem analysis.

2. Experimental

As our previous experiments [21, 22], commercial prismatic $\text{LiCoO}_2/\text{MCMB}$ batteries (CP 475148AR) were used and the rated capacity of designed battery at 1C was 1.150 Ah. At first, the battery was charged to 4.2 V at 0.6C (CC mode) and kept at 4.2 V until the charge current reached to 23 mA (CV mode). After a rest of 2 min, the battery was discharged to 3.0 V at 0.6C, and was considered as activated battery. 0.6C rate means the current was 690 mA. Before the over-charging, the battery was charged/discharged for two times at 0.6C between 3.0 V and 4.2 V, and the measured capacity was considered as the initial capacity of the battery. After that, the battery was over-charged at 0.6C to 4.4 V, 4.5 V, 4.6 V, and 4.7 V, respectively, and then the

over-charged battery was discharged to 3.0 V. The battery was over-charged and discharged for ten times using the same mode. After that, the battery was charged/discharged at 0.6C between the voltage range of 3.0 and 4.2 V for two cycles to determine reversible capacity after over-charging. To analyze the effect of over-charging on long-term cycling, the over-charged battery was cycled 1000 times at 0.6C with 30% depth of discharge (DOD). During each cycle, the batteries were charged to 4.2 V using CC-CV mode at 0.6C, then was discharged to release 30% of the initial capacity. Every 100 cycles, two full charge/discharge cycles were performed in order to estimate reversible capacity during cycling. To simplify, the battery over-charged for ten times was labeled as BO and the battery, which was over-charged for ten times and then cycled 1000 times, was labeled as BOC. The activated battery was also cycled for 1000 times as a comparison with BOC and was labeled as blank battery.

To access the contribution of electrodes to full battery behavior, the activated batteries, blank battery and over-charged batteries before and after 1000 cycles were disassembled in discharge state in an Ar-filled glove box (<1 ppm H_2O , <10 ppm O_2). Morphologies of the obtained LiCoO_2 and MCMB electrodes were recorded by digital camera. The electrodes were immersed in DMC solution to extract the lithium salt and dried in a vacuum oven. Active materials on one side of electrodes were removed using a cotton-based tissue soaked in 1-methyl-2-pyrrolidinone (NMP) to dissolve the polyvinylidene fluoride (PVDF) binder [2, 21, 22], then the electrode with 14 mm diameter were punched out. Coin cells were assembled with a lithium metal foil as the

counter electrode, polyethylene separator (Celgard 2400) as separator, and using fresh electrolyte. The Li/LiCoO₂ (or Li/MCMB) coin cells were cycled in order to check the reversible capacity of LiCoO₂ (or MCMB) electrodes at 0.05C. The Li/LiCoO₂ cells were charged/discharged using CC-CV protocol at 0.05C between 3.0 and 4.3 V and the Li/MCMB cells within the voltage range of 0.01~1.5 V. All the above operations were conducted at the test temperature of 25 ± 2 °C.

The structural characterization of the active materials was carried out by X-ray diffraction (XRD) using a Rigaku D/max- γ B diffractometer (Cu K α radiation). Rietveld refinement for XRD patterns was performed using the GSAS/EXPGUI package. The surface morphology of the electrode material was studied by scanning electron microscopy (SEM) using a Helios Nanolab600i microscope equipped with energy dispersive spectrometry (EDS).

Soft XAS measurements were performed on the bending magnet beamline 8-2 at Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 500 mA and a 1100 l·mm⁻¹ spherical grating monochromator with 20 μ m entrance and exit slits, which provide $\sim 0.5 \times 10^{10}$ ph·s⁻¹ at 0.2 eV resolution in a 1 mm² beam spot. Data were acquired under 10⁻⁹ Torr in a single load at room temperature using AEY mode [23].

The anode dismantled from blank battery and BOC to 4.5 V and 4.7 V was further soaked in H₂O in order to remove SEI film and lithium dendrites [24]. These anodes were assembled into coin cells, then charged/discharged using the same method with described above.

3. Results and discussion

3.1 Electrochemical tests

The discharging profiles of the batteries, which are over-charged to different voltage (4.4 V, 4.5 V, 4.6 V, and 4.7 V), are shown in Fig. 1a. When the over-charging voltage is 4.4 V or 4.5 V, the discharging curve has no obvious difference with that of the activated battery. While the initial profile of battery over-charged to 4.6 V or 4.7 V has obvious plateau, indicating that the presence of metallic lithium on the MCMB electrode [25]. Moreover, the length of the plateaus is proportional to the amount of metallic lithium over the MCMB electrode, which hints more lithium deposition under 4.7 V than others.

These over-charged batteries were cycled for 1000 times at 0.6C with 30% DOD. Normalized charging/discharging profiles of BO and BOC are shown in Fig. 1b. Compared with other conditions, the lithium-intercalation platform rises and lithium-deintercalation platform drops for the battery over-charged to 4.6 V and 4.7 V, indicating that the increasing of polarization [26]. The polarization of BO increases with the increase of over-charging voltage, and similar situations appear in BOC. In addition, the battery over-charged to 4.7 V and then cycled 1000 times shows the biggest polarization among all batteries, indicating that cycling can intensify the polarization of over-charged battery.

Fig. 1. (a) Normalized discharging profiles of batteries after different over-charge, (b) Normalized charging/discharging profiles of BO and BOC.

The capacity loss of over-charged battery is 1.01% for 4.4 V, 1.13% for 4.5 V, 2.42% for 4.6 V, and 12.75% for 4.7 V, respectively, indicating that serious over-charging can reduce the battery capacity obviously. The cycling performance of over-charged battery is shown in Fig. 2a. During cycling, all batteries undergo capacity fade and the degradation is gradually aggravating as the increase of over-charging voltage. The capacity loss of battery over-charged to 4.4 V, 4.5 V, and 4.6 V is 9.28%, 9.83%, and 10.68% after 1000 cycles, respectively, which is higher relative to blank battery (6.94%). The capacity loss of over-charged to 4.7 V is up to 20.22%. Results show that slight over-charging has a little effect on capacity fading of

LiCoO₂/MCMB battery during long-term cycling, while serious over-charging can accelerate the worse of battery performance.

The discharging voltage of these over-charged batteries during 1000 cycles is shown in Fig. 2b. The end-of-discharge voltage of over-charged battery (4.4 V, 4.5 V, 4.6 V, and 4.7 V, respectively) is reduced by 0.01 V, 0.01 V, 0.02 V, and 0.07 V, respectively. This leads to the conclusion that a high degree of polarization occurs due to serious over-charging and cycling can lead to the increase of polarization of the battery along with the increase of over-charging voltage. These results indicate the over-charging can result in capacity loss of batteries, increasing of polarization and accelerating capacity decay during long-term cycling. The over-charging has important effect on the capacity fading, so the BO and BOC are further analyzed in order to investigate the capacity fading mechanism after long-term cycling of the over-charged battery.

Fig. 2. LiCoO₂/MCMB batteries over-charged to different voltage: (a) cycle performance, (b) the end-of-discharge voltage.

3.2 Morphology of the electrodes

The BO and BOC were dismantled in discharge state in order to analyze the change of electrode material and capacity fading mechanism after long-term cycling of over-charged battery.

The color and surface morphology of LiCoO₂ electrodes dismantled from BO and BOC have no remarkable difference by digital photograph (Fig. S1c) and SEM images (Fig. S2). However, the cathode dismantled from BOC to 4.7 V is much easier peeled from the Al-substrate than blank LiCoO₂ electrode using the automatic digital tension tester (ZCDS-50N). It suggests that the over-charging reduces the adhesion of cathode materials and substrate, which may be related with the release of gas caused by over-charging [19].

After 1000 cycles, there is no obvious difference in electrode color and the surface appearance of MCMB electrode when the over-charge voltage is not more

than 4.5 V from digital photograph. MCMB materials dismantled from battery over-charged to 4.4 V and 4.5 V present regular and smooth surfaces (Fig. S3b and c), and the particles have much more roughen than that of blank MCMB after 1000 cycles by SEM images (Fig. S3d-f).

However, the color of anode dismantled from BOC to 4.6 V and 4.7 V is similar and has obvious difference with that of blank anode by digital photograph. Moreover, the color of MCMB electrode dismantled from BOC to 4.7 V turns into clay bank (area B) and gray (area A) with discontinuous distribution (Fig. S1d). The local deviations on the surface imply more lithium deposition than an ideal surface [27-29].

Fig. 3. SEM morphologies of MCMB electrodes dismantled from BO (a-d) and BOC (e-h) to different voltage: (a, e) 4.6 V (area A), (b, f) 4.6 V (area B), (c, g) 4.7 V (area A), and (d, h) 4.7 V (area B).

Fig. 3 shows the SEM morphology of MCMB materials dismantled from BO and BOC to 4.6 V and 4.7 V. There are small amounts of needle-like feature on the surface of MCMB particles from battery over-charged to 4.6 V in area A (Fig. 3a) while the particle in area B (Fig. 3b) has no obvious change with activated MCMB. A lot of needle-like carbonitrides can be clearly observed on the surface of the MCMB

particles dismantled from BO to 4.7 V in area A (Fig. 3c) than that in area B (Fig. 3d). The needle-like feature is also observed on the surface of the lithium metal after cycles in the lithium battery, which is attributed to the lithium dendrite formation [30]. The growth of dendrites result in the loss of active lithium and the reaction between lithium and electrolyte, which lead to the growth of SEI film and contribute to capacity fading [11, 12]. The dendrites can still be observed on the surface of the MCMB particles dismantled from BOC to 4.6 V and 4.7 V in area A (Fig. 3e and g). The MCMB particles in area B (Fig. 3f and h) become much rougher after 1000 cycles. The EDS results obtained from analysis of the surface of MCMB electrodes are listed in Table 1. It is clearly observed that the content of oxygen in the anode of BO increases with the rise of the over-charging voltage. This result suggests that the growth of SEI film on the surface of over-charged electrodes [31]. In addition, the cobalt can be detected on the surface of MCMB electrode dismantled from BO to 4.7 V. Li_xCoO_2 particles react with the HF, which are inevitably present in LiPF_6 solutions in the electrolyte, which may lead to a change in the oxidation state of the cobalt metal, and to dissolution of cobalt metal ions into the solution. Cobalt ions in solutions are partially reduced at the negative electrode [32-34]. The content of oxygen increases after 1000 cycles, suggesting that the long-term cycling can lead to the growth of SEI film.

Table 1.

3.3. XRD measurements

Structural changes in LiCoO_2 and MCMB electrodes in response to over-charging and cycling are investigated by XRD. Fig. 4 shows the full spectra of LiCoO_2 and MCMB electrode dismantled from BO and BOC in the discharged state. All over-charged LiCoO_2 electrodes show hexagonal crystal structure without secondary phases. The characteristic peaks of LiCoO_2 have no change, suggesting that the bulk structure of LiCoO_2 has no obvious change after 1000 cycles. The ratio of peak (003) and peak (104) is nearly identical for all the samples, indicating that the degree of transition metal lithium ion intermixing remained roughly constant [35]. The lattice parameters of blank battery and BOC to 4.7 V are estimated by Rietveld refinement (Fig. S4), and the results are listed in Table S1. The refinement results show that there was a little difference in the ion intermixing. Meanwhile, the characteristic peak positions of MCMB dismantled from BO and BOC remained unchanged from Fig. 4b. However, based on previous EDS results (table 1), cobalt was detected on the surface of the MCMB and was only supplied by the cathode material. Thus, XAS was used for analyzing and verifying the change of the cathode.

Fig. 4. XRD patterns of the fully discharged electrodes dismantled from BO and BOC:

(a) LiCoO_2 , (b) MCMB.

3.4 X-ray Absorption Spectroscopy (XAS) measurements

XAS is suitable for probing electronic and/or structural gradient, so XAS is performed to elucidate the change of the LiCoO_2 dismantled from BO and BOC. The measurements were performed on the electrodes in the fully discharged state, and the Co L2,3-edge spectra of activated battery, BO, blank battery, and BOC were obtained by the AEY mode in Fig.5. Two peaks appear at the same energies for all samples, indicating cobalt mainly shows oxidation states of Co^{3+} , in good agreement with previous literature reports [36-38].

Fig. 5. (a) Normalized Co L2,3-edge XAS/AEY spectra of LiCoO₂ electrode dismantled from activated electrode, BO, blank battery and BOC electrodes, (b) partial enlarged drawing of Fig. 5a.

The low energy shoulders of Co L3-edges grow when the battery is over-charged to 4.6 V, indicating an evolution of transition metal 3d bands to higher occupancies, suggesting that over-charged reaction causes some of the Co³⁺ ions at the electrode surface to be reduced. The valence state may be related with the formation of inert material formation (e.g., Co₃O₄), which can cause a capacity imbalance between the electrodes further lead to the capacity loss [39]. The low energy shoulders clear intensify with the increase of over-charging voltage. The cobalt of BOC goes significant changes by comparing that of blank battery, indicating that the cycling intensifies the reduction of Co³⁺ in over-charged LiCoO₂. In the above discussion, these results suggest the chemical evolution at the vicinity of LiCoO₂ particle surfaces. The changes in electronic structures may be associated with the collapse and rearrangement of local crystal structures [40]. Comprehensive above analysis, the capacity loss of LiCoO₂ electrode may be related to the reduction and the dissolution

of cobalt.

3.5. Coin cell tests

The coin cell is used to test the performances of LiCoO_2 and MCMB electrode dismantled from BO and BOC, which will distinguish the contribution of cathode and anode. Normalized charging/discharging profiles of LiCoO_2 and MCMB electrode dismantled from BO and BOC are presented in Fig. 6. The charged/discharged profiles of the LiCoO_2 electrodes have no noticeable change in batteries over-charged to 4.4 V and 4.5 V. The obvious voltage drop is shown in 4.6 V and 4.7 V, which is attributed to polarization of LiCoO_2 . Similar phenomena occur in BOC batteries. Correspondingly, the polarization of LiCoO_2 dismantled from BOC to 4.6 V and 4.7 V increases, indicating that the cycling can increase the polarization of over-charged LiCoO_2 . The charged/discharged profiles of the MCMB electrodes dismantled from BO and BOC have no noticeable change. These results indicate that the polarization of full battery is mainly caused by the LiCoO_2 electrode.

Fig. 6. Normalized charged/discharged profiles of (a) LiCoO₂ electrode and (b)

MCMB electrode dismantled from BO and BOC.

Fig. 7 shows the capacity loss of LiCoO₂ and MCMB electrode dismantled from BO and BOC at 0.05C. For BO batteries, the capacity loss of MCMB electrode dismantled from BO to 4.4 V and 4.5 V is higher than that of LiCoO₂ electrode. Moreover, the capacity loss of LiCoO₂ electrode from BO to 4.6 V is almost same with that of MCMB electrode. While LiCoO₂ electrode from BO to 4.7 V exhibits marked capacity fade (12.68%) relative to MCMB (1.69%). LiCoO₂ and MCMB electrode dismantled from BOC shows similar results and the LiCoO₂ electrode dismantled from BOC to 4.7 V exhibits marked capacity fade (16.03%) than MCMB electrode (6.21%). The capacity loss upon over-charging voltage was much pronounced for the LiCoO₂ electrodes than that of MCMB electrode, whose fading tendency is maintained without abrupt change. These results indicate different degradation mechanisms of battery upon different over-charging voltage during long-term cycling. The capacity fading of LiCoO₂/MCMB batteries over-charged to 4.6 V and 4.7 V is attributed primarily to the LiCoO₂ electrode, which may be related to the reduction and the dissolution of cobalt. However, the capacity fading of

LiCoO₂/MCMB battery over-charged to 4.4 V and 4.5 V can be mainly attributed to the MCMB electrode. Base on previous work [28], SEI film of MCMB electrode plays an important role, which will grow and deteriorate the performance of battery during long-term cycling. According to our previous work [22-24], the water washing is an effective method to remove the SEI film and lithium dendrites, which will make sure the contribution of SEI film to capacity fading of battery.

Fig. 7. The capacity loss of LiCoO₂ and MCMB electrode dismantled from BO and BOC.

3.6 water washed tests

The MCMB electrodes dismantled from blank battery and BOC to 4.5 V and 4.7 V are washed with water to remove the SEI film and lithium dendrites. The water washed MCMB electrodes were used as the working electrode to assembled half-cells with fresh electrolyte, and the specific capacities are shown in Fig. 8. After being washed with water, the specific capacity of MCMB can increase from 306.90 Ahg⁻¹ to 328.00 mAhg⁻¹ for blank battery, 305.37 mAhg⁻¹ to 325.85 mAhg⁻¹ for BOC to 4.5 V, and 296.38 mAhg⁻¹ to 322.80 mAhg⁻¹ for BOC to 4.7 V, respectively. As a result, it is

clear that the SEI film and lithium dendrites, which are mainly generated by the over-charging and long-term cycling, has a pronounced effect on the capacity fading of anode. The observations from various methods (SEM, EDS, XRD, and water washed experiment) made here in support the fact that the growth of SEI film and the generation of lithium dendrites after over-charging and long-term cycling are the governing factors of performance deterioration of MCMB electrode.

Fig. 8. Charge/discharge profiles of MCMB electrode dismantled from blank battery (A), BOC to 4.5 V (B), and BOC to 4.7 V (C) before/after water washing at 0.05C.

4. Conclusion

This study presents the degradation mechanism after long-term cycling of over-charged $\text{LiCoO}_2/\text{MCMB}$ batteries. When the over-charging voltage is 4.4 V or 4.5 V, over-charging nearly has no influence on long-term cycling. While the over-charging voltage is 4.6 V or 4.7 V, the over-charging can deteriorate the performance of the battery. Upon over-charging voltage, different degradation mechanisms of electrochemical performances occur after long-term cycling. The capacity fading during long-term cycling of batteries undergone the over-charging of 4.4 V or 4.5 V, is mainly caused by the MCMB electrode, whereas, capacity fading of

battery over-charged to 4.6 V or 4.7 V is primarily attributed to the LiCoO₂ electrode. The capacity loss of MCMB is mainly attributed to the appearance of lithium dendrite and the SEI film on the surface of MCMB electrode generated by over-charging and long-term cycling. For the LiCoO₂ electrodes, the degradation after long-term cycling of battery over-charged to 4.6 V or 4.7 V is related to the reduction and the dissolution of cobalt.

Acknowledgments

This work was funded by the National High Technology Research and Development Program (863 Program) of China (No. 2012AA110203) and the National Science Foundation of China (No. 51202047). The synchrotron X-ray portion of this work was carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University that is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [2] Y.Z. Cui, C.Y. Du, G.P. Yin, Y.Z. Gao, L.L. Zhang, T. Guan, L.J. Yang, F.P. Wang, J. *Power Sources* 279 (2015) 123–132.
- [3] L.G. Wang, P.J. Zuo, G.P. Yin, Y.L. Ma, X.Q. Cheng, C.Y. Du, Y.Z. Gao, J. *Mater. Chem. A* 3 (2015) 1569–1579.

- [4] Y. Zhao, X.F. Li, B. Yan, D.B. Xiong, D.J. Li, S. Lawes, X.L. Sun. *Adv. Energy Mater.* 6 (2016) 1502175.
- [5] X.F. Li, J. Liu, M. N. Banis, A. Lushington, R.Y. Li, M. Cai, X.L. Sun. *Energy Environ. Sci.* 7 (2014) 768–778.
- [6] C.K. Lin, Y. Ren, K. Amine, Y.Q., Z.H. Chen, *J. Power Sources* 230 (2013) 32–37.
- [7] S. Tobishima, K. Takei, Y. Sakurai, J. Yamaki, *J. Power Sources* 90(2000) 188–195.
- [8] S.I. Tobishima, J.I. Yamaki, *J. Power Sources* 81–82 (1999) 882–886.
- [9] R. Spotnitz, J. Franklin, *J. Power Sources* 113 (2003) 81–100.
- [10] F. Xu, H. He, Y.D. Liu, C. Dun, Y. Ren, Q. Liu, M.X. Wang, J. Xie, J. *Electrochem. Soc.* 159(2012) A678–A687.
- [11] W.Q. Lu, C.M. López, N. Liu, J.T. Vaughey, A. Jansen, D.W. Dees, J. *Electrochem. Soc.* 159 (2012) A566–A570.
- [12] D. Belov, M.H. Yang, *J. Solid State Electrochem.* 12 (2008) 885–894.
- [13] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, *J. Power Sources* 97–98 (2001) 681–683.
- [14] N. Schweikert, A. Hofmann, M. Schulz, M. Scheuermann, S.T. Boles, T. Hanemann, H. Hahn, S. Indris, *J. Power Sources* 228 (2013) 237–243.
- [15] L. Croguennec, C. Poullerie, C. Delmas, *J. Electrochem. Soc.*, 147 (2000) 1314–1321.
- [16] J.N. Reimers, J.R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2091–2097.

- [17]G.G. Kumar, W.H. Bailey, B.K. Peterson, W.J. Casteel, J. Electrochem.Soc. 158 (2011) A146–A153.
- [18]K. Mahera, R. Yazami, Electrochim. Acta 101 (2013) 71–78.
- [19]J.F. Dahn, E.W. Fuller, M. Obravae, U.V. Sacken, Solid State Ionics 69 (1994) 265–270.
- [20]T. Ohsaki, T. Kishi, T. Kuboki, N. Takami, N. Shimura, Y. Sato, M. Sekino, A. Satoh, J. Power Sources 146 (2005) 97–100.
- [21]L.L. Zhang, Y.L. Ma, X.Q. Cheng, C.Y. Du, T. Guan, Y.Z. Cui, S. Sun, P.J. Zuo, Y.Z. Gao, G.P. Yin. J. Power Sources 293 (2015) 1006–1015.
- [22]L.L. Zhang, X.Q. Cheng, Y.L. Ma, T. Guan, S. Sun, Y.Z. Cui, C.Y. Du, P.J. Zuo, Y.Z. Gao, G.P. Yin. J. Power Sources 318 (2016) 154–162.
- [23]F. Lin, D. Nordlund, T.C. Weng, Y. Zhu, C. Ban, R.M. Richards, H.L. Xin Nat. Commun. 5 (2014) 3358.
- [24]L.J. Yang, X.Q. Cheng, Y.Z. Gao, P.J. Zuo, Y.L. Ma, C.Y. Du, B. Shen, Y.Z. Cui, T. Guan, G.P. Yin, Appl. Mater. Interfaces 6 (2014) 12962–12970.
- [25]C.S. Kim, K.M. Jeong, K. Kim, C.W. Yi, Electrochim. Acta 155 (2015) 431–436.
- [26]L.J. Yang, X.Q. Cheng, Y.L. Ma, S.F. Lou, Y.Z. Cui, T. Guan, G.P. Yin, J. Electrochem. Soc. 160 (2013) A2093–A2099.
- [27]J. Christensen, P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, J. Electrochem. Soc. 159(2012) R1–R30.
- [28]A. Schechter, D. Aurbach, Langmuir 15 (1999) 3334–3342.

- [29] Y.S. Cohen, Y. Cohen, D. Aurbach, J. Phys. Chem. B 104 (2000) 12282–12291.
- [30] C.C. Chang, T.K. Chen, J. Power Sources 193 (2009) 834–840.
- [31] M. Kassem, C. Delacourt. J. Power Sources 235 (2013) 159–171.
- [32] D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, D. Kovacheva. J Power Sources 165 (2007) 491–499.
- [33] G.G. Amatucci, J.M. Tarascon, L.C. Klein. Solid State Ionics 83 (1996) 167–173
- [34] X.F. Li, J. Liu, X.B. Meng, Y.J. Tang, M. Norouzi Banis, J.L. Yang, Y.H. Hu, R.Y. Li, M. Cai, X.L. Sun. J. Power Sources 247 (2014) 57–69.
- [35] S. Patoux, M.M. Doeff, Electrochem. Commun. 6 (2004) 767–772.
- [36] F. Lin, D. Nordlund, T.J. Pan, I. M. Markus, T.C. Weng, H.L. Xin, M.M. Doeff, J. Mater. Chem. A, 2 (2014) 19833–19840.
- [37] B. Gilbert, B.H. Frazer, A. Belz, P.G. Conrad, K.H. Nealson, D. Haskel, J.C. Lang, G. Srajer, G.D. Stasio, J. Phys. Chem. A 107 (2003) 2839–2847.
- [38] W.S. Yoon, K.B. Kim, M.G. Kim, M.K. Lee, H.J. Shin, J.M. Lee, J.S. Lee, C.H. Yo, J. Phys. Chem. B 106 (2002) 2526–2532.
- [39] P. Arorat, R.E. White. J. Electrochem. Soc. 145 (1998) 3647–3667.
- [40] F. Lin, I.M. Markus, D. Nordlund, T.C. Weng, M.D. Asta, H.L. Xin, M.M. Doeff. Nat. Commun. 5 (2014) 3529.

List of table captions

Table 1. EDS results on the surface of the MCMB electrodes dismantled from activated battery, BO, blank battery, and BOC.

Table 1

	C	O	F	P	Co
activated battery	92.97	3.90	3.14	-	-
BO to 4.6 V(area A)	82.48	9.10	8.28	-	-
BO to 4.7 V(area A)	63.02	30.79	5.79	0.12	0.28
blank battery	89.30	6.90	3.80	-	-
BOC to 4.6 V(area A)	79.92	16.27	4.62	-	-
BOC to 4.7 V (area A)	54.70	38.21	6.34	0.17	0.58

[41]