Aging-invariance of the open-circuit-voltage of NMC-lithium-ion-cells

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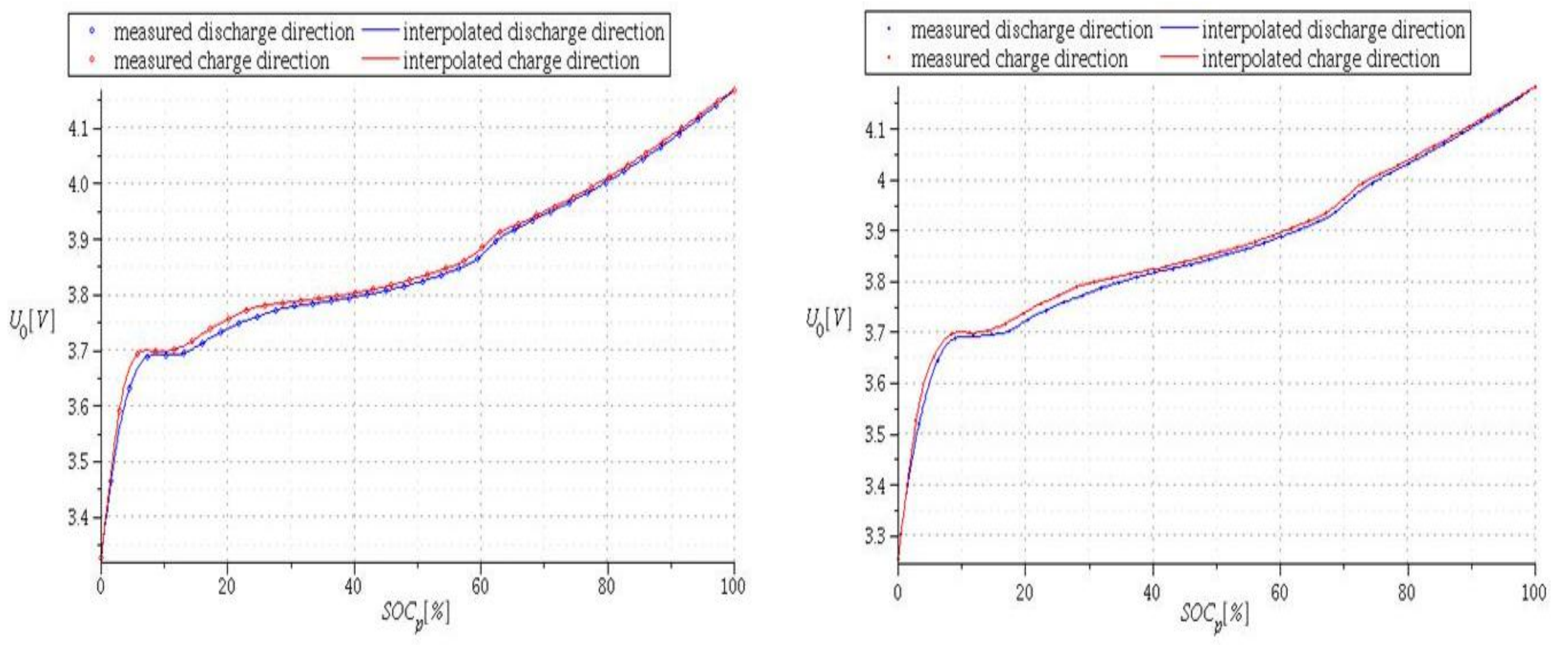
Introduction

Most methods for determination of the state-of-charge (SOC) of lithium-ion cells are based on the (equilibrium) open-circuit voltage (OCV or U_0). The one-to-one relation between SOC and U_0 can be used for recalibration of ampere-hour counting methods or as a part of model-based methods. In order to provide accurate estimations over the lifetime of a battery, the algorithms must be invariant under the state-of-health (SOH). This invariance under SOH is either an intrinsic property of the algorithm or must be explicitly built by its adaptivity. It is a common approach to assume (implicitly or explicitly) that the U_0-SOC relation is invariant under the aging of the cell. In this note we investigate the influence of different aging mechanisms on the OCV of high-energy lithium-ion cells in NMC-technology.



(a) New (b) 14 days deep discharge

Figure 1: $U_0(SOC_p)$-hysteresis (SOC_p := practical SOC)
(a) New, (b) 14 days deep discharged
NMC-lithium-ion cells

Experimental and methods of investigation

Accelerated aging of NMC-lithium-ion cells was performed by the following tests: cycling, deep-discharge and storage. In order to obtain statistical relevant results, we used three cells for each test. The $U_0(SOC_p)$-curves are measured in both charge and discharge direction. The resulting OCV hysteresis are shown in Fig.1. The influence of aging on OCV is measured by the relation $U_0(SOC_p)$ and compared in terms of the properties of its hysteresis of new and aged cells in the following way:

Definition 1. Let $U_{0,max}$,$U_{0,min}$ be the lowest or the highest measured OCV of a cell between $0\% \leq SOC_p \leq 100\%$, and $\Delta U_0 := U_{0,max} - U_{0,min}$. Then we define the real numbers

$$\varepsilon_{\text{area}} := \int_{U_{0,\min}}^{U_{0,\max}} \Delta SOC_p(U_0)dU_0, \quad (1)$$

$$\text{RMS} := \sqrt{\frac{1}{\Delta U_0}\int_{U_{0,\min}}^{U_{0,\max}} (\Delta SOC_p(U_0))^2 dU_0}, \quad (2)$$

$$\varepsilon_{\max} := \max_{U_{0,\min}\leq U_0 \leq U_{0,\max}} |\Delta SOC_p(U_0)|, \quad (3)$$

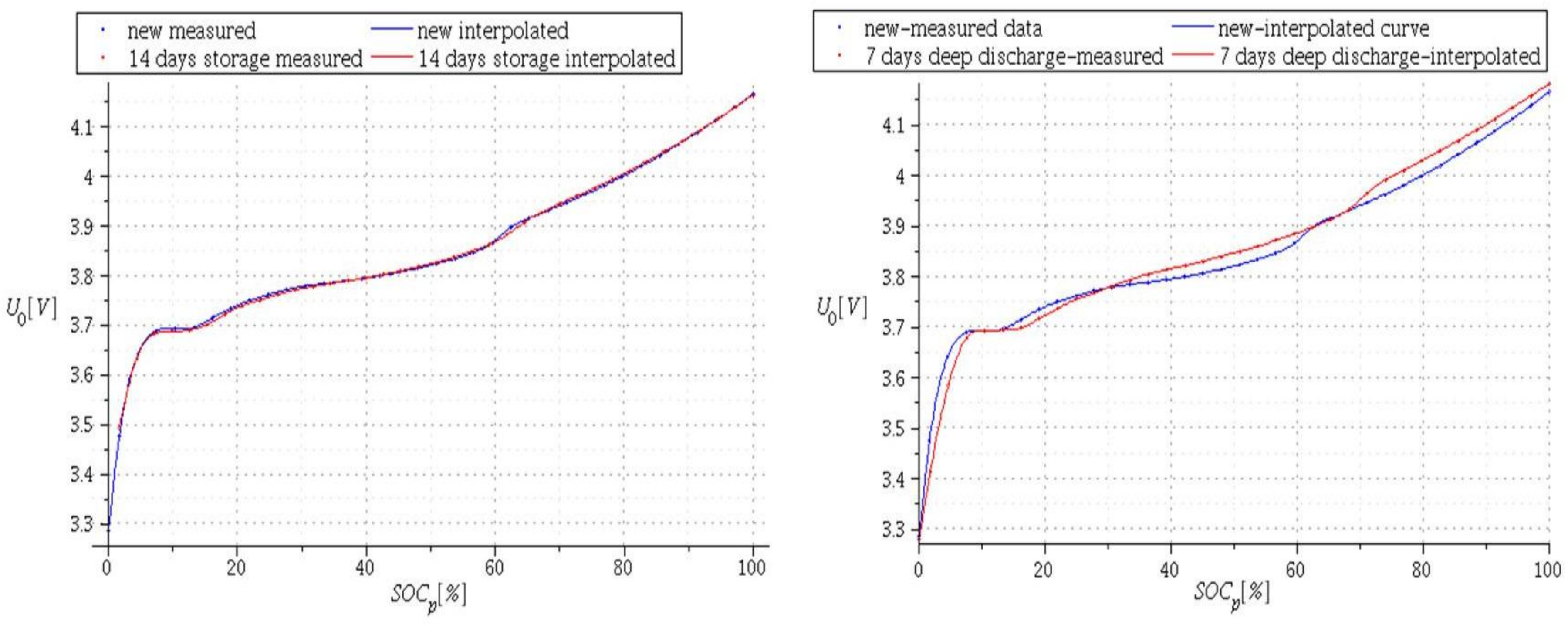
whereby the function $\Delta SOC_p : [U_{0,max},U_{0,min}] \rightarrow \mathbb{R}$,
$U_0 \rightarrow \Delta SOC_p(U_0) := |SOC_{p,new}(U_0) - SOC_{p,aged}(U_0)|$ is obtained by the experimental relations $U_0(SOC_p)$ of new and aged cells; (or $\Delta SOC_p(U_0) := |SOC_{p,ch}(U_0) - SOC_{p,dis}(U_0)|$ for consideration of hysteresis properties.)
The results are quantitative estimations of the SOH dependence in the $U_0(SOC_p)$-relation in terms of error SOC_p magnitudes as defined in def.1.

Results

It is important to note, that the degree of specific aging mechanism has never produced a total damaged cell, so it make sense to speak of pre-aging. The capacity-loss of the pre-aged cells was always less than 20% of the nominal capacity, which implies the relevance of the results in the regular liftime of the battery.

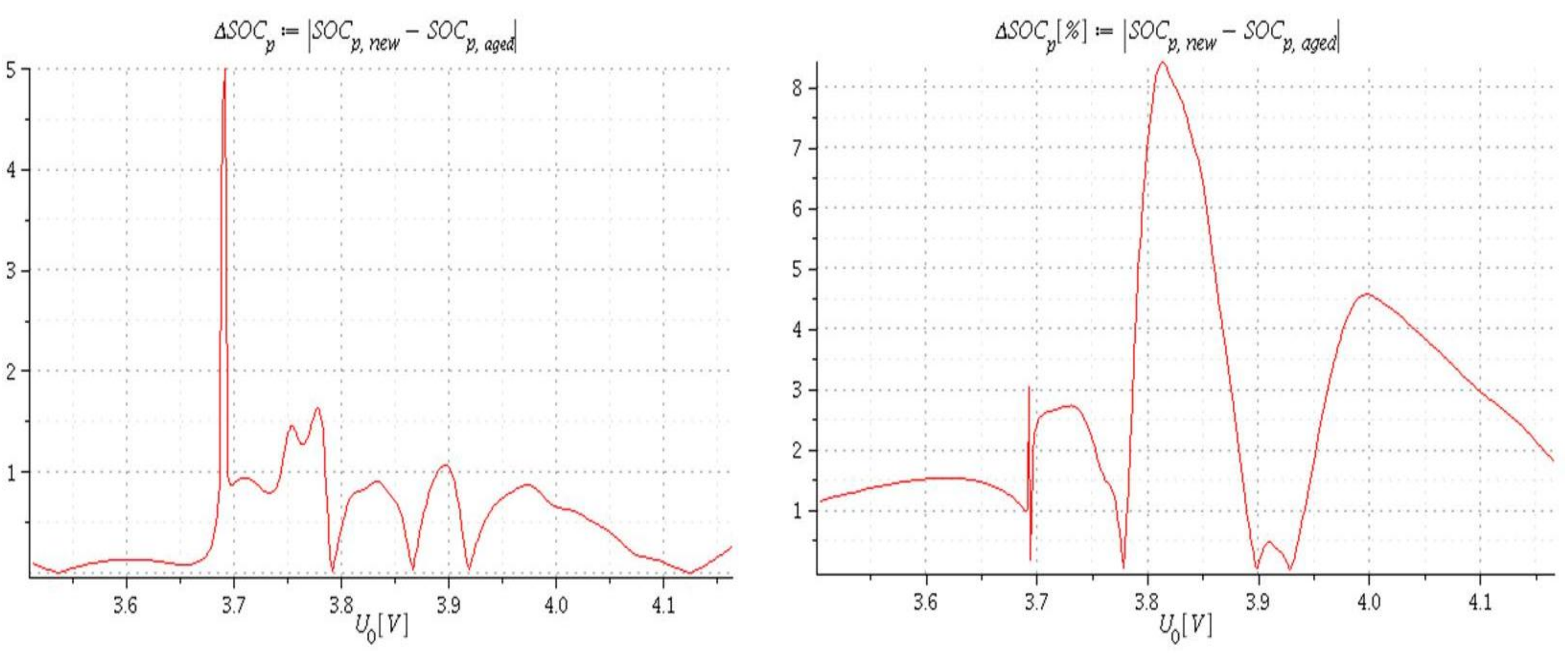
	Stored	Deep Discharged	Cycled
ε_{max} [%]	5 - 7	8	4
RMS [%]	1 - 2	4	1.6
ε_{area} [V%]	0.3 - 1	1.8	0.7

Table 1: Influence of pre-aging to the OCV-SOC characteristic



(a) 14 days stored (b) 7 days deep discharge

Figure 2: Comparison of $U_0(SOC_p)$-discharge curves
(a) new and14 days stored cells or
(b) new and 7 days deep discharged cells.



(a) 14 days stored (b) 7 days deep discharge

Figure 3: ΔSOC_p error in % of 14 days stored and 7 days deep discharged NMC-cells as shown in Fig.2

To summarize:
Deep discharge has the most significant influence to $U_0(SOC_p)$, Fig.2b,3b. The very tight and sharp ε_{max} of stored cells in Fig. 3a lies always in first plateau (Fig.2a) about $U_0 \approx$ 3.7V in $SOC_p(U_0)$; the SOC-deviation at the other OCV-points is less then 2%, measured until 60 days storage-time. The influence of cycling to OCV-SOC is similar to deep discharge; the more depth of discharge (DoD) the more influence to OCV-SOC is observable.

Conclusion

Compared to the 5% – 10% SOC-accuracy in recent publications which use SOC determination based on the OCV, one can conclude that influence of pre-aging is not negligible and also the broad made assumption of constant OCV-SOC characteristic over batteries lifetime is often not correct.