



Analysis and prediction of the open circuit potential of lithium-ion cells



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HIGHLIGHTS

- ▶ A model for the quantitative OCV analysis of Li-ion cells is introduced.
- ▶ In-situ diagnosis of aging mechanisms is experimentally verified.
- ▶ Loss of active lithium and contact loss of active material are separated.
- ▶ A novel model to describe the OCV of a blend cathode is introduced.
- ▶ The active masses of the blend components are determined using the OCV model.

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ABSTRACT

A model is presented, which allows quantitative analysis as well as prediction of the open circuit potential of lithium-ion cells. Furthermore, the model determines half-cell potentials of already stressed lithium-ion cells, using a data set accomplished just once from half-cell potentials of a new reference cell. Its capability to describe thereby two relevant degradation processes, namely, (i) loss of active mass, and, (ii) loss of active lithium, is experimentally verified on a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)/ LiCoO_2 (LCO) blend cell.

A further extension of the model allows the prediction of the open circuit potential of a blend cathode with various blend ratios as well as the analysis of unknown blend ratios. This ability is experimentally verified for cathodes made of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)/ LiMn_2O_4 (LMO) blends.

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1. Introduction

Two relevant degradation processes, namely, (i) loss of active mass, and, (ii) loss of active lithium, affect the open circuit potential (OCV) of lithium-ion cells. In experimental cells, these changes are usually monitored by a standard reference electrode [1], using a piece of metallic lithium attached to a copper wire [2,3], electrochemically deposited lithium [4] or lithium-metal alloy [5,6]. However, the reference electrode itself is a source of error, since the reference material may interfere with the chemical and electrical electrode characteristics. However, reference electrodes are widely used to extract the half-cell potentials of anode and cathode in experimental cells, but their applicability in commercial cells is of questionable value.

In this case, the commercial cell (i) has to be opened, (ii) the reference electrode has to be inserted in the electrode stack or role, (iii) lost electrolyte has to be refilled, and finally, (iv) the cell has to be sealed again [7]. This rather complicated process influences the cell behavior, as the content of active lithium may be changed, and thus, the half-cell potentials of the electrodes deviate from the original course.

To overcome those obstacles, we apply a model based on [8], which enables online analysis of the half-cell potential of commercial cells during cycling with small currents. The model requires a data set containing the half-cell potentials of the relevant anode and cathode materials, which has to be determined over SOC by a separate measurement. Therefore, and just once, a commercial cell has to be opened, and both electrodes are measured in experimental half-cells. This data set is then available for calculating the change of half-cell potentials of new cells during their entire lifetime. Thus, a real-time analysis of degradation mechanisms

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becomes possible, as a recent publication of Dubarry et al. [9] has already shown by simulation. Herein, loss mechanisms became identifiable from OCV-curve measurements, on condition that the half-cell potentials are known. For the first time, our findings proof the applicability to real measurements.

In case of a lithium-ion cell with a cathode blend, which usually consists of two active materials [10,11], the mixed open circuit potential depends on blend ratio and material chemistry. Thereby, tailoring of open circuit potentials becomes possible. It is evident, that a model which predicts the open circuit potential of arbitrary blends is beneficial to determine the blend ratio prior to manufacturing.

Likewise such a model can be potentially applied to determine the composition and blend ratio of unknown cathodes. Furthermore, such a model can identify the degradation of single blend components using differential capacity plots [12].

In the following, we introduce first the so-called *OCV-model full cell* for analysis and prediction of the open circuit potential a full cell. Second, we introduce a sub-model called *OCV-model blend electrode*, which is tested on cathode blends. Its outcome is an OCV-curve, where the half-cell potential of the blend electrode is measured versus lithium, which is then integrated into the *OCV-model full cell*.

2. OCV-model full cell

2.1. Theory

The potential of a full cell $U_{full}(Q)$ in dependence of the charged capacity Q is expressed as the potentials of the half-cells:

$$U_{full}(Q) = U_{cat}(Q) - U_{an}(Q). \quad (1)$$

If the potential $U_{cat}(Q)$ and $U_{an}(Q)$ vs. lithium of the half-cells is measured as function of the charged capacity, the full cell potential can then be calculated [8,13,14] using Equation (1). For different capacities of anode $Q_{0,an}$ and cathode $Q_{0,cat}$, the smaller electrode or the available amount of lithium-ions determines the full cell capacity. Thereby, the OCV curve of the full cell is calculated by using a set of measured OCV curves of anode and cathode.

However, if the capacity of one electrode is altered, the actual OCV curve of the corresponding half-cell must be measured. To avoid any new measurement over time, it is much advantageous to multiply the charged capacity Q by a scaling factor α_{cat} and α_{an} in Equation (2). This multiplication results in a scaling of the OCV curve with the Q -axis, as it is shown in Fig. 1. The capacity ratio of the simulated full cell can then be easily calculated as

$$c_{an/cat} = \frac{Q_{0,an} \cdot \alpha_{an}}{Q_{0,cat} \cdot \alpha_{cat}}. \quad (2)$$

Furthermore, as the cathode is not necessarily completely discharged, when the anode is charged and the full cell state is completely charged. This is sometimes called “alignment” of the electrodes. To account for that, the two parameters ν_{cat} and ν_{an} are introduced. Equation (3) describes now the complete model for the potential of a full cell $U_{full}(Q)$, and the resulting OCV curve is illustrated in Fig. 1.

$$U_{full}(Q) = U_{cat}(\alpha_{cat}Q - \nu_{cat}) - U_{an}(\alpha_{an}Q - \nu_{an}) \quad (3)$$

The model Equation (3) is now applicable for the simulation of full cell potentials for electrode combinations of any chemistry. Furthermore, if the OCV curves of the chosen anode and cathode material are available from separate measurements, these data sets can be used to identify the model parameters α_{cat} , α_{an} , ν_{cat} and ν_{an} . These parameters are obtained by fitting the resulting full cell

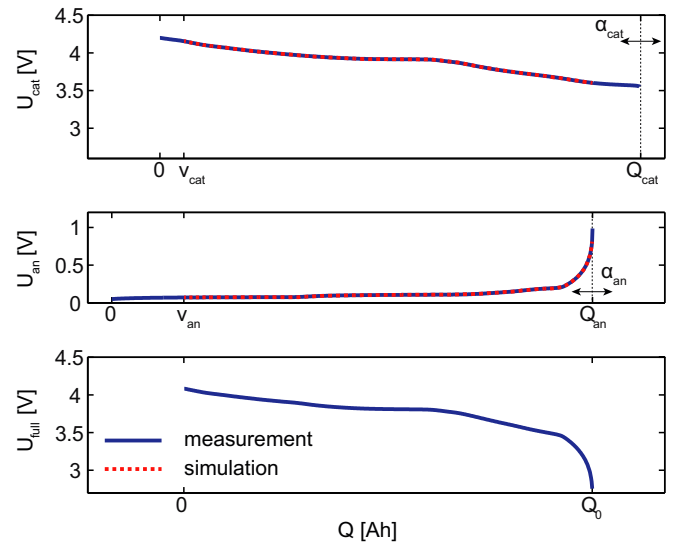


Fig. 1. Schematic of the OCV model full cell, which is calculated from two separate OCV curves of cathode and anode. The parameters α_{cat} and α_{an} are used to scale the capacity and ν_{cat} and ν_{an} to adjust the alignment of the single electrodes. The resulting full cell OCV curve is computed by subtracting the cathode from the anode potential.

potential from Equation (3) and the underlying anode and cathode OCV-curves to the measured full cell potential. With those parameters the half-cell potential for every charged capacity can now be evaluated by separately evaluating the terms for U_{cat} and U_{an} .

Since Equation (3) is only valid at equilibrium, all OCV-curves, from half- and full-cells, have to be obtained with low discharge or charge rates, ensuring close-to-equilibrium conditions. At higher currents the characteristic steps in the OCV-curves are flattened, which complicates the identification of the model parameters. Furthermore, overpotentials arising from solid-state diffusion and charge transfer are superimposed to the open circuit voltage. The effect on the fitting result can be alleviated to some extent by choosing identical C-rates for the measurement of the OCV-curves of the half-cells and the full cell.

2.2. Experimental

All electrodes were obtained from Kokam SLPB834374H lithium-ion cells with a capacity of 2 Ah. They were disassembled in an Argon filled Glovebox (Braun, Germany) and experimental cells with a diameter of 18 mm were built immediately. The cell housings ECC-Ref (el-cell, Germany) were equipped with a lithium reference electrode. As separator three Freudenberg FS2190 were used and 250 μ l of LP50 (Merck, Germany) was used as electrolyte. The liquid electrolyte was composed of a 1 mol l^{-1} LiPF₆-solution in a 1:1 mixing ratio with ethylene carbonate:ethylmethyl carbonate (EC:EMC).

At first, two experimental cells were built with anode and cathode material from the commercial cell versus a lithium counter electrode. Then half-cell potentials during constant current charge and discharge with a C-rate of C/40 were recorded.

These two measurements are of great importance, as they serve as reference OCV curves of anode and cathode for the once required parameterization of the *OCV model full-cell*.

The next step, the validation of the *OCV model full-cell*, required two further experiments, namely, a variation in (a) the active mass of lithium and (b) the active mass of the cathode. The variation in (a) the active mass of lithium represents cell aging correlated to

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