



Short communication

Lithium ion battery cells under abusive discharge conditions: Electrode potential development and interactions between positive and negative electrode



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HIGHLIGHTS

- Electrode potential interactions of counter- and working electrodes.
- Competitive reactions on positive electrode surface.
- Reasonable selection of electrochemical discharge cut-off criteria for full cells.

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ABSTRACT

Increasing specific energy of lithium ion battery cells (LIBs) and their cycle life requires deeper understanding of complex processes taking place during the cell operation. This work focuses on the electrode potential development and the interactions between negative and positive electrode in a quasi LIB full cell by applying over-discharge conditions. By analysis of the potential profiles, a characteristic potential plateau at ≈ 3.56 V vs. Li/Li⁺ was detected at the graphite negative electrode, which can be assigned to the Cu oxidation process of the negative electrode current collector. Also at the positive electrode, a time shifted potential plateau was observed, which could be attributed to a competitive reaction between conventional discharge (lithiation) and parasitic Cu reduction (plating) on the positive electrode surface. The proposed mechanism involving the presence of elemental Cu on the positive electrode surface was confirmed by SEM-EDX mapping experiments. The relevance of Cu dissolution and deposition as well as possible solution approaches are discussed.

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1. Introduction

The need for advanced electronic energy storage systems for stationary, automotive and portable applications combining increased gravimetric/volumetric energies with a sufficient cycle life has been significantly grown over the past decades [1–4]. With this in line, lithium ion battery (LIB) is considered as key

electrochemical energy storage technology [5]. Nevertheless, LIBs are still far from being a mature technology in stationary and automotive applications, thus requiring intense research and development efforts [4,6,7].

For systematic research and development of advanced LIBs, understanding of the complex and mostly interconnected electrode processes during cell operation is inevitable [8]. Among a wide range of possible investigation tools, the monitoring of the voltage profiles during operation is considered as a simple and reliable “*in situ* method” [9,10]. From the voltage vs. time development (at known specific current values), performance relevant information can be determined [9–13]. In a three-electrode cell set-up, the use of a reference electrode (RE) enables the investigation of aging phenomena of the each individual electrode *via* monitoring the

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respective potential profiles [9,14–17]. However, compared to half cells, using a Li metal counter electrode (CE) and thus an excess of lithium, the individual electrode investigation is challenging within a LIB full cell, as changes/consumption of the active Li^+ amount ($\text{Li}^+ + \text{e}^-$) within the full cell significantly alter the performance of each electrode in a direct and/or indirect way [9,18]. Therefore, to obtain insight in the material related aspects of each electrode, the basic investigation is commonly carried out in Li half cells [17,19]. Here, the operation is controlled by a fixed potential range *via* the use of a RE, which enables reliable potential comparison conditions for the investigated working electrode (WE) and the lack of active Li^+ is excluded by the use of a Li metal CE.

With regard to abusive conditions in LIBs, the focus is usually set on the charge (overcharge), which indeed leads to severe stability and safety hazards [20–22]. However, the rarely investigated abuse at discharge (over-discharge), which can easily happen when more than two cells are connected in series [23], can reveal undesired side phenomena, as well [24–27]. One of these phenomena, Cu dissolution from the negative current collector, was extensively investigated by He et al. for a LiFePO_4 (LFP) based full cell system [28]. However, unlike for the Al current collector at the positive electrode [29,30], thorough investigations on the Cu current collector are missing, in particular investigations focusing on the electrode interactions based on voltage/potential data have not

been carried out, yet. Among others, there is an ambiguity, whether the onset of over-discharge of the negative electrode somehow can affect the conventional positive electrode discharge process.

In this work, a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111)/graphite quasi-full-cell, in which the potential is controlled by the use of a Li metal RE, is selected to study interactions between the negative and positive electrode in a systematic way, especially with regard to the Cu dissolution as well as Cu plating processes while consciously over-discharge the graphite electrode.

2. Experimental

Constant current charge/discharge cycling experiments were performed in a three-electrode cell set-up (Swagelok®) [31]. $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) and TIMREX SFG6 graphite electrodes, purchased by respectively BASF and Imerys, were house made; the detailed preparation process is described elsewhere [17]. Lithium metal (Albermarle) was used as a RE. In all investigations, battery grade electrolyte, 1 M LiPF_6 in EC:EMC (1:1, by wt.), (LP50 Selectolyte™) from BASF was used. All constant current experiments were conducted on a Maccor Series 4000 battery cell test system under temperature control (20 °C) in a climate chamber (Binder KB400). The electrochemical conditions are emphasized within the respective figures/text. Cu deposition was investigated by means of

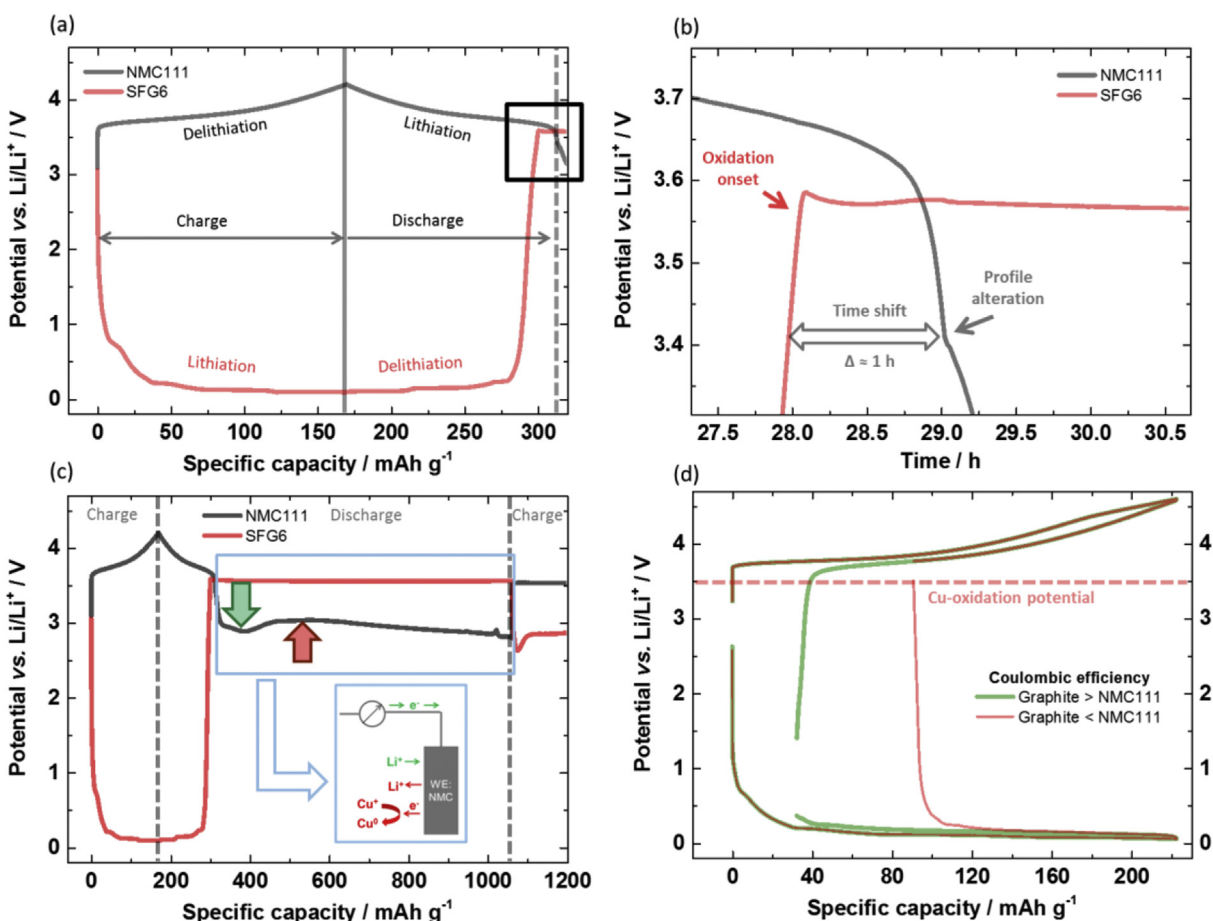


Fig. 1. (a) Potential profiles of the WE (NMC111) and CE (SFG6 graphite) during the initial charge/discharge cycle. The charge and discharge cut-off potentials are set to 4.2 and 2.8 V vs. Li/Li^+ , respectively, for a specific current of 15 mA g^{-1} . The potential profile for SFG6 graphite is obtained *via* an additional auxiliary measurement vs. the RE. The salient potential behavior during over-discharge is marked within the black box and is magnified in (b). Inset of the potential vs. time plot of a NMC111/SFG6 cell during discharge process. 1 h after the onset of an “untypical oxidation process” of the SFG6 CE, a distinct kink in the slope of the NMC111 WE potential profile is observed (marked by a grey arrow). (c) Extended potential profiles of the complete charge/discharge cycle. The processes occurring at the NMC111 within the marked potential plateau are schematically depicted. (d) Schematic illustration of the initial charge/discharge cycle for graphite with higher and lower Coulombic efficiency compared to NMC111.

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