Improving cycle life of layered lithium transition metal oxide (Li*MO*$_2$) based positive electrodes for Li ion batteries by smart selection of the electrochemical charge conditions

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HIGHLIGHTS

- NMC622 reveals best compromise between specific energy and its retention up to 60 °C.
- NMC622 specific capacity fade is of almost reversible nature.
- NMC622 specific capacity fade mostly induced by delithiation (charge) hindrance.
- Modification of charge cut-off criteria and formation cycles can improve cycle life.

ARTICLE INFO

ABSTRACT

Increasing the specific energy of a lithium ion battery and maintaining its cycle life is a predominant goal and major challenge for electrochemical energy storage applications. Focusing on the positive electrode as the specific energy bottleneck, cycle life characteristics of promising layered oxide type active materials (Li*MO*$_2$) has been thoroughly investigated. Comparing the variety of Li*MO*$_2$ compositions, it could be shown that the "Ni-rich" (Ni $\geq$ 60% for M in Li*MO*$_2$) electrodes expectably revealed best performance compromises between specific energy and cycle life at 20 °C, but only LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622) could also maintain sufficient cycle performance at elevated temperatures. Focusing on NMC622, it could be demonstrated that the applied electrochemical conditions (charge capacity, delithiation amount) in the formation cycles significantly influence the subsequent cycling performance. Moreover, the insignificant transition metal dissolution, demonstrated by means of total X-ray fluorescence (TXRF) technique, and unchanged lithiation degree in the discharged state, determined by the measurement of the Li$^+$ content by means of the inductively coupled plasma optical emission spectroscopy (ICP-OES) technique, pointed to a delithiation (charge) hindrance capacity fade mechanism. Considering these insights, thoughtful modifications of the electrochemical charge conditions could significantly prolong the cycle life.

1. Introduction

The success of renewable energies and of 'electro-mobility', i.e., of electric vehicles, is intertwined with the effective storage of energy [1]. In this regard, many research and development efforts focus on lithium ion batteries (LIBs) as the current state-of-the-art (SOTA) technology [2]. Here, the enhancement of specific energy and of cycle life still remains as predominant challenge [3,4].

The specific energy is defined as the product of the specific capacity and mean cell voltage (difference between the mean potential of the negative and positive electrode) [5]. The use of graphite as the negative electrode enables a relative high specific capacity (372 mAh g^{-1}), as well as an operation potential almost

equal to Li metal [6,7]. Graphite is the unrivaled SOTA negative electrode active material in LIBs; consequently, apart from irreversible reactions during cell operation [8–10], the specific energy of a LIB depends largely on the choice of the positive electrode [2]. In general, the numerous positive electrode active material types can be distinguished and categorized by the kind of pathway for solid state Li^+ diffusion and transport: one dimensional (olivines), two dimensional (layered oxides), and three dimensional (spinels) [11]. The combination of high specific capacity, excellent manufacturability, sufficient solid state Li^+ diffusivity and transport as well as relative high mean working potential led to the implementation of the layered oxides represented by $LiCoO_2$ (LCO) in the 1st generation of commercial LIBs [12].

However, the main drawbacks, besides the toxicity and costs of Co, are the structural instabilities and safety hazards of LCO at abuse conditions [11,13]. The necessary limitation of the practical specific capacity utilization thus prevents the step towards increased specific energy in this case [13]. Promising alternative layered oxides could be obtained by the substitution of Co with Mn and Ni, presented by the $LiNi_{1-x-z}Mn_xCo_zO_2$ (NMC) family [14]. In NMC, each transition metal (*M*) can characteristically influence the electrode behavior, thus having possible advantages and drawbacks [12]. NMC including Ni in trivalent state (Ni^{3+}) is chemically more stable than $LiCoO_2$, thus enabling higher delithiation amounts without gassing in the cell [15]. However, Ni^{3+} suffers from structural instability due to Jahn Teller distortion [12]. The less toxic and cheaper Mn increases the structural stability and safety aspects, but only in tetravalent state (Mn^{4+}) [15,16]. Therefore, the structural incorporation of Mn must be accompanied with at least the same amount of Ni, which permits the required intrinsic electron exchange according to the crystal field theory, exhibiting the advantageous Mn^{4+} and divalent Ni (Ni^{2+}) [17]. However, due to size similarities [18], the Ni^{2+} partly exchanges its respective structural site with Li^+ [19]. This "Li^+/Ni^{2+} mixing" effect is known for deteriorating the rate performance and to a large extent even the structural stability [11]. The incorporation of Co can decrease the Li^+/Ni^{2+} mixing extent but at the expense of all the disadvantages associated with Co itself [20]. Overall, since each *M* in NMC material has its respective advantages and drawbacks, the optimal *M* ratio needs to be selected to obtain high structural stability and thus maximum possible reversible energy for a given application [21].

The structural stability of layered oxides predominantly depends on the delithiation amount (Li^+ extraction ratio) [15,21,22]. Thus, the stability comparison in dependence of the charge cut-off potential is not reasonable since different NMC compositions have different Li^+ extraction ratios for a set charge cut-off potential [23]. Our previous work showed parasitic reactions (e.g., electrolyte oxidation) to be negligible up to a charge cut-off potential of 4.6 V *vs.* Li/Li^+, which in turn implies that the specific charge capacity can be equated to the delithiation amount [21,22]. The specific capacity loss could be assigned to incomplete lithiation during discharge [22]. The associated kinetically lithiation hindrances of respective active material domains lead to Li^+ site vacancies in the discharged state [22,24]. Facilitating the kinetics *via* decreasing the specific current, temperature increase and/or introduction of a constant potential step during discharge, leads to an increase in specific discharge capacity [22]. These insights enabled a convenient calculation of the Li^+ extraction ratio obtained by a simple conventional constant current (galvanostatic) measurement, namely by the simple division of the measured specific charge capacity and calculated specific theoretical capacity [21,22]. Based on these results it could be shown that both, the Li^+ extraction ratio as well as the charge time, affect the specific capacity loss, thus the specific energy [23]. In further report, it was shown that specific capacity losses/fading during ongoing galvanostatic charge/discharge

cycling have an overwhelming reversible origin, as they can mostly be recovered when facilitating the kinetics [25]. The rise in internal resistances could be attributed to the intrinsic changes of the active material [25]. These insights enabled a modified comparison between structural stability, reversible specific energies as well specific energy efficiencies for different layered oxides [21]. However, to the best of our knowledge, a thorough investigation of different layered oxide materials, comparing cycle life based on these novel insights has not been reported, yet.

In this work, following layered oxides were evaluated with respect to their cycle life behavior: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111), $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811). Additionally, based on the specific capacity fading characteristics and results from our previous work [21,25], we have introduced effective strategies to prolong the cycle life at elevated specific energies, by simply modifying external electrochemical charge conditions. Overall, our intention is to bring this work to the scientific community for a deeper understanding of specific capacity fading characteristics, that can systematically assist further improvement with regard to specific energy and cycle life of the LIB technology.

2. Experimental

Galvanostatic (constant current) charge/discharge cycling experiments were performed in a three electrode cell set-up (Swagelok®). In this cell set-up it is possible to apply both, half- and full cell measurements. The benefit of the used three electrode set-up is the possibility to simultaneously monitor supportive potential values of each electrode for both, half- and full cell measurements *via* a reference electrode (Li metal from Albermale). The benefit of the half cell measurement is the use of Li metal also as the counter electrode, which ensures sufficient active Li^+ amount. Consequently, the working electrode (in this work $LiMO_2$ type based positive electrode) can be investigated without any interference from the counter electrode, enabling insights on electrode level. For the used two electrode application, natural graphite was used as the negative electrode. For reasons of monitoring the potential of the operated two electrode set-up, also a Li metal reference electrode was conducted. Battery grade 1 M $LiPF_6$ in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (1:1, by wt.) (LP50 Selectilyte™, BASF) was used as electrolyte. Battery cell test measurements were performed on a Maccor Series 4000 system. In all experiments, the discharge cut-off potential was set to 3.0 V *vs.* Li/Li^+. The discharge cut-off voltage for the two electrode set-up was set to 2.5 V. The electrochemical conditions (specific current, cut-off conditions) for charge were varied described in the respective figures of this manuscript. All experiments proceeded in a climate chamber (Binder KB400) under temperature control (20 °C if not other denoted). BMW Group provided the NMC111 and NMC532 electrodes. The NMC622, NCA and graphite electrodes were purchased from Customcells. NMC811 was purchased from Shanshan technology. All electrodes had an active mass ratio between 86% and 92%, thus including a sufficient amount of inactive materials. The slight differences in the active mass ratios are not significant for the here applied specific currents [26,27]. Prior the measurement of the lithiation degree, the discharged positive electrodes after 53 charge/discharge cycles were (microwave assisted) acid digested [22]. Afterwards, the Li/*M* ratio was determined by means of inductively coupled plasma optical emission spectroscopy (ICP−OES) [22]. The investigation of *M* dissolution occurred by analyzing of the digested cell components by means of total X-ray fluorescence (TXRF) after 53 charge/discharge cycles [25,28]. The respective deviations are given in the results and discussion part. The