1 Supplementary Experimental Part

a. Galvanostatic measurements

The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) electrodes were provided by BMW Group whereas the MCMB graphite (MTI cooperation) based electrodes were in-house made. NCM and MCMB graphite based electrodes had an active mass loading of 15 mg cm^{-2} and 11 mg cm^{-2}, respectively. In the full cell the MCMB electrode was 25% oversized in specific capacity. Battery grade solvent 1 M $LiPF_6$ in EC:EMC (1:1, by wt.) (LP50 Selectilyte™) from BASF was used as electrolyte. Galvanostatic charge/discharge cycling experiments were performed in a three electrode cell set-up (Swagelok®). Lithium metal (Rockwood Lithium) was chosen as a counter- and reference electrode. Maccor Series 4000 was used as battery cell test system. Charge cut-off potentials have been varied in this work. The discharge cut-off potential was set to 3.0 V *vs.* Li/Li^+. In several experiments a constant potential (CP) step at the discharge cut-off potential was set for 24 h. The full cell investigations were performed at a similar test procedure, but with a charge cut-off voltage of 4.55 V and a discharge cut-off voltage of 2.40 V. A constant voltage (CV) step at the discharge cut-off voltage was set for 24 h.

b. ICP-OES analysis

i. Measurement

A Spectro ARCOS ICP-OES (Spectro Analytical Instruments, Kleve, Germany) instrument with axial plasma viewing was used for element determination. A standard Fassel type torch was employed. For sample introduction, the system's peristaltic pump with a cross flow nebulizer and a double-pass spray chamber (Scott type) was used. Li (670.870 nm), Co (228.616 nm), Ni (221.648 nm) and Mn (260.596 nm) emission was detected at different individual emission lines simultaneously. Operating conditions for ICP-OES measurements are shown in Table 1.

Table 1 Instrument parameters (Spectro ARCOS ICP-OES, axial plasma viewing).

ICP-OES system	Conv. ICP-OES
Rf power (W)	1400
Argon flow (L/min)	13.65
Sample carrier gas (L/min)	0.85
Auxiliary plasma gas (L/min)	0.80
Outer plasma gas (L/min)	12.0
Torch geometry	Fassel type
Torch injector tube i.d. (mm)	1.8
Nebulizer	CrossFlow

ii. Sample Preparation

The NCM cathodes were dissolved by microwave assisted acid digestion using a Mulitwave 3000SOLV (Anton Paar) with each 3 ml nitric and hydrochloric acid (Suprapur®, Merck). The digestion was performed with a ramp up to 1300 W, holding time of 38 minutes and finally a cooling step down to 50°C.

Further dilutions were performed with deionized water (18.2 mΩ/cm^2, 5 ppb TOC, Millipore Corporation) in order to obtain an acidic concentration of 2-3 %. Furthermore an external calibration was performed using lithium, cobalt, nickel and manganese standards (1000 mg/L, Centripur®, Merck).

c. On-line MS analysis

i. Measurement

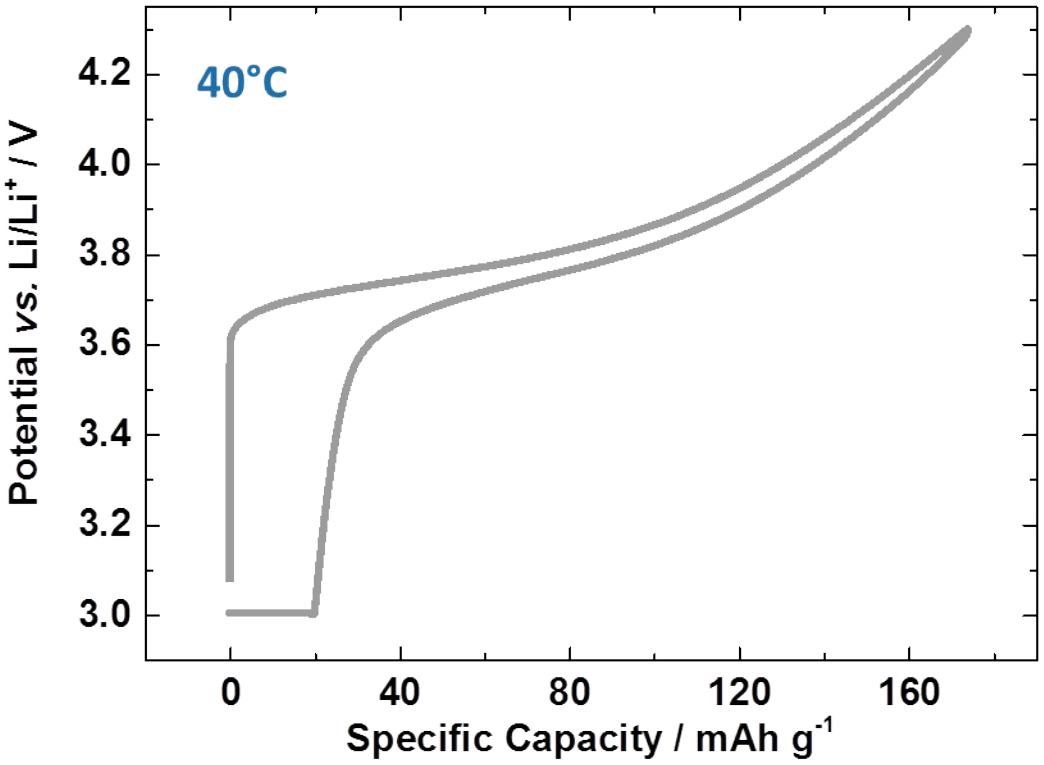
The Online MS experiments were carried out on a modified GCMS-QP2010 Ultra System from Shimadzu®. An unoccupied capillary column from CS (12 m × 100 µm × 360 µm) served as a pressure restriction. Measurements run without additional carrier gas and the column oven temperature was set isocratic to 200°C. The mass spectrometer was operating in electron ionization (EI) mode with an *m/z* scan range of 15-300. The ion source temperature was set to 250°C, the filament voltage to 70 V

and the absolute detector voltage to 0.7 kV. As software for compound identification and system controlling, GCMS Real Time Analysis and GCMS Postrun Analysis, which includes the NIST 08 library, were used.

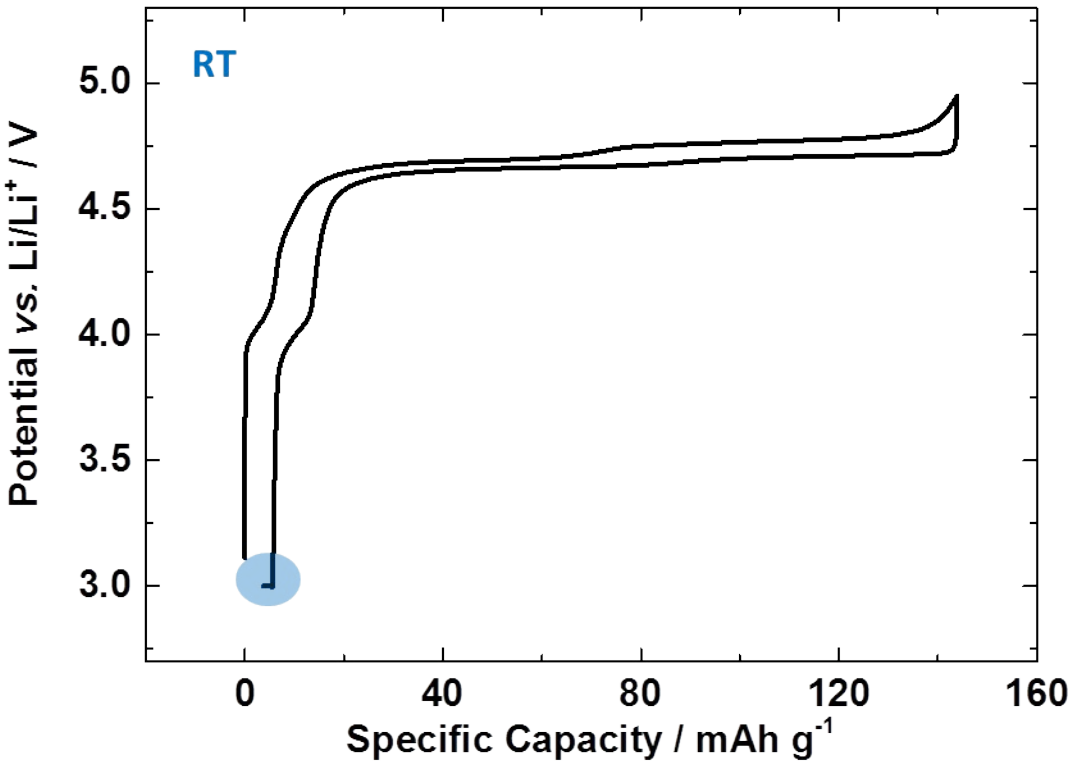
ii. Preparation

A three electrode cell set-up (Swagelok®) was used with an additional orifice for the capillary. The three electrode cell was assembled as described above.

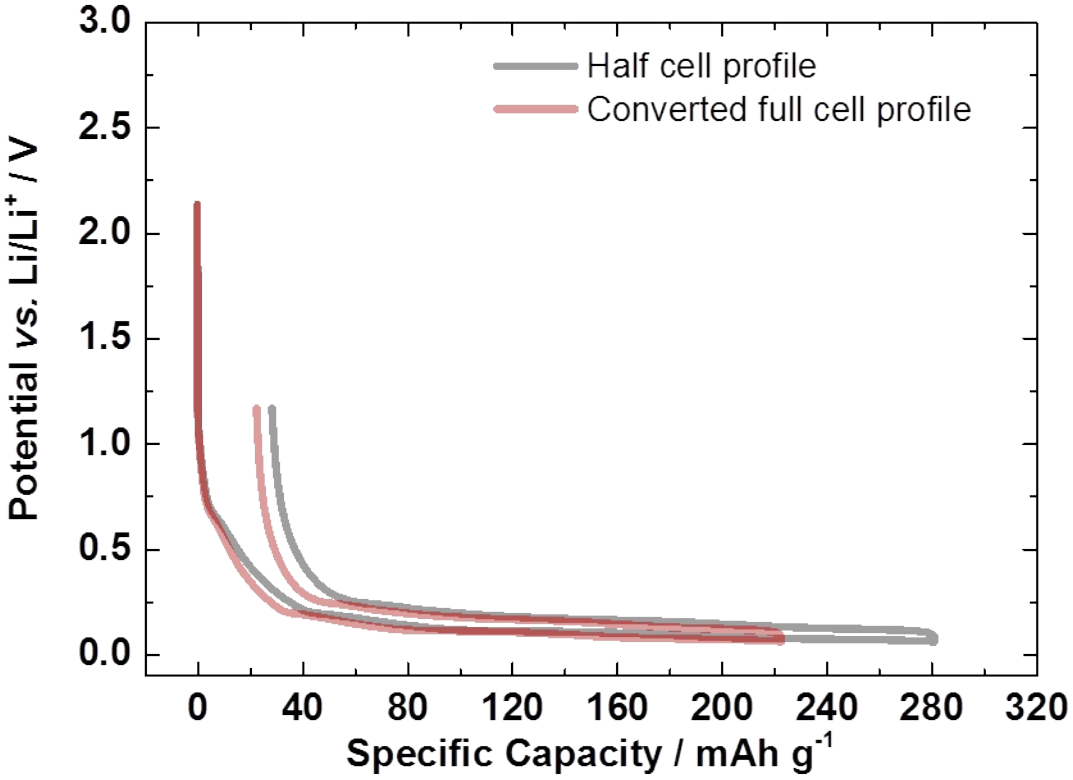
2 Supplementary Figures



Supplementary Figure 1: 1st cycle potential profile of a NCM/Li half cell at cut-off potentials of 4.3 - 3.0 V *vs.* Li/Li+ at 40°C. The discharge includes a CP step at the discharge cut-off potential of 3.0 V *vs.* Li/Li+ for 24 h. During the CP step a specific capacity of 16.3 mAh g-1 could be regained from the initial apparent overall specific capacity loss of 16.9 mAh g-1. Merely 0.6 mAh g-1 seem to be irreversibly reasoned which corresponds to a 1st cycle CE of 99.7%.



Supplementary Figure 2: 1st cycle potential profile of a LNMO/Li half cell at cut-off potentials of 4.95 - 3.0 V *vs.* Li/Li$^+$ at RT. The discharge includes a CP step at the discharge cut-off potential of 3.0 V *vs.* Li/Li$^+$ for 24 h. During the CP step a specific capacity of 1.8 mAh g^{-1} could be regained from the initial apparent specific capacity loss of 5.6 mAh g^{-1}. Hence, the remaining irreversible capacity amounts to 3.8 mAh g^{-1}.



Supplementary Figure 3: 1st cycle potential profile of a MCMB/Li half cell simulating the full cell conditions with the charge cut-off potential of 0.05 V *vs.* Li/Li+ at RT using a specific current of 23 mA g^{-1} (Specific current for a 30% oversized graphite, when using specific current of 30 mA g^{-1} for NCM). The half cell capacities (grey) are converted to full cell capacacities (red) (specfic capacity ratio of graphite:NCM is 1:0.79, considering a 30% oversized graphite). The corresponding converted full cell capacity loss amounts to 22.6 mAh g^{-1} which is in accordance to the real full cell capacity loss detremined after the CV step at 2.4.