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Supporting Information

Failure mechanism of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathodes in aqueous/non-aqueous hybrid electrolyte

Leilei Du[a],[1] Xu Hou[b],[1] Debbie Berghus[a], Lars Frankenstein[a], Richard Schmuch[a], Jun Wang[c], Elie Paillard[d], Martin Winter[ab], Tobias Placke[a,*], Jie Li[b,d,*]

[a] MEET Battery Research Center, Institute of Physical Chemistry, University of Münster, Corrensstr. 46, Münster 48149, Germany

[b] Helmholtz-Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149, Münster, Germany

[c] School of Innovation and Entrepreneurship, Southern University of Science and Technology, Shenzhen 518055, China

[d] Department of Energy, Politecnico di Milano, Via Lambruschini 4, Milano, 20156, Italy

* Corresponding author: tobias.placke@uni-muenster.de (T. P.), jie1.li@polimi.it (J. L.)

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1. Experimental

1.1 Preparation of electrolyte and electrodes

Lithium bis (trifluoromethane sulfonyl) imide ($LiN(SO_2CF_3)_2$, LiTFSI) (purity: >98%) and ethoxy-(pentafluoro)-cyclotriphosphazene (PFN; purity: >98%) were purchased from Tokyo Chemical Industry, dimethyl carbonate (DMC; BASF SE; battery grade) was used as co-solvent. The formulation of 13M basic electrolyte is, dissolving 13M LiTFSI into 1 kg bi-solvent of milli-Q H_2O/DMC (1:1, molar ratio). 20 wt.% of PFN were added to 13M electrolyte to prepare the '13M20' electrolyte.[1]

The $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622, Lot. No.: LT-170961715, specific surface area: 0.24 m^2 g^{-1}) cathode material was purchased from Hunan Shanshan Energy Technology Co., Ltd. The NCM622 electrodes consisted of 80 wt.% NCM622, 10 wt.% polyvinylidene difluoride (PVdF) binder (Kynar® FLEX 761A, Arkema Group) and 10 wt.% carbon black (Super C65, Imerys Graphite & Carbon) which were cast onto titanium foil (25 μm, Ti-shop.com), and the corresponding XRD pattern is shown in **Figure S10**. The solvent for the cathode paste was *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich, purity: 99.5 %). Thereafter, the electrodes were punched into Ø12 mm disks and dried in a *Büchi* B-585 glass drying oven under 120°C in the reduced pressure at least 5 hours until all solvent was evaporated. The mass loading of average active materials was ≈2.88 mg cm^{-2}. Before use, all electrodes were pressed under 2 bars for 5 seconds.

The TiO_2@$LiTi_2(PO_4)_3$ anode material was synthesized according to the previous work,[2] and the electrode paste was prepared by same method as for the cathode, but was cast onto aluminum foil (15 µm; Nippon Foil). The anode was composed of 80 wt.% active material, 10 wt.% PVdF and 10 wt.% Super C65. The average mass loading of the anode active material was ≈2.4 mg cm^{-2}.

1.2 Experimental Equipment and Materials Characterization

The surface morphology of the NCM622 electrode was analyzed by high-resolution scanning electron microscopy (SEM, Carl Zeiss AURIGA). The crystalline structure of the NCM622 was characterized using an X-ray diffractometer (Bruker D8 Advance X-ray) with Cu Kα radiation (λ = 0.15418 nm) in the 2θ range from 10° to 90°. For the thermogravimetric analysis, TGA-MS measurements were carried out on a TGA Q5000IR (TA Instruments) coupled with a ThermoStar GSD 301 T3 (Pfeiffer Vacuum) mass spectrometer under helium gas flow. Cycled cathodes were taken from NCM622 || TiO_2@$LiTi_2(PO_4)_3$ full-cells after 100 cycles by disassembling cells in a dry room and washing the electrode surface with 100 µL DMC to remove residual salts.

1.3 Electrochemical measurements

For CR2032-type coin cells (two-electrode configuration, full-cell setup [3]), NCM622 and TiO_2@$LiTi_2(PO_4)_3$ electrodes were used as positive electrode (cathode) and negative electrode (anode), respectively. A positive-to-negative areal capacity balancing ratio (P/N) of 1.2:1 (NCM622, 1C =150 mA g^{-1} charge to 4.3 V, TiO_2@$LiTi_2(PO_4)_3$, 1C =150 mA g^{-1}) was used, thus the cells were anode limited. A glass fiber (Whatman, GF/A) was used as separator in combination with 100 µL of the

‘13M20’ electrolyte. For Swagelok cells (three-electrode configuration, full-cell setup), Ag|AgCl was used as reference electrode (RE) with glass fiber (Whatman, GF/D) as separator. Galvanostatic charge/discharge cycling measurements were carried out on MACCOR series 4000 battery testers (Maccor Inc.) in cell voltage operation ranges of 0.7-2.9 V or 0.7-2.8 V for the full-cells at 0.5C for two formation cycles and at 1C for 98 cycles (1C =150 mA g^{-1} based on the mass of the capacity-limiting anode). At least three cells have been evaluated to ensure a good reproducibility of the electrochemical results.

Electrochemical impedance spectroscopy (EIS) was performed at an EC-lab electrochemical workstation in a frequency range from 100 kHz to 5 mHz at the potential amplitude of 10 mV. The galvanostatic intermittent titration technique (GITT) was carried out on VMP3 (BioLogic Science Instruments, France). Therefore, the cell was firstly charged to 2.8 V or 2.9 V at a rate of 0.5C and hold at cut-off voltage for 48 h. Thereafter, a discharge pulse was employed at a rate of 0.5C for 15 min until reaching 0.7 V, and the relaxation time was two hours between each pulse. The operating temperature was 20 °C for all electrochemical measurements.

2. Supplementary Figures and Tables

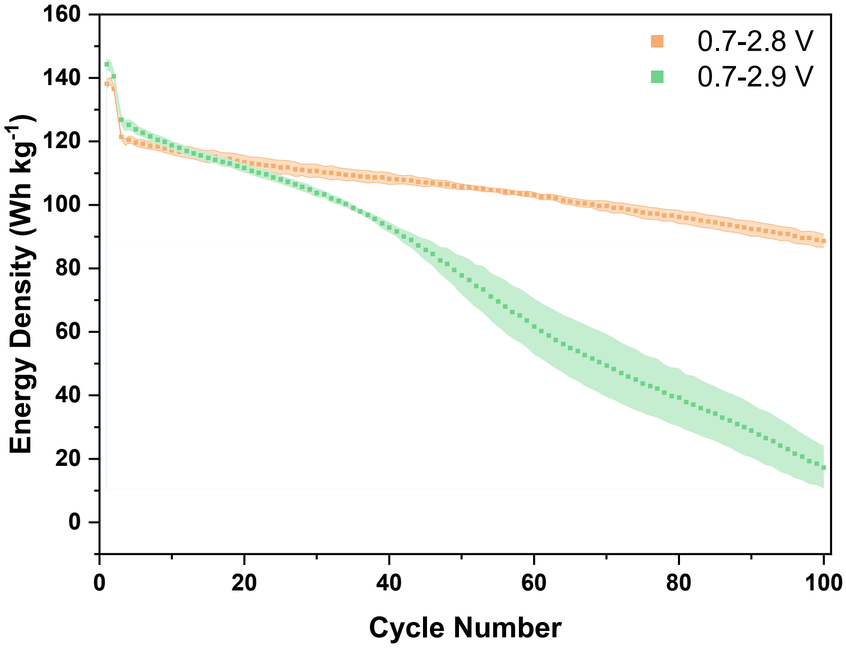

Figure S1. Charge/discharge cycling performance during 100 cycles with specific energy density.

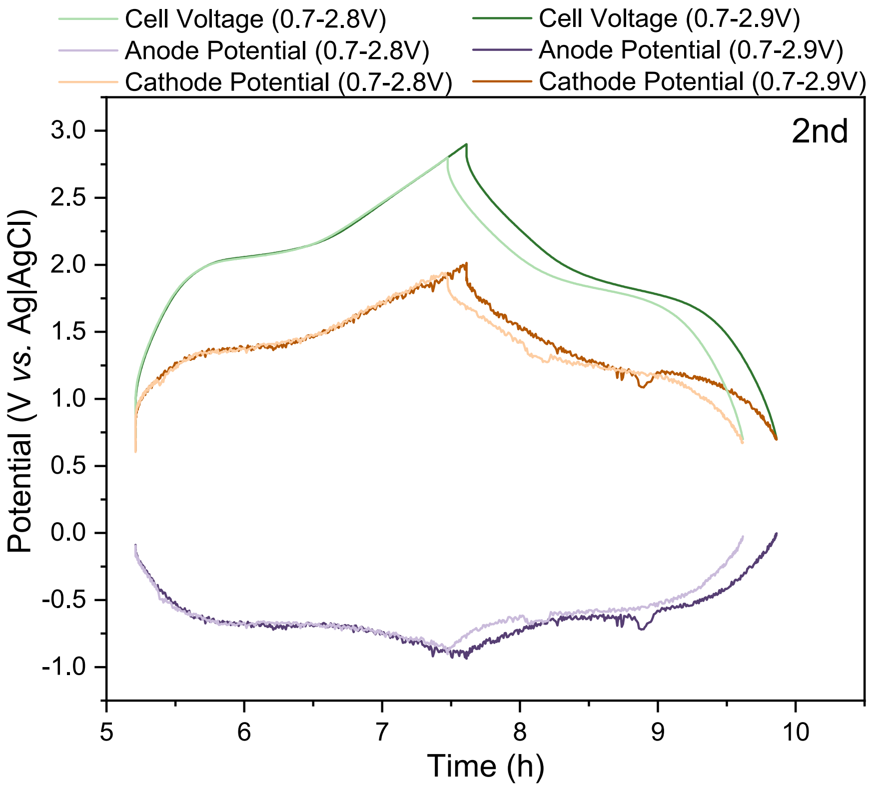

Figure S2. Charge/discharge cell voltage and potential *vs.* time curves for the 2nd cycle in Swagelok-type cells (three-electrode configuration), which use NCM622, $TiO_2@LiTi_2(PO_4)_3$ and Ag|AgCl electrodes as cathode, anode and reference electrodes, respectively. Cell voltage ranges: 0.7-2.8 V and 0.7-2.9 V.

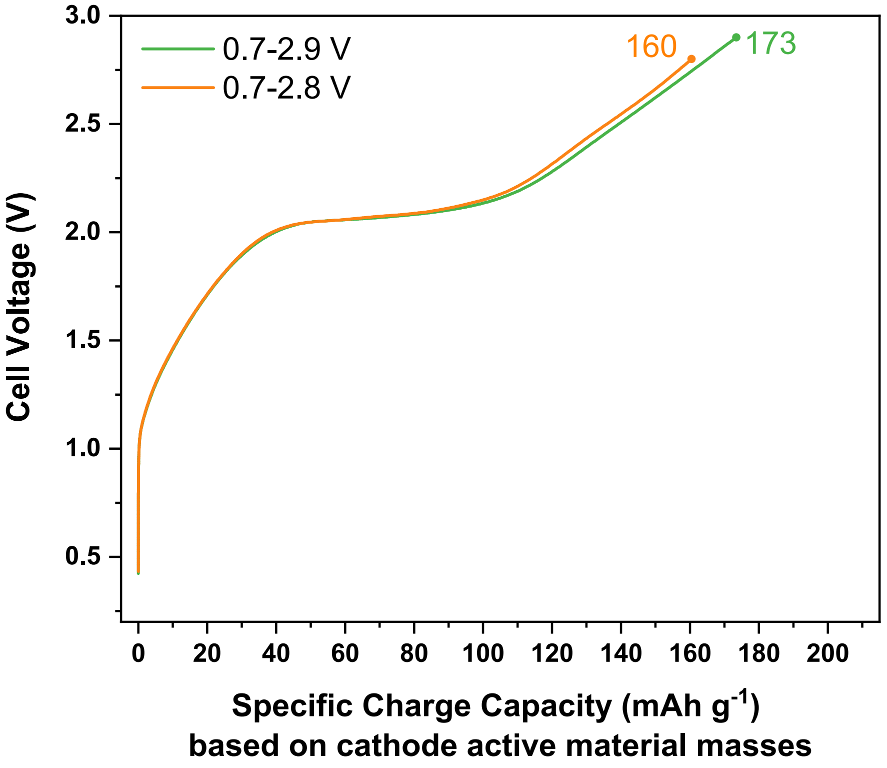

Figure S3. Cell voltage curves of NCM622 || TiO_2@$LiTi_2(PO_4)_3$ full-cells during the 1st charge with 2.8 or 2.9 V upper cut-off cell voltage, showing the specific capacities based on the cathode active material mass loading.

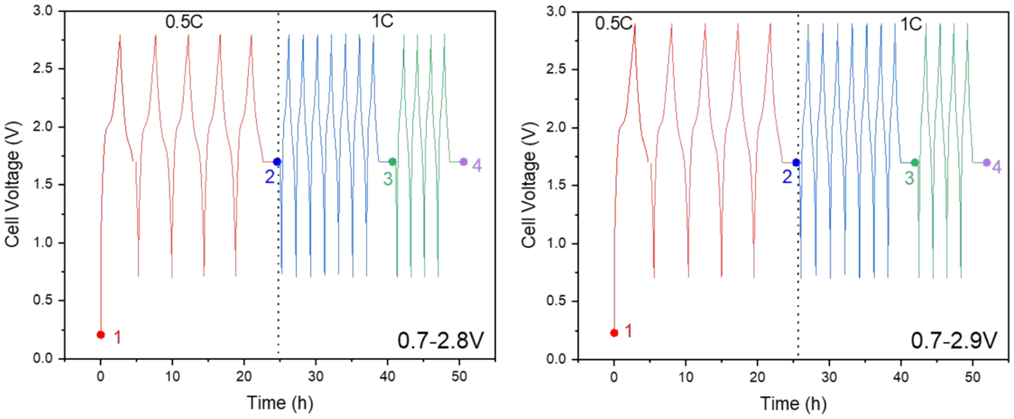

Figure S4. Cell voltage *vs*. time cycling curves for NCM622 || TiO_2@$LiTi_2(PO_4)_3$ full-cells. Points (1-4) indicate times at which EIS measurements were made.

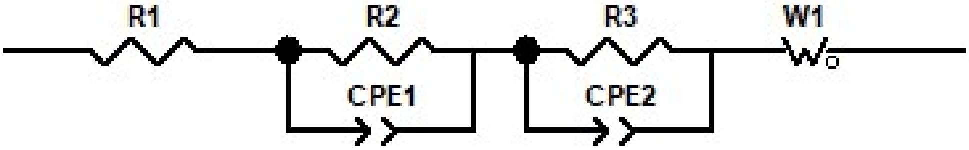

Figure S5. Equivalent circuit model for fitting of EIS data of NCM622 || $TiO_2@LiTi_2(PO_4)_3$ full-cells, as shown in **Figure 2**. R1: bulk resistance of the cell; R2 and CPE1: resistance and capacitance of the interphasial layer; R3 and CPE2: charge transfer resistance and double layer capacitance; W: Warburg impedance.

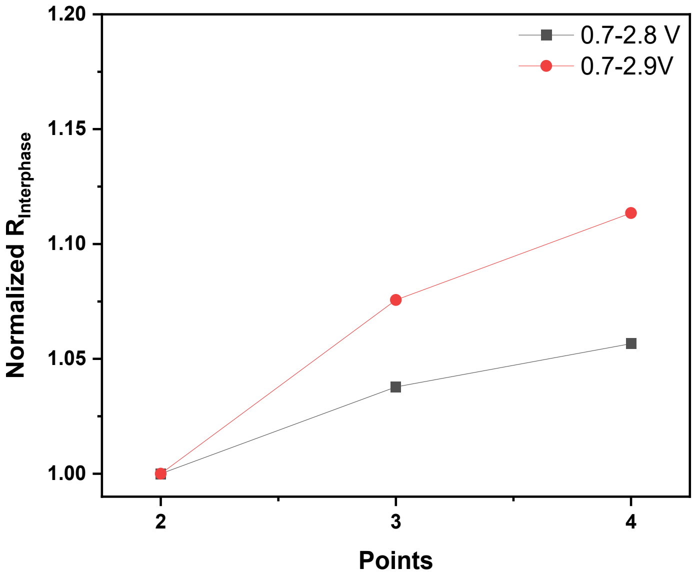

Figure S6. Normalized $R_{Interphase}$ fitting values from EIS data of NCM622 || $TiO_2@LiTi_2(PO_4)_3$ cells (**Figure 2a, b**) from point 2 to point 4 (**Figure S5**).

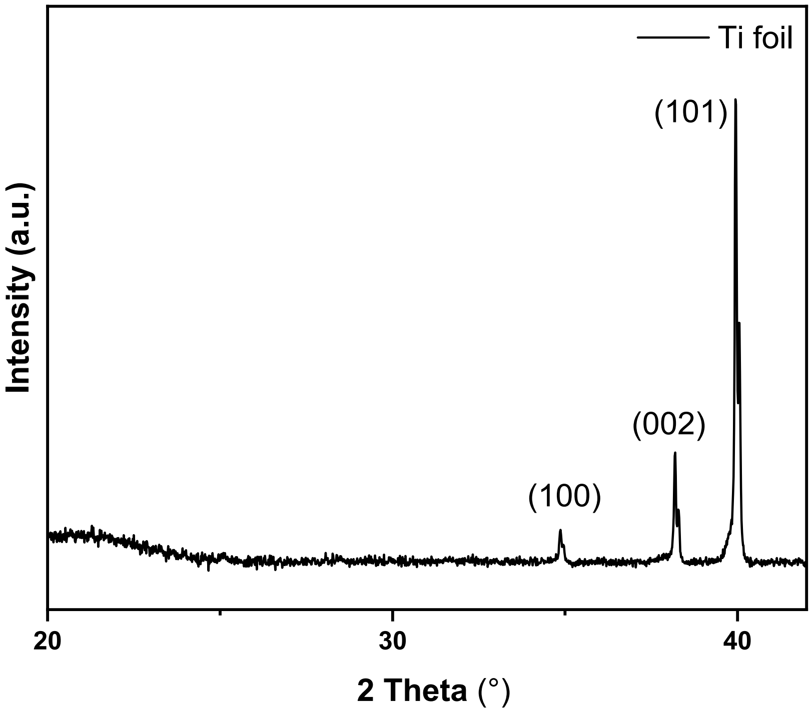

Figure S7. XRD pattern of titanium foil which has been used as current collector of NCM622 cathode.

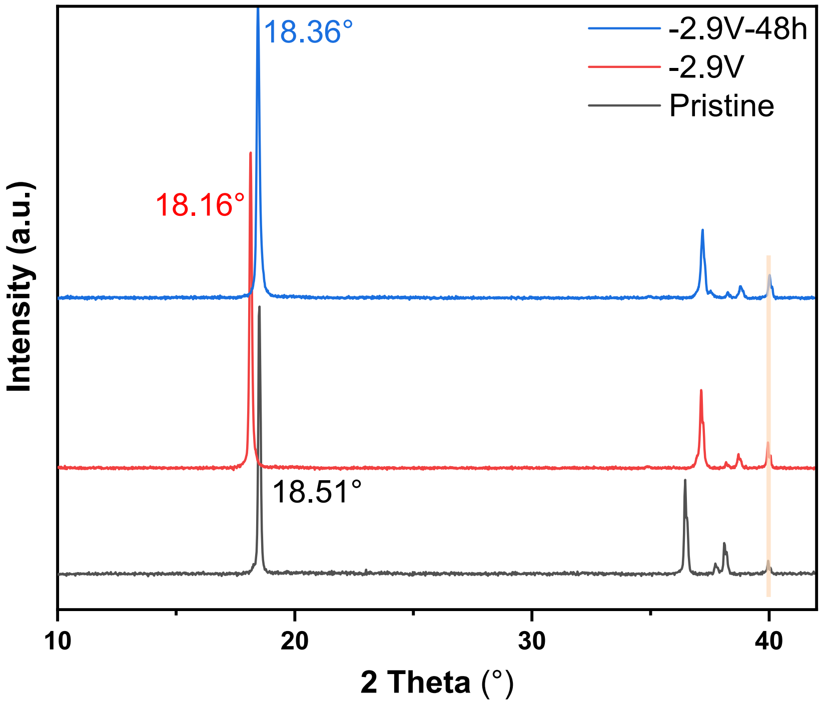

Figure S8. XRD patterns of NCM622 cathodes from 10° - 42° 2θ, including the pristine NCM622 cathode, and NCM622 cathodes charged to 2.9V without or with an additional 48 hours holding step (after 1st charge).

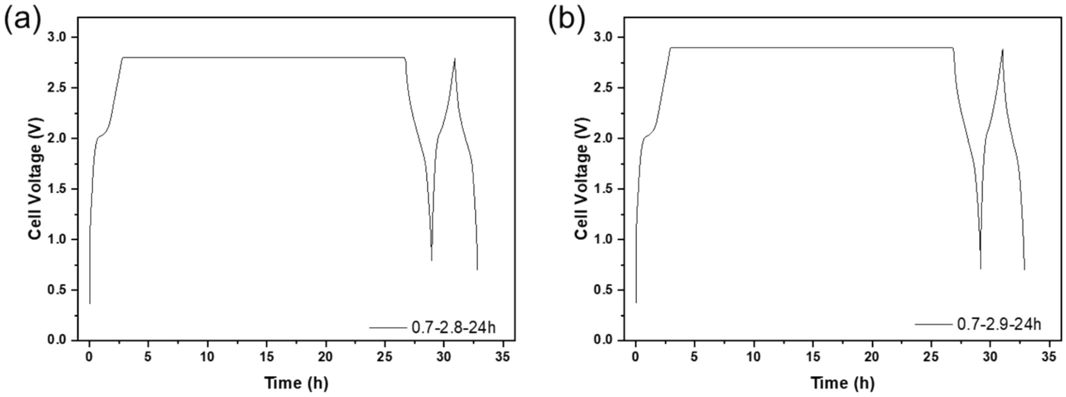

Figure S9. Cell voltage *vs.* time curve for a 24 h holding measurement of NCM622 || $TiO_2@LiTi_2(PO_4)_3$ full cells after charging to 2.8 V(a) or 2.9 V(b).

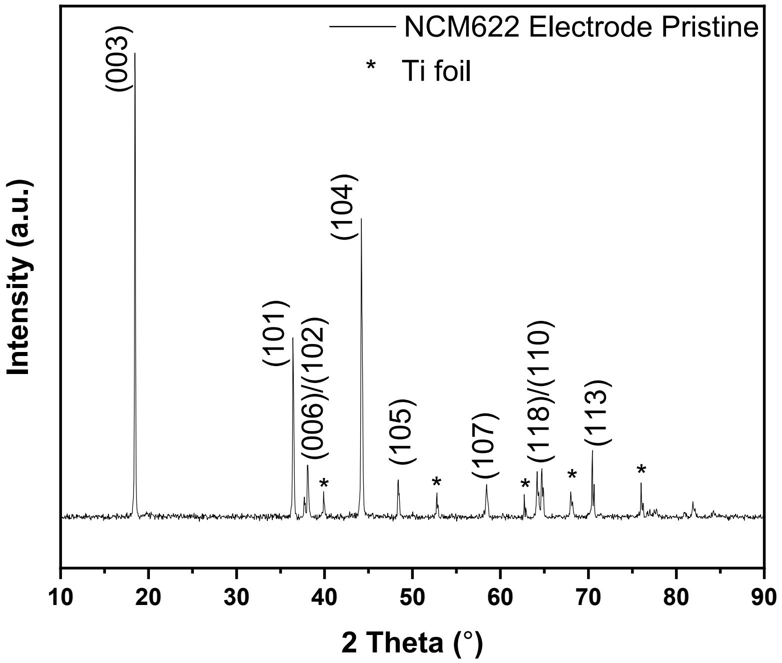

Figure S10. XRD pattern of the pristine NCM622 electrode.

3. References

[1] L. Du, X. Hou, W. Zhao, L. Haneke, J. Wang, X. Ju, X. Liu, Y. Yang, J. M. Wrogemann, S. Künne, *Journal of Power Sources* 2022, *541*, 231670.

[2] X. Hou, X. Ju, W. Zhao, J. Wang, X. He, L. Du, B. Yan, J. Li, E. Paillard, J. Sun, H. Lin, M. Winter, J. Li, *Journal of Power Sources* 2021, *484*, 229255.

[3] R. Noelle, K. Beltrop, F. Holtstiege, J. Kasnatscheew, T. Placke, M. Winter, *Materials Today* 2020, *32*, 131-146.

4. Author Contributions

L.D. performed the experiments and wrote the original draft. X.H. gave advice for the paper structure. D.B. performed TGA-MS measurement, L.F., R.S., J. W., E. P. gave lab work or writing supports. T. P. and J. L. proposed the topic and supervised the work. M. W., T. P. and J. L. corrected the original draft. All authors discussed the results and reviewed the final manuscript.