High Voltage All-Solid-State-Lithium-Battery with Sulfide-based Electrolyte: Challenges for the Construction of a Bipolar Multi-Cell-Stack and How to Overcome Them

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Keywords

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Abstract

Solid electrolytes can be the key for the desired goal of increased safety and specific energies of batteries. On cell and battery pack level, the all-solid nature and absence of liquid electrolyte leakage is considered to enable the safe and performant realization of the rechargeable Li metal electrode and bipolar cell stacking, respectively. Well performing Li metal cells with high energy/voltage positive electrodes like $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) can already be cycled when using a blend of the sulfidic solid electrolyte like β-Li_3PS_4 (LPS) and Li salt in poly(ethylene)oxide (PEO). However, operation of a bipolar stack using these cell materials using the common Al/Cu clad as bipolar plate results in an immediate short-circuit, because of an ionic inter-cell connection *via* molten LiTFSI/PEO. Oversizing the area of the bipolar plates can prevent such short-circuit and indeed enables a partial charge of the stack, but after a certain time, the next cell failure is observed consisting of severe, sulfur caused, corrosion of copper which was used as metal substrate for the lithium anode. The exchange of the sulfide incompatible Cu collector by (also area-oversized) stainless steel can finally enable a failure-free performance of the bipolar cell stack, which performs similar to a single cell with regard to cycling stability.

Introduction

The increase in specific energy and safety of batteries by at the same time decreased costs is the main motivation for research and development.[1] State-of-the-art (SOTA) active materials are reaching their calculated energy limits. Interestingly, an inactive material, the electrolyte, is assumed to be key for the next targeted development.[2]

The SOTA electrolyte is liquid and composed of $LiPF_6$ dissolved in a liquid ethylene carbonate/linear carbonate (e.g. dimethyl carbonate) solvent mixture.[3-4] Though it reveals good physical (*e.g.* wetting ability),[5] physicochemical (*e.g.* ionic conductivity)[6-7] and electrochemical properties (*e.g.* oxidative stability,[7-9] passivation of graphite as SOTA negative electrode,[3, 10] passivation of Al current collector[11]), its main drawback is the insufficient component safety because of high flammability and reactivity.[3, 12] In addition, used in combination with rechargeable Li metal electrodes, liquid electrolytes rather fast result in unsafe high surface area (HSAL) Li deposition morphologies, which finally motivates research on solid electrolytes.[13] In addition, solid electrolytes can provide opportunities to further increase specific energies.[2, 14]

On cell level, solid electrolytes can enable Li as the negative electrode by mechanically suppressing HSAL (dendrite) formation and growth.[15] The use of metallic Li can increase the specific energy because of its theoretically 10 times higher specific capacity and ca. 100 mV lower working potential compared to the graphite-based negative electrode.[16] On battery pack level, the absence of any possibility of leakage of solid electrolytes may enable a bipolar cell stacking without short circuit concerns, contrary to liquid electrolytes, where a serial connection can only be realized in a mono-polar manner.[17-18] Bipolar stacking reduces the amount of inactive materials necessary for each cell (*e.g.* for housing, wiring) and additionally can decrease resistive losses (short electron pathways, higher contact area), which is beneficial for both, specific energy and costs.[19-20] However, bipolar design requires a very accurate cell capacity reproducibility as the cells, unlike in mono-polar pack design, cannot be controlled and monitored individually and thus are more sensitive to overcharge/over-discharge in a bipolar series arrangement. Still the development of an appropriate solid electrolyte remains a challenge, both on cell and battery level independent of the use of mono-/bipolar design.

Common solid electrolytes can be roughly divided into two substance classes, namely organic (*e.g.* solid polymers) and inorganic (*e.g.* ceramics, glasses) solids.[2] While solid polymer-based electrolytes like lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in poly(ethylene)oxide (PEO) can be cycled with Li metal, they suffer from poor room temperature ionic conductivities and apparent issues with high voltage positive electrodes *e.g.* the promising $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622).[21-23] In contrast, some inorganic electrolytes like β-Li_3PS_4 (LPS) can provide good ionic conductivities as well as sufficient oxidative stabilities, but show stability issues with Li metal.[14, 24-26] Given the different pros and cons on negative and positive electrodes, different solid electrolyte classes have recently been successfully combined to a multi-layer and implemented in a "high energy" all-solid-state-lithium-battery cell with NMC622 electrode, where the respective side of the LiTFSI/PEO faces the Li electrode and LPS faces the NMC622 electrode.[27]

Even though bipolar stacking has been reported in literature for solid state batteries,[14] to our knowledge no stack studies have been reported for sulfide electrolytes with high energy/voltage positive electrodes like NMC622 and Li as negative electrode. Indeed, as will be shown in this work, bipolar stacking is more challenging for sulfide-containing solid electrolytes compared to sulfide-free ones.[28] The aim of this diagnostic work is not only to reveal and understand the issues and failure origins (causing problematic short-circuits), but

to improve the battery and battery cell design to finally realize a failure-free bipolar stack using the promising sulfide electrolytes.

Experimental

a) Materials

Poly(ethylene oxide) (PEO, M_w 300000 Da) and vapor-grown-carbon-fibers (VGCFs) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%) was purchased from Solvay, France. Toluene (99.85%, extra dry) was purchased from Fisher Scientific. The active material $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622), β-$LiPS_4$ (LPS) and Oppanol (= polyisobutylen based) binder was provided by BASF. Lithium metal was used as foil without further treatment and was purchased from Albemarle. Stainless steel is the commercial 316L type. Material storage and sample preparations was performed in an argon-filled glovebox (GS-Glovebox MEGA M-Line, ≤1 ppm O_2, ≤1 ppm H_2O). PEO was dried under vacuum (10^{-7} mbar) at 45 °C and LiTFSI at 110 °C for 2 days before use. All other chemicals were used as received. The used material discs for cell assembly was as follows: Cu (15 µm), Li (500µm), PEO/LiTFSI membrane (100 µm), LPS (44 µm), NMC622 (60 µm), Al (20 µm), Stainless steel (20 µm).

b) LiTFSI/PEO membrane preparation

Free-standing LiTFSI/PEO polymer membranes were prepared by dry-mixing of PEO and LiTFSI in a mortar using an EO:Li ratio of 12:1. The mixture was annealed in an oven at 60 °C for 2 days and the resulting gum-like material was hot-pressed for 10 min at 100 °C with an applied pressure of 15 bar, resulting in a final membrane thickness of 100±5 µm.

c) Electrode preparation and cell assembly

The NMC622 composite electrodes were prepared consisting of 67.2wt% NMC 622, 28.8wt% β-LPS, 2wt% VGCFs and 2wt% Oppanol according to literature.[27] The average active mass loading of NMC622 composite electrodes was 4.1 mg cm^{-2}. D50 value of the secondary NMC622 particle was 20 µm.

d) LPS membrane preparation and transfer on NMC622 electrode

LPS solid electrolyte membranes consisting of 95wt% β-LPS and 5wt% binder were prepared using the (scale-able) solvent-based preparation process.[27] The prepared electrolyte paste was casted on polished aluminum foil with a wet-coating thickness of 400 µm and dried under reduced pressure. The resulting dry β-LPS membranes were punched into circular disk (12 mm diameter) and pressed with an applied pressure of 8 t for 10 s. On pressure release, the aluminum substrate loses contact and free-standing β-LPS membranes with an average thickness of 44±3 µm can be obtained. The contact between the NMC 622 composite electrode and the β-LPS membrane was ensured by stacking a free-standing β-LPS membrane with a NMC 622 composite electrode (12 mm diameter) and pressing the stack with the parameters mentioned above.

e) Electrochemical measurements

Constant current cycling experiments were conducted on a Maccor Series 4000 battery cell test system at 60 °C in a climate chamber (Binder KB400) including 24 h resting time prior operation. The used C-Rates and corresponding specific currents are mentioned within text and/or figure caption.

f) Differential scanning calorimetry (DSC)

DSC measurements were performed using a TA Instruments Discovery DSC 2500 (TA Instruments, USA) in the temperature range of -100 °C to 120 °C with a scan rate of 10 °C min^{-1}. The samples of ≈ 2 mg were sealed in hermetic aluminum pans (TA Instruments, USA). Helium was used as sample gas (25 mL min^{-1}). Three cycles of heating and cooling within the given temperature range were performed.

g) Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX)

SEM micrographs were obtained using a Carl Zeiss AURIGA CrossBeam® workstation (Carl Zeiss SMT AG) with an acceleration voltage of 20 kV at a working distance of 5 mm under a vacuum of 10^{-6} bar. EDX elemental mapping was conducted to analyze composition of the surface of interest using an integrated EDX-detector INCA X-max 80 mm^2 (Oxford Instruments).

Results and discussion

a) Preparation of singleNMC622||Li cell

The assembled cell consists of a Li metal layer, a LiTFSI/PEO layer, a LPS sheet (with binder), a NMC622 composite electrode (with VGCF, LPS and binder) and Al foil, which is schematically shown in Figure 1 (a). The direct transfer of LPS layer on NMC622 electrode *via* cold pressing occurred from an Al substrate. Galvanostatic charge/discharge cycling was performed in the voltage range of 4.2 – 3.0 V with a specific current of 15 mA g^{-1}, as shown in Figure 1 (b).

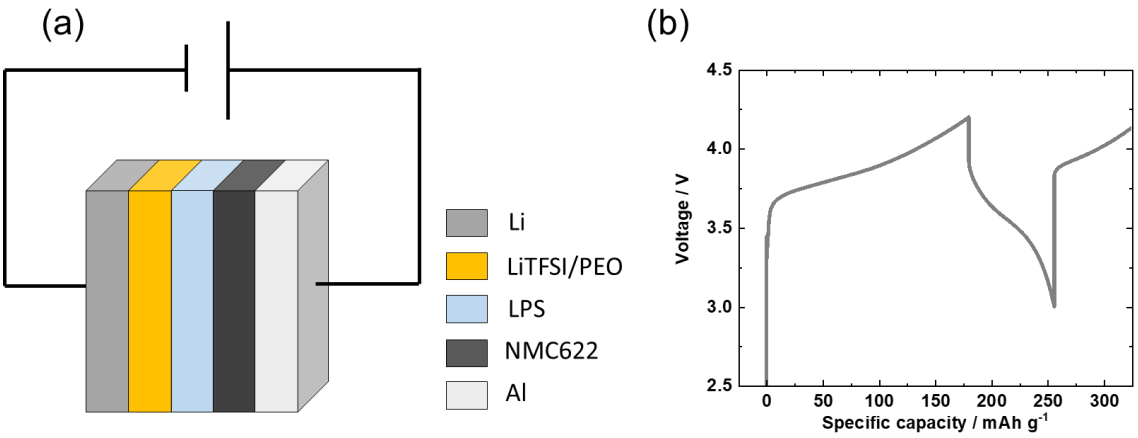

Figure 1: (a) Cell concept of the single NMC622 // Li cell. (b) Galvanostatic charge/discharge profiles of the respective cell in the voltage range of 4.2 -3.0 V using a specific current of 15 mA g^{-1} at 60 °C. The shown performance of a single cell serves as orientation (benchmark) for the upcoming development of bipolar stack design.

NMC622 characteristic voltage curves are obtained (no short-circuits), which demonstrates feasibility on cell level and serves as performance/capacity reference for the design of the bipolar stack set-up. The focus of this work is the design of the bipolar stack set-up based on the shown single cells, which thus can maximally reveal the performance of this single cell

with respect to e.g. specific capacities. In detail, the predominant challenge is a stack design with the absence of short-circuits. The challenging further improvement of the performance and cycle life is related to improvement of single cells and is beyond the scope of this thesis. For this reason and reasons of effectiveness of the cell stack development (reproducibility, experiment duration), only the initial charge/discharge cycle is carried out.

b) Designing a bipolar stack with sulfide electrolytes: challenges

In the ideal case during operation of a bipolar stack, the electrons only move outside the individual cells and between neighboring cells, while the Li ions only move within the individual cells (Figure 2 (a)). However, in practice several challenges occur. A simple bipolar stack of the shown single cells may lead to formation undesired Li-Al alloys.[14] To avoid this, Cu can be inserted between Li and Al, as reported in literature for a bipolar stack using a sulfide-free solid electrolyte (Figure 2 a).[28] However, this rather simple bipolar set-up results in a failure already after cell assembly during open circuit voltage (OCV), even before charge, as shown in in Figure 2 (b). First, the connection of the 3-cell stack reveals a reasonable OCV of ≈ 7.8 V (OCV of single cells between 2.3 and 2.7 V). However, after only ≈ 0.6 h under OCV conditions, the OCV rapidly decreases by 2.6 V (red arrow in Figure 2 b, the value exactly corresponds to the voltage of a single cell). In contrast, the OCV remains failure free (no short circuits) at 20 °C. As seen in differential scanning calorimetry (DSC) in Figure 2 (c) the melting of LiTFSI/PEO appears at 51 °C. Thus, at 60 °C the molten LiTFSI/PEO can connect two neighboring cells and create a short circuit, as schematically illustrated in Figure 2 (d). As a result, the two short-circuited cells behave as one cell and lead to a voltage decay.

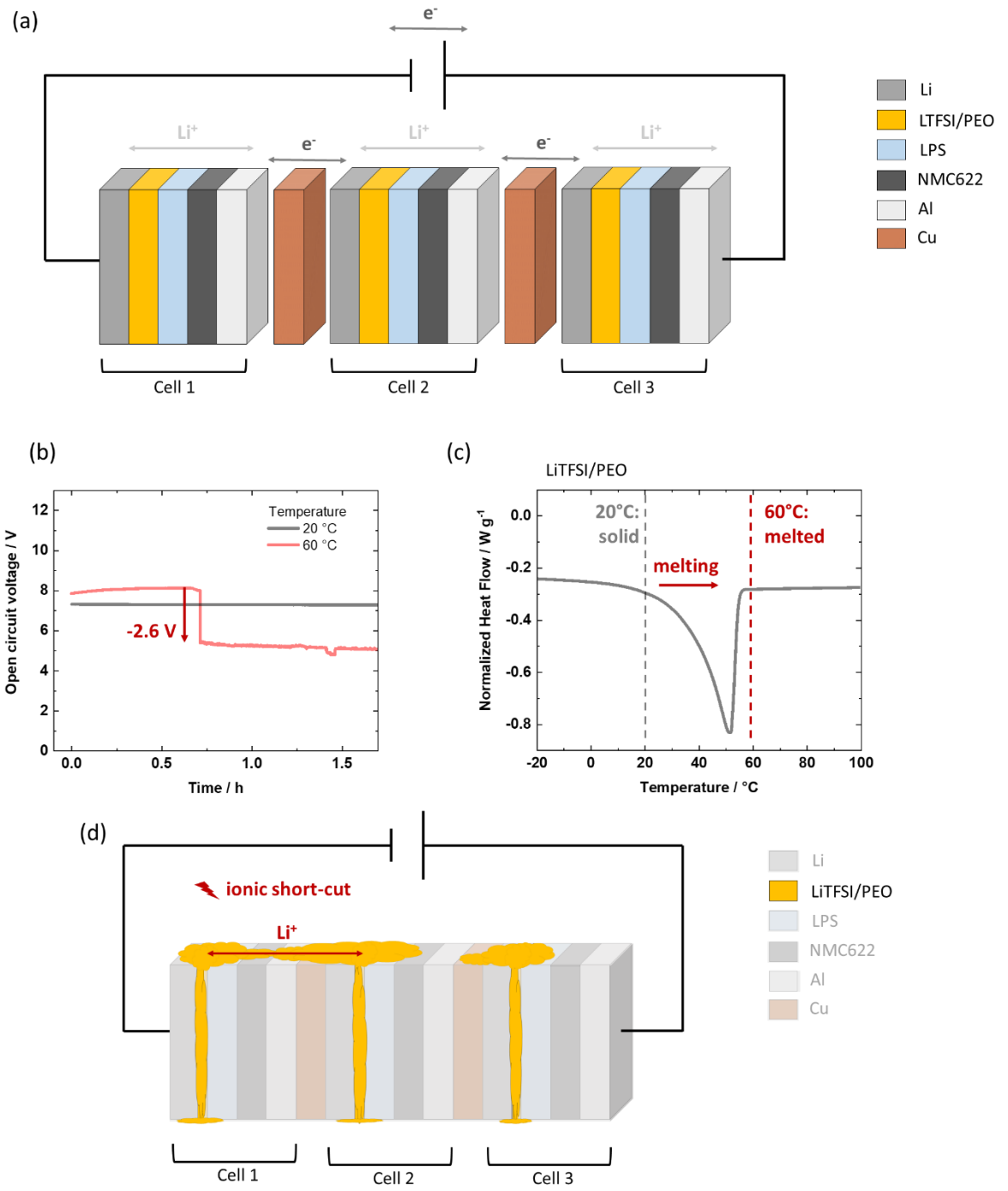

Figure 2: (a) During ideal operation of a bipolar multi stack (here, a triple stack), electrons only move outside the individual cells and between neighboring cells, while the Li ions only move within the individual cells. (b) OCV as a function of time at 20 °C and 60 °C. Already after ≈ 0.6 h at 60 °C the OCV decreases by 2.6 V (this values corresponds to the OCV of a single cell), which points to ionic short-cut between two cells, while the OCV remains constant at 20 °C. (c) DSC measurement (scan rate 10 °C min^{-1}) as a function of temperature reveals melting of LiTFSI/PEO at 51 °C. (d) A connection of molten LiTFSI/PEO can explain the short circuit via the detrimental Li ion connection between the cells.

To prevent the issue of LiTFSI/PEO connection, a more effective separation of neighboring cells *via* an area-oversized current collector (Cu) is applied as shown in Figure 3 (a). By oversizing the diameter of Cu by e.g. 6% (12.7 vs. 12.0 mm), a partial charge reaction can be obtained in this way before appearance of a next failure, resulting in an overall specific charge capacity of only ≈ 15 mAh g^{-1} (Figure 3 b). Short circuits due to LiTFSI/PEO melting in the Cu separated stack set-up are rather unlikely to be responsible for the observed failure, as no

voltage decay is observed in the OCV during the 24 h resting time. An increase of the specific current to 150 mA g^{-1} (Figure 3 (b)) results in an increased specific capacity of ≈ 80 mAh g^{-1} at a stack voltage of ≈ 12.5 V before the failure appears. Obviously this failure has an electrochemical relation (occurring after charge onset) and chemical relation (showing a time dependence; as the failure appears after 30 to 60 min after charge reaction onset). In addition, Cu collector corrosion was observed after disassembly of the failed cell stack (Figure 3 (d)). Cu corrosion can be attributed to the generally known chemical instability of Cu with sulfides, which corrodes even without direct contact between Cu and LPS layers (Figure 2 a); that is, given the sensitivity of this chemical reaction already sulfide traces in the gas phase (*e.g.* H_2S) can be sufficient for the observed corrosion reaction, which is known to form electric (ionically and electronically) conductive Cu_xS dendrites. [29] These can lead to ionic (between the cells) and/or electronic (within the cell) micro-short-circuits, showing a characteristic "voltage noise" during the cell failure (Figure 3 b) and c). This reaction can be facilitated by increase in potential differences and/or onset of current flow,[30] thus gets significantly obvious after onset of the charge process. Indeed, those dendrites can be visualized *via* scanning electron microscopy (SEM) *post mortem* in a shortened cell, as shown in Figure 3 (e). As anticipated, those dendrites are composed of Cu and S elements, as demonstrated *via* SEM energy dispersive X-ray microscopy (EDX), shown in Figure 3 (f).

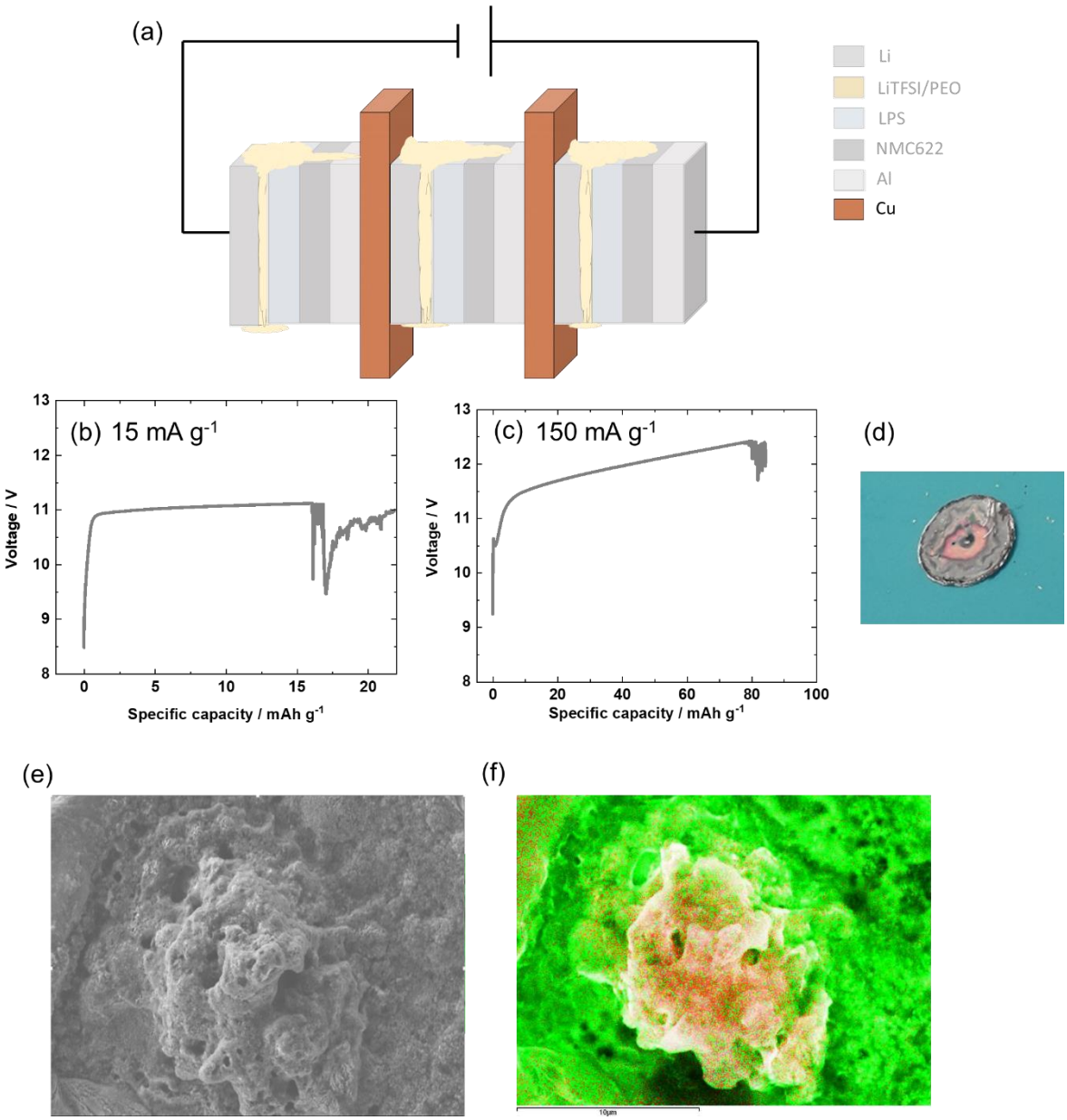

Figure 3: (a) Triple cell stack in bipolar design with area-oversized current collector (Cu) to verify and counteract the issue of molten LITFSI/PEO connection. (b) Indeed, a small charge capacity could be obtained with a specific charge current of 15 mA g^{-1} before the appearance of a failure yielding a specific capacity of only ≈ 15 mAh g^{-1}. (c) A significantly higher specific charge capacity of ≈ 80 mAh g^{-1} could be obtained after increasing the specific current to 150 mA g^{-1}, pointing to a time-dependence of this reaction causing cell failure. (d) Disassembly after post mortem of the cell revealed an almost fully corroded Cu collector, pointing to a chemical side reaction. (e) SEM revealed dendrites on the Cu current collector. (f) These dendrites are composed of Cu (green color) and S (red color) as revealed by SEM-EDX, which are likely responsible for the failure as discussed in main text.

Obviously, in addition to the design modification of the bipolar stack (Figure 3), also a material modification of the bipolar plates is necessary. To prevent corrosion reactions with sulfides, the area-oversized Cu is exchanged with (area-oversized) stainless steel, which is chemically more inert.[14] Indeed, failure-free charge discharge cycling performance is obtained (Figure 4 (a)), which even performs similar to the single cell (Figure 2). The similar performance demonstrates that the developed design of the bipolar stack is adequate.

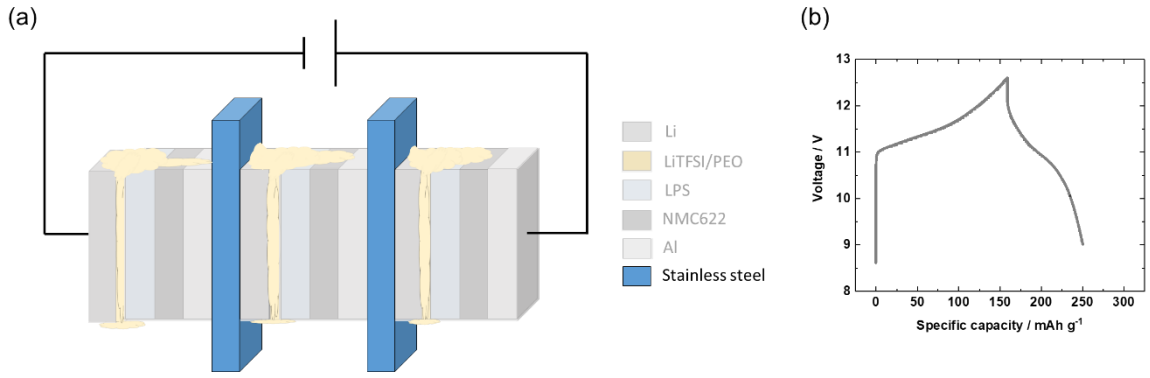

Figure 4: (a) Triple stack with area-oversized current collector (stainless steel). (b) The set-up reveals a failure-free galvanostatic charge/discharge, performing similar to the single cell shown in Figure 1.

Conclusion

The use of solid electrolytes in rechargeable Li metal batteries can have beneficial effects on cell and pack level. On cell level, their inflammable and mechanically rigid nature may help to realize Li metal as negative electrode, while on pack level their solid nature can realize the bipolar series stacking of cells. In this work, we can show that a simple triple cell stack of NMC622|LPS|LiTFSI/PEO|Li cell cells in bipolar configuration using a common Al/Cu clad as bipolar plate results in a short circuit even before the cell is charged. This can be attributed to an ionic connection between neighboring cells due to molten LiTFSI/PEO, as evidenced by differential scanning calorimetry (DSC). To prevent this, the cells were separated *via* an area-oversized Cu current collector. This design modification indeed results in a partial charge reaction, before another, in this case time dependent failure appears, which hints at an additional chemical origin of the observed failure. The disassembly of the failed cell reveals an almost fully corroded Cu collector, which may be attributed to the reaction with sulfides leading to the formation of Cu_xS based dendrites as visualized by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDX) technique. The replacement of Cu by chemically more inert stainless steel finally lead to failure-free charge-discharge cycling, with the stack having similar performance as a single cell. The performance similar to single cell proves sufficient functionality on pack level of the cell stack design obtained by the reported current collector measures

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References

1. Winter, M.; Barnett, B.; Xu, K., Before Li Ion Batteries. *Chemical Reviews* **2018,** *118* (23), 11433-11456.
2. Janek, J.; Zeier, W. G., A Solid Future for Battery Development. *Nature Energy* **2016,** *1*, 16141.
3. Xu, K., Nonaqueous Liquid Electrolytes for Lithium-based Rechargeable Batteries. *Chemical Reviews* **2004,** *104* (10), 4303-4417.

4. Tarascon, J. M.; Guyomard, D., New Electrolyte Compositions Stable Over The O-V to 5-V Voltage Range and Compatible With The $Li_{1+x}MN_2O_4$ Carbon Li-Ion Cells. *Solid State Ion.* **1994,** *69* (3-4), 293-305.
5. Zheng, H. H.; Tan, L.; Liu, G.; Song, X. Y.; Battaglia, V. S., Calendering Effects on the Physical and Electrochemical Properties of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Cathode. *J. Power Sources* **2012,** *208*, 52-57.
6. Kasnatscheew, J.; Rodehorst, U.; Streipert, B.; Wiemers-Meyer, S.; Jakelski, R.; Wagner, R.; Laskovic, I. C.; Winter, M., Learning from Overpotentials in Lithium Ion Batteries: A Case Study on the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) Cathode. *J. Electrochem. Soc.* **2016,** *163* (14), A2943-A2950.
7. Kasnatscheew, J.; Streipert, B.; Röser, S.; Wagner, R.; Cekic Laskovic, I.; Winter, M., Determining Oxidative Stability of Battery Electrolytes: Validity of Common Electrochemical Stability Window (ESW) Data and alternative Strategies. *Phys. Chem. Chem. Phys.* **2017,** *19* (24), 16078-16086.
8. Kasnatscheew, J.; Evertz, M.; Streipert, B.; Wagner, R.; Klopsch, R.; Vortmann, B.; Hahn, H.; Nowak, S.; Amereller, M.; Gentschev, A. C.; Lamp, P.; Winter, M., The Truth about the 1st Cycle Coulombic Efficiency of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) Cathodes. *Phys. Chem. Chem. Phys.* **2016,** *18* (5), 3956-3965.
9. Kasnatscheew, J.; Evertz, M.; Streipert, B.; Wagner, R.; Nowak, S.; Cekic Laskovic, I.; Winter, M., Changing Established Belief on Capacity Fade Mechanisms: Thorough Investigation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111) under High Voltage Conditions. *The Journal of Physical Chemistry C* **2017,** *121* (3), 1521-1529.
10. Kasnatscheew, J.; Börner, M.; Streipert, B.; Meister, P.; Wagner, R.; Cekic Laskovic, I.; Winter, M., Lithium Ion Battery Cells under Abusive Discharge Conditions: Electrode Potential Development and Interactions between Positive and Negative electrode. *J. Power Sources* **2017,** *362*, 278-282.
11. Streipert, B.; Röser, S.; Kasnatscheew, J.; Janßen, P.; Cao, X.; Wagner, R.; Cekic-Laskovic, I.; Winter, M., Influence of LiPF6 on the Aluminum Current Collector Dissolution in High Voltage Lithium Ion Batteries after Long-Term Charge/Discharge Experiments. *J. Electrochem. Soc.* **2017,** *164* (7), A1474-A1479.
12. Kasnatscheew, J.; Wagner, R.; Winter, M.; Cekic-Laskovic, I., Interfaces and Materials in Lithium Ion Batteries: Challenges for Theoretical Electrochemistry. *Topics in Current Chemistry* **2018,** *376* (3), 16.
13. Bieker, G.; Winter, M.; Bieker, P., Electrochemical In Situ Investigations of SEI and Dendrite Formation on the Lithium Metal Anode. *Phys. Chem. Chem. Phys.* **2015,** *17* (14), 8670-8679.
14. Jung, K. N.; Shin, H. S.; Park, M. S.; Lee, J. W., Solid-State Lithium Batteries: Bipolar Design, Fabrication, and Electrochemistry. *ChemElectroChem* **2019,** *6* (15), 3842-3859.
15. Kerman, K.; Luntz, A.; Viswanathan, V.; Chiang, Y. M.; Chen, Z. B., Review-Practical Challenges Hindering the Development of Solid State Li Ion Batteries. *J. Electrochem. Soc.* **2017,** *164* (7), A1731-A1744.
16. Kasnatscheew, J.; Placke, T.; Streipert, B.; Rothermel, S.; Wagner, R.; Meister, P.; Laskovic, I. C.; Winter, M., A Tutorial into Practical Capacity and Mass Balancing of Lithium Ion Batteries. *J. Electrochem. Soc.* **2017,** *164* (12), A2479-A2486.
17. Hao, F.; Han, F. D.; Liang, Y. L.; Wang, C. S.; Yao, Y., Architectural Design and Fabrication Approaches for Solid-State Batteries. *MRS Bull.* **2018,** *43* (10), 775-781.
18. Schnell, J.; Gunther, T.; Knoche, T.; Vieider, C.; Kohler, L.; Just, A.; Keller, M.; Passerini, S.; Reinhart, G., All-Solid-State Lithium-Ion and Lithium Metal Batteries -Paving the Way to Large-Scale Production. *J. Power Sources* **2018,** *382*, 160-175.
19. Wiesener, K.; Ohms, D.; Benczur-Urmossy, G.; Berthold, M.; Haschka, F., High Power Metal Hydride Bipolar Battery. *J. Power Sources* **1999,** *84* (2), 248-258.
20. Karami, H.; Mousavi, M. F.; Shamsipur, M., A Novel Dry Bipolar Rechargeable Battery Based on Polyaniline. *J. Power Sources* **2003,** *124* (1), 303-308.
21. Appetecchi, G. B.; Hassoun, J.; Scrosati, B.; Croce, F.; Cassel, F.; Salomon, M., Hot-Pressed, Solvent-Free, Nanocomposite, PEO-based Electrolyte Membranes II. All Solid-State Li/$LiFePO_4$ Polymer Batteries. *J. Power Sources* **2003,** *124* (1), 246-253.

22. Zaghib, K.; Shim, J.; Guerfi, A.; Charest, P.; Striebel, K. A., Effect of Carbon Source as Additives in $LiFePO_4$ as Positive Electrode for Lithium-Ion Batteries. *Electrochem. Solid State Lett.* **2005,** *8* (4), A207-A210.
23. Kasnatscheew, J.; Röser, S.; Börner, M.; Winter, M., Do Increased Ni Contents in $LiNi_xMn_yCo_zO_2$ (NMC) Electrodes Decrease Structural and Thermal Stability of Li Ion Batteries? A Thorough Look by Consideration of the Li^+ Extraction Ratio. *ACS Applied Energy Materials* **2019**.
24. Tachez, M.; Malugani, J. P.; Mercier, R.; Robert, G., Ionic-Conductivity of and Phase-Transition in Lithium Thiophosphate LI_3PS_4. *Solid State Ion.* **1984,** *14* (3), 181-185.
25. Lee, K.; Kim, S.; Park, J.; Park, S. H.; Coskun, A.; Jung, D. S.; Cho, W.; Choi, J. W., Selection of Binder and Solvent for Solution-Processed All-Solid-State Battery. *J. Electrochem. Soc.* **2017,** *164* (9), A2075-A2081.
26. Zhang, W. B.; Weber, D. A.; Weigand, H.; Arlt, T.; Manke, I.; Schroder, D.; Koerver, R.; Leichtweiss, T.; Hartmann, P.; Zeier, W. G.; Janek, J., Interfacial Processes and Influence of Composite Cathode Microstructure Controlling the Performance of All-Solid-State Lithium Batteries. *Acs Applied Materials & Interfaces* **2017,** *9* (21), 17835-17845.
27. Ates, T.; Keller, M.; Kulisch, J.; Adermann, T.; Passerini, S., Development of an All-Solid-State Lithium Battery by Slurry-Coating Procedures using a Sulfidic Electrolyte. *Energy Storage Mater.* **2019,** *17*, 204-210.
28. Shin, H. S.; Ryu, W. G.; Park, M. S.; Jung, K. N.; Kim, H.; Lee, J. W., Multilayered, Bipolar, All-Solid-State Battery Enabled by a Perovskite-Based Biphasic Solid Electrolyte. *Chemsuschem* **2018,** *11* (18), 3184-3190.
29. Graedel, T. E.; Franey, J. P.; Kammlott, G. W., The Corrosion of Copper by Atmospheric Sulfurous Gases. *Corrosion Sci.* **1983,** *23* (11), 1141-&.
30. Qiu, P.; Agne, M. T.; Liu, Y.; Zhu, Y.; Chen, H.; Mao, T.; Yang, J.; Zhang, W.; Haile, S. M.; Zeier, W. G.; Janek, J.; Uher, C.; Shi, X.; Chen, L.; Snyder, G. J., Suppression of Atom Motion and Metal Deposition in Mixed Ionic Electronic Conductors. *Nature Communications* **2018,** *9* (1), 2910.

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