

# Table of Contents

|  |     |
|--|-----|
| Acknowledgment .....   | III |
| Synopsis .....   | V   |
| Zusammenfassung .....  | VII |
| Table of Contents .....  | IX  |
| 1 Introduction – the supremacy of lithium-ion batteries .....  | 1   |
| 1.1 Inside Li-ion batteries .....  | 3   |
| 1.1.1 Physico-chemical principles .....  | 4   |
| 1.1.2 Electrode materials .....  | 5   |
| 1.1.3 Significance and challenges of state-of-the-art liquid electrolytes .....                                    | 6   |
| 1.2 The emergence of all-solid-state batteries .....   | 8   |
| 1.2.1 Concept and motivation .....   | 8   |
| 1.2.2 Solid electrolyte .....  | 9   |
| 1.3 All-solid-state batteries with a sulfide-based solid electrolyte .....   | 15  |
| 1.3.1 Electrochemical characterization of SSB with a sulfide-based SE .....  | 15  |
| 1.3.2 Interfacial reactivity between AM and SE .....   | 16  |
| 1.3.3 Mechanical deformation in SSB .....  | 19  |
| 1.4 The scope of the thesis .....  | 23  |
| 2 Materials and methods .....  | 25  |
| 2.1 Synthesis and characterization of glass amorphous $(\text{Li}_2\text{S})_x\text{-(P}_2\text{S}_5)_{1-x}$ ..... | 26  |
| 2.2 High-throughput SSB cell design and assembly .....   | 28  |
| 2.3 Electrochemical testing .....  | 30  |
| 2.3.1 Galvanostatic cycling and cyclic voltammetry .....   | 30  |

|       |  |    |
|-------|--|----|
| 2.3.2 | Electrochemical Impedance Spectroscopy .....   | 31 |
| 2.4   | Materials characterization .....   | 34 |
| 2.4.1 | Surface and interface characterization – X-ray photoelectron spectroscopy (XPS) .....  | 34 |
| 2.4.2 | Fundamental principles of <i>operando</i> XPS applied to SSB .....   | 37 |
| 2.4.3 | Imaging of complete SSB cell – X-ray tomographic microscopy .....  | 43 |
| 2.4.4 | Other characterization methods .....   | 49 |
| 3     | Development of the all-solid-state battery measurement platform .....  | 51 |
| 3.1   | Benchmark electrochemical performance of LPS75-based SSB cells with various active materials .....   | 51 |
| 3.1.1 | The drawback of metallic lithium as a counter electrode .....  | 52 |
| 3.1.2 | In-Li alloy as a suitable counter electrode .....  | 53 |
| 3.1.3 | $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{TiS}_2$ as low voltage benchmark active material .....  | 55 |
| 3.1.4 | $\text{LiFePO}_4$ and $\text{LiCoO}_2$ as high voltage cathode active material .....   | 57 |
| 3.2   | Optimization of the electrode microstructure .....   | 59 |
| 3.2.1 | Influence of active material particle size (micro- vs. nano-LTO) .....   | 59 |
| 3.2.2 | Influence of cell pressure on LPS .....  | 60 |
| 3.2.3 | Influence of electrode composition .....   | 61 |
| 4     | <i>Operando</i> and ex-situ XPS investigation of the interfacial reactivity between active materials and the LPS solid electrolyte .....                                       | 63 |
| 4.1   | Cathodic reactivity of LPS: Reactivity and potential profile across the electrochemical solid-solid interface between LCO and LPS directly probed by <i>operando</i> XPS ..... | 64 |
| 4.1.1 | Introduction .....   | 64 |
| 4.1.2 | Limitations of <i>ex-situ</i> XPS on the LCO-LPS interface .....   | 65 |
| 4.1.3 | <i>Operando</i> XPS observation of the reactivity of the LPS/LCO interface .....   | 67 |
| 4.1.4 | Potential gradient across the interface .....  | 73 |
| 4.1.5 | Conclusions .....  | 74 |

|       |   |     |
|-------|---|-----|
| 4.2   | Anodic reactivity of LPS75: Insights on the chemical and electronic evolution of cycled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in $\text{Li}_2\text{S-P}_2\text{S}_5$ enabled by <i>operando</i> XPS ..... | 76  |
| 4.2.1 | Introduction .....  | 76  |
| 4.2.2 | Electrochemical performance of the <i>operando</i> XPS cell .....   | 76  |
| 4.2.3 | <i>Operando</i> XPS on the LTO/LPS/VGCF interface .....   | 77  |
| 4.2.4 | LPS electrochemical stability below the LTO cycling voltage .....   | 81  |
| 4.2.5 | Limitations of <i>post-mortem</i> XPS experiments .....   | 83  |
| 4.2.6 | Impact of the LPS reduction byproducts on the cell electrochemical performance .....  | 85  |
| 4.2.7 | Conclusion .....  | 85  |
| 4.3   | <i>Ex-situ</i> XPS observation of LPS reactivity with LFP .....   | 87  |
| 4.4   | General conclusion .....  | 89  |
| 5     | Li migration and electro-mechanical deformation in all-solid-state batteries observed by <i>operando</i> X-ray tomography .....   | 91  |
| 5.1   | Motivation .....  | 91  |
| 5.2   | Pristine sample morphology .....  | 92  |
| 5.3   | Electrochemical performance of $\mu\text{-Sn/LPS/VGCF}$ WE in SSB .....   | 93  |
| 5.4   | Real-time observation of the electromechanical deformation in SSB .....   | 95  |
| 5.4.1 | Visualization of the deformation phenomena .....  | 95  |
| 5.4.2 | Morphological evolution of active materials particles .....   | 97  |
| 5.5   | Quantification of volume expansions .....   | 99  |
| 5.5.1 | Anisotropic volume expansion of $\mu\text{-Sn}$ particles .....   | 99  |
| 5.5.2 | Volume changes of the working electrode .....   | 100 |
| 5.6   | Lithium migration through a thick electrode .....   | 103 |
| 5.6.1 | Visualization of the lithium gradient .....   | 103 |
| 5.6.2 | Increased tortuosity hinders ion transport .....  | 104 |
| 5.7   | Conclusion .....  | 106 |

|       |  |     |
|-------|--|-----|
| 6     | Conclusion and Outlook .....   | 107 |
| 6.1   | Conclusion .....   | 107 |
| 6.2   | Outlook I: Further development of characterization techniques for all-solid-state batteries<br>109   |     |
| 6.2.1 | Electrochemical impedance spectroscopy of SSB .....  | 109 |
| 6.2.2 | Surface and near-surface characterization of the interfacial chemistry between the<br>active material and solid electrolyte .....  | 114 |
| 6.2.3 | Morphological characterization of the electrode-electrolyte interface .....  | 115 |
| 6.3   | Outlook II: towards a more viable all-solid-state battery .....  | 117 |
| 6.3.1 | Improved electrochemical performance with LiNbO <sub>3</sub> -coated LCO .....   | 117 |
| 6.3.2 | Infiltration of standard LiB electrode with solution processable SE .....  | 118 |
| 6.3.3 | A practical SSB cell architecture .....  | 119 |
| 7     | Annex .....  | 122 |
| 7.1   | Annex – Chapter 2 .....  | 122 |
| 7.1.1 | Surface morphology of solid electrolyte and composite working electrode .....  | 122 |
| 7.1.2 | Fundamental principles of <i>operando</i> XPS applied to SSB .....   | 123 |
| 7.1.3 | Operando X-ray tomographic microscopy on SSB .....   | 127 |
| 7.2   | Annex – Chapter 3 .....  | 128 |
| 7.3   | Annex – Chapter 4 .....  | 129 |
| 7.3.1 | Cathodic reactivity of LPS: Reactivity and potential profile across the electrochemical<br>solid-solid interface between LCO and LPS directly probed by <i>operando</i> XPS .....  | 129 |
| 7.3.2 | Anodic reactivity of LPS75: Insights on the chemical and electronic evolution of cycled<br>Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> in Li <sub>3</sub> S-P <sub>2</sub> S <sub>5</sub> enabled by <i>operando</i> XPS ..... | 134 |
| 7.4   | Annex – Chapter 5 .....  | 139 |
| 7.5   | Annex figures – Chapter 6 .....  | 142 |
| 7.5.1 | Electrochemical impedance spectroscopy performed on SSB .....  | 142 |

|       |  |     |
|-------|--|-----|
| 7.5.2 | Experimental procedure for the infiltration of solution-processable Li <sub>6</sub> PS <sub>5</sub> Cl into<br>standard LiB electrodes ..... | 144 |
| 7.6   | Annex Tables .....   | 147 |
| 7.7   | List of physical quantities .....  | 158 |
| 7.8   | List of abbreviations .....  | 159 |
| 7.9   | List of Figures .....  | 160 |
| 7.10  | References .....   | 169 |