# Summary

This work collects the outcomes of the research activity carried out to develop lab-scale ionic liquid- and polymer-based electrolytes, in the framework of workpakage 2 (WP2) as part Si-DRIVE project.

Si-DRIVE is a European project granted in 2019 in the framework of Horizon 2020, involving industrial and academic partners.

The ambition of Si-DRIVE is the development up to the TRL5 prototype demonstration of next-generation, cost-competitive rechargeable Li-ion battery cells for the EVs market, with demonstrated recyclability and manufacturable within Europe.

The Si-DRIVE consortium includes partners with expertise in the fields covering all the necessary steps, including material design and synthesis, electrochemical testing, prototype formation and production method validation, life-cycle assessment, and recycling process development. Si-DRIVE proposal built on existing lab-scale demonstrations of the concept for all the components, as part of the partners' expertise.

The technology includes a silicon-based negative electrode. Si is an earth-abundant material that can form alloys with Li, working in conveniently low electrochemical potentials window (between ≈0.01 and 0.6 V $Li^+/Li$), and having an ultrahigh theoretical specific capacity of 4200 mAh $g^{-1}$ in the highest lithiated form (i.e. $Li_{22}Si_5$). This is more than ten times higher than that of commercial graphite anodes relying on the intercalation paradigm, which can deliver a maximum of 372 mAh $g^{-1}$, corresponding to $LiC_6$. The main disadvantages of Si are the poor ionic and electronic conductivities and huge (< 300%) volume variations upon lithiation-delithiation cycles. The positive electrode consists of a high voltage lithium-rich layered oxide having a high specific capacity of ≥ 250 $mAhg^1$, which is devoid of Co to address cost and sustainability.

To address safety and improve cycle life, the electrolyte concept relies on highly conductive and thermally stable ionic liquid-based electrolytes1 for the first generation of cells. The second generation includes self-standing gel (and composite) polymer electrolytes encompassing the optimal ionic liquid solution, preferably obtained by solvent-free upscalable process, and allowing for in-situ deposition on top of the electrode to maximize the interfacial contact with the active materials.

The targets set by WP2 include the achievement of ionic conductivity values as high as 0.1 $mScm^{-1}$ at -10 °C and 1 mScm-1 at room temperature, thermal stability up to at least 150 °C, wide electrochemical stability, and compatibility with silicon-based negative electrodes, and high voltage lithium-rich layered oxide positive electrodes.

The polymer-based electrolytes were developed starting from ionic liquid solutions meeting the targets and using commercially available precursors for the polymer matrix using preparation processes relying on UV-light-induced free radical polymerization. The systems were developed pursuing improved electrochemical performance and compatibility with the electrode materials, notably exploiting in-situ polymerization, keeping in mind the need for easy scalability and sustainability in the preparation process.

The evolution of electrodes throughout the project was tackled by the investigation of Li salt solutions in different ionic liquids, and polymer-based electrolytes in cooperation among partners, towards the selection of the optimal combination for upscaling. The pursuit of the project targets drove the selection among the different systems investigated.

Covid-19 pandemic caused delays in the production at scale of nanostructured silicon anodes. Therefore, different kinds of silicon-based anodes were used by the partners, causing further delays and requiring more efforts to harmonize the results and select the optimal electrolyte composition. The characterizations reported in this work are mostly electrochemical ones, and based on the comparison of the different systems. Notably, the parent ionic liquid solutions served as a benchmark for the polymer-based electrolytes.

Broad investigation of different formulations for each system, and in-depth physico-chemical characterization could not be covered in the timeframe of the project considering the scope and is a possible basis for future works. This was

also due to the lack of promptly accessible facilities for the physico-chemical characteristics of the polymer electrolytes.

Following the overview of the global research context given above, Chapter 1 summarizes some electrochemical notions underlying the experimental work carried out. Chapter 2 deals with the investigation of ionic liquid-based electrolytes in combination with silicon-based negative electrodes and layered oxide positive electrodes. Chapter 3 reports the use of different polymer-based electrolytes in combination with silicon-based electrodes and high-voltage layered oxides. In chapter 4 it is demonstrated a multi-layer electrolyte approach, tackling the compatibility with the electrode materials.