Batteries, of different technologies, must operate for thousands of cycles at variable temperature to meet application requirements. Performance degradation is due to complex physico-chemical processes, involving active and non-active electrode components, as well as the electrolyte. In part, these phenomena occur at the electrode/electrolyte interface, owing both to the evolution of the active material and its electrochemical interaction with the electrolyte, potentially leading to electrode shape changes and passivation, but quite often involve the modification of the electrolyte bulk or separator, as well as transfer of materials across the cell - resulting in electrode poisoning - and current-collector corrosion. Furthermore, the mechanical failure of the electrode and the loss of electric contact can generate electrochemically inactive areas. This scenario is particularly critical in applications that require high stability and reliability, such as, prototypically, space ones, which fully lie in the field of topics targeted by DM n.352 (09/04/2022), Art.s 1.7 and 6.4a, specifically "Green revolution and energy transition". Among battery chemistries that are currently adopted for satellite applications, Li-based systems currently play a pivotal role. Commercial Li-ion batteries generally employ liquid electrolytes, which show poor stability in contact with the electrodes: this makes them often inappropriate for the relevant scenarios. In this field, solid-state batteries, with both Li and post-Li technologies, are a
promising solution for next-generation energy storage in which reliability, durability, high energy density and light weight are crucial aspects. Nevertheless, the above-mentioned material-evolution and degradation issues are even more crucial and less understood in solid-state Li batteries, than in liquid-based ones. Thus a special application-oriented research effort is needed in order to bring these chemistries to the stage at which they can be implemented in real-scale systems. In view of these tasks, often, accelerated ageing protocols are performed to speed-up the degradation processes, in view of assessing the impact on performance of common operating parameters, such as temperature, discharge/charge rates, cut-off voltage and depth of discharge, and predicting lifetime. Purely electrical tests are typically not enough to gain a thorough understanding of degradation processes and next-generation research will require extensive input is required regarding the evolution of materials under realistic conditions.

Initially, the research focus will be on materials synthesis, cell assembly/testing and post mortem analysis of single cells. Post mortem analysis will be carried out with both laboratory and commercial scale single cells. The cells will be aged with charge/discharge protocols, representative of real-life operation. Ageing tests will be followed by cell disassembly and autopsy. Portions of the cell components, especially the electrodes, will be analysed in the pristine state and after ageing, with common materials-science methods, such as X-ray micro-computed tomography (XmCT), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Moreover, they will be used to reassemble laboratory cells, to determine the nature and evolution of their electrochemical properties. The tests will be conducted using electrode parts taken from different portions of the cells and from different positions in the electrodes, to detect non-homogeneous ageing effects. At a more advances stage of research, imaging and spectroscopy tools methods will the used for the study of battery materials both, mainly in context, thanks to XmCT, but also with an appropriate selection of approaches, as per results of electrochemical testing.
such as: Raman spectroscopy, optical spectroscopies, X-ray photoemission spectroscopy microscopy and X-ray absorption spectroscopy. Finally, in operando monitoring tools, chiefly based on X-ray and neutron tomography and spectroelectrochemical approaches, will be developed in model cells in view of extending the protocol to real-life devices.

The PhD candidate will develop an interdisciplinary approach for tackling battery studies from the point of view of materials engineering, will set up the methodology and protocols for the morpho-electrochemical analysis of battery metarials as implemented in real devices and will devise novel routes towards next-generation in operando monitoring. Thin solid-state batteries will be fabricated by sputter-deposition, electrodeposition or functionally equivalent methods and will be investigated with a suite of characterization methods, both ex situ and in operando. After having tackled the fabrication issues and electrochemical and functional characterization, the research will be centred around electrochemical investigations and an appropriate selection of spectroscopies and micro-spectroscopies, according to the specific issues raised by electrochemical screening, such as: soft X-ray absorption microspectroscopy and X-ray fluorescence for the assessment of the morphochemical evolution of the battery materials during operation, especially tracking the chemical state and space distribution of the electrodis metals at the electrode-electrolyte interface. After this first-stage investigation, the characterisation of materials in device context will be refined with complementary techniques, aimed at clarifying open issues, e.g. with a selection of approaches akin to the ones listed below. (i) X-ray micro-computed tomography will allow to follow the evolution of the electrode-electrolyte interface and the formation of mechanical damaging resulting from battery cycling. (ii) Post-mortem TEM morphological analyses will allow an in-depth understanding of the microstructural damaging processes resulting, e.g. from intercalation-deintercalation sequences or phase transformations of conversion electrodes, and from mechanical mismatch of
the anode, electrolyte and cathode materials. (iii) The space distribution of the oxide types and other inorganic functional groups, as well as the chemical structure at electrode/electrolyte interphase will be analyzed by FT-IR microscopy and nanoscopy under different working conditions. (iv) Local environment of lithium atoms will be studied by ex-situ NMR spectroscopy, e.g. $^6\text{Li}$ and/or $^7\text{Li}$ magic-angle spinning (MAS) NMR spectroscopy. NMR analysis will enable us to study electrolyte and electrodes interaction, and degradation products. (v) In operando SAXS measurements to investigate structural and electrochemical performances of the batteries. 6 months of training at Thales Alenia Space Italia s.p.a., will be a specific qualifying educational objective of this PhD project.

Job opportunities

The PhD candidate will develop a joint approach for tackling battery studies from materials synthesis to in operando characterization, and will consolidate battery-oriented scientific and technological skills, including electrochemical cell fabrication, experimental protocols, data analysis and modelling. The candidate's profile will be highly attractive both in the research environment, where cross-disciplinary skills are more and more appreciated, and in the rapidly expanding industrial field of battery design, production and management.

Composition of the research group

1 Full Professors
2 Associated Professors
0 Assistant Professors
6 PhD Students

Name of the research directors

Benedetto Bozzini

Contacts

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Email benedetto.bozzini@polimi.it
phd-STEN@polimi.it

Additional support - Financial aid per PhD student per year (gross amount)

| Housing - Foreign Students | -- |
| Housing - Out-of-town residents (more than 80Km out of Milano) | -- |
**Scholarship Increase for a period abroad**

<table>
<thead>
<tr>
<th>Amount monthly</th>
<th>700.0 €</th>
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<tbody>
<tr>
<td>By number of months</td>
<td>6</td>
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</table>

**National Operational Program for Research and Innovation**

<table>
<thead>
<tr>
<th>Company where the candidate will attend the stage (name and brief description)</th>
<th>Thales Alenia Space Italia s.p.a.</th>
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</thead>
<tbody>
<tr>
<td>By number of months at the company</td>
<td>6</td>
</tr>
<tr>
<td>Institution or company where the candidate will spend the period abroad (name and brief description)</td>
<td>ZAG - Slovenian National Building and Civil Engineering Institute, Dimiceva ulica 12, 1000 Ljubljana, Slovenia</td>
</tr>
<tr>
<td>By number of months abroad</td>
<td>6</td>
</tr>
</tbody>
</table>

**Additional information: educational activity, teaching assistantship, computer availability, desk availability, any other information**

**Educational activities:** Financial aid per PhD student is available for purchase of study books and material, funding for participation in courses, summer schools, workshops and conferences, instrumentations and computer, etc. The amount is about Euro 5700.

**Teaching assistantship:** Availability of funding in recognition of supporting teaching activities by the PhD student. There are various forms of financial aid for activities of support to the teaching practice. The PhD student is encouraged to take part in these activities, within the limits allowed by the regulations.

**Computer availability:** individual use.

**Desk availability:** individual use. Accommodation in Politecnico’s Residences (http://www.residenze.polimi.it) is available for PhD candidates; special rates will be applied to selected out-of-town candidates (detailed info in the call for application).

**Research period abroad:** Our candidates are strongly encouraged (6 months minimum is mandatory) to spend a research period abroad, joining high-level, research groups in the specific PhD research topic, selected in agreement with the Supervisor. An increase in the scholarship will be applied for periods up to 6 months (approx. 700 euro/month- net amount).