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*Editorial*

# Study of Rechargeable Batteries Using Advanced Spectroscopic and Computational Techniques

**Bernardo Barbiellini [1,2,*], Jan Kuriplach [3] and Rolando Saniz [4]**

[1] Department of Physics, School of Engineering Science, LUT University, FI-53851 Lappeenranta, Finland
[2] Department of Physics, Northeastern University, Boston, MA 02115, USA
[3] Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-180 00 Prague, Czech Republic; Jan.Kuriplach@mff.cuni.cz
[4] Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium; rolando.saniz@uantwerpen.be
* Correspondence: Bernardo.Barbiellini@lut.fi

**Abstract:** Improving the efficiency and longevity of energy storage systems based on Li- and Na-ion rechargeable batteries presents a major challenge. The main problems are essentially capacity loss and limited cyclability. These effects are due to a hierarchy of factors spanning various length and time scales, interconnected in a complex manner. As a consequence, and in spite of several decades of research, a proper understanding of the ageing process has remained somewhat elusive. In recent years, however, combinations of advanced spectroscopy techniques and first-principles simulations have been applied with success to tackle this problem. In this Special Issue, we are pleased to present a selection of articles that, by precisely applying these methods, unravel key aspects of the reduction–oxidation reaction and intercalation processes. Furthermore, the approaches presented provide improvements to standard diagnostic and characterisation techniques, enabling the detection of possible Li-ion flow bottlenecks causing the degradation of capacity and cyclability.

**Keywords:** Li-ion battery; Na-ion battery; Li-air battery; spectroscopy techniques for batteries; first-principles calculations; cathode materials; anode materials; electrolytes; Li diffusion and intercalation



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## 1. Introduction

Energy storage systems are commonplace in small handheld devices, but they are being used more and more as a power source in larger scale applications, as an alternative or complement to fossil fuels. Examples include electric vehicles and balancing in electrical power grids. Li-ion battery (LIB) technology [1–4] is largely used for such applications. This technology, however, has several shortcomings, the most important being its limited energy density and lifetime, the latter currently in the range of a few years. Hopes are high for other technologies as well, such as Na-ion, Li-air and Li-sulphur batteries [5]. However, the understanding of the functioning of these technologies and of the related obstacles to their wider adoption is still lacking. This holds in many respects for LIB technologies as well. The objective of current research is to provide answers to the basic questions posed by the ageing mechanisms in Li-ion batteries [6]: How to detect early signs and what are the reasons for the degradation of a battery? How to improve the lifetime of a battery? How to recycle the expensive battery packs, making the best use of their possible second life? Answering these questions in a way relevant to the lithium industry can have important societal impacts [7,8]. The challenges in this endeavour are many. It is important to first realise that the challenges faced present a complexity implicating a hierarchy of scales, i.e., from the atomic scale [9] to the macroscopic scale [10]. Their study calls for joint experimental and theoretical work, as well as an interdisciplinary approach, involving physics, chemistry, materials science, and engineering, as the various scale hierarchies are coupled to each other and to the functionality of the Li-ion batteries in an intricate manner.

The research activities reported in this Special Issue tackle these challenges at different levels using various approaches.

## 2. Advanced Battery Characterisation

In situ and in operando X-ray techniques available at synchrotron radiation facilities provide powerful tools for battery material research, allowing a deep understanding of structural evolution, redox processes, and transport properties during cycling [11], and present us with a new avenue for battery technology characterisation [12]. As an example, in operando X-ray diffraction (XRD) and X-ray absorption have been useful to understand the reversible electrochemical lithiation of potassium iron hexacyanocobaltate [13]. Moreover, X-ray resonant inelastic scattering (RIXS) at the oxygen K edge is an experimental soft X-ray technique capable of directly probing the oxygen activity in the redox processes [14]. On the other hand, the use of high-energy X-ray scattering at synchrotron radiation facilities has enabled the study of the electronic wavefunctions associated with redox processes by means of Compton scattering [9,15–17]. An advantage of X-ray Compton scattering is that it can be effectively applied to commercial batteries, thanks to the high penetration power of high-energy X-rays [18,19]. In addition, the large reciprocal space range accessible to high-energy X-rays allows acquiring total scattering data for the analysis of the pair distribution function to study battery materials having short-range order only [20].

The role of internal interfaces in Li migration occurring in Li-ion batteries can be studied using first-principles simulations based on density functional theory (DFT) combined with positron annihilation spectroscopy [21]. The latter can be viewed as a cousin technique of Compton scattering, involving $\gamma$-rays instead of hard X-rays, allowing the identification of defects (that are often attractive for positrons) and their chemical surroundings in materials [22,23]. DFT-based simulations in conjunction with Mössbauer spectroscopy, moreover, can be applied to study the deep connection between magnetism, electronic, and atomic structure in cathode materials [24] allowing the identification of the redox state of cathodes. DFT-based simulations are also able to provide precious information regarding the effect of the local atomic environment and structural deformations on the electrochemical redox potentials [17]. This is well illustrated further by a computational study of the electrochemical potentials in a metal–organic framework used as cathode for Li-ion batteries [25]. In addition, DFT-based methods are used to explain the experimentally measured conductivity and capacity of anode materials, such as in high-capacity Na-ion batteries [26]. Most interestingly, such methods have also shown the potential of topological materials, such as $Na_3Bi$, to be used as anode materials [27].

## 3. Conclusions

The results presented in this Special Issue show important advances in research on rechargeable batteries. We can look into the mechanisms at the heart of battery technologies by applying a combination of quantum mechanical calculations and spectroscopic techniques, practically reconstructing the redox processes. The ultimate goal of this body of research is the development of a probe ensemble capable of visualising lithium insertion in real time and on an atomic scale, in order to enable systematic routes to better battery diagnostics and to improve the efficiency and performance of batteries.

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