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The ENEA's 2019–2021 Three-Year Research Project on Electrochemical Energy Storage

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This work describes the research activities carried out by ENEA in the three-year period 2019–2021 as a part of the Electrochemical Storage project. The project was part of a larger and more integrated project for energy storage, itself contained in the Electric System Research program. Within the project, various research lines were carried out: From the development of materials for electrodes to the testing of electrolytes and separators, both for lithium and sodium-ion batteries, evaluation of the use of lithium metal batteries, and studying how to give a second life to used batteries. Dissemination of the results was an integral part of the program. The reasons that have been adduced to articulate the research plan and the main results obtained are reviewed in this concept.

1. Introduction

The Electric System Research is a national program which includes a series of research and development activities aimed at reducing the cost of electricity and improving the reliability and quality of the service for the end users. The objectives of the program are the reduction of the impact of the electricity system on the environment and on the health of citizens.[1] These objectives can be achieved through the rational use of energy resources to guarantee Italy the conditions for sustainable development. Research and development activities, objectives, and economic allocations are defined through three-year plans approved by the Ministry of Economic Development (and starting from 2020 onwards by the Ministry of Ecological Transition) once the observations resulting from a public consultation have been acquired and after having obtained the opinion of the Italian Regulatory Authority for Energy, Networks, and the Environment (ARERA). For the implementation of the research activities defined in the three-year plans, the competent ministry stipulates a program agreement with the three entrusted subjects, namely Ricerca sul sistema energetico (RSE S.p.A), Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile (ENEA), and Consiglio nazionale delle ricerche (CNR). These latter then elaborate triennial implementation plans, articulated in research projects. In the triennial plan covering the period 2019–2021, ENEA has divided their activities into ten projects. Eight projects are addressed to develop product and process technologies essential for the energy transition while two are oriented to introduce models functional to the energy transition and security in the sectors of technologies and systems. One of the projects, called Storage Systems and Related Interfaces with the Networks, dealt with energy storage. This project was divided into three subprograms dedicated respectively to Electrochemical Storage, Thermal Storage, and Power-to-Gas Conversion which also includes the production of hydrogen from renewable sources. In this paper, the Electrochemical Storage project will be reported in detail.

2. Outcomes of the Project

At the basis of the research Electrochemical Storage project there are a series of considerations that will be quickly exposed in the following. Lithium-ion battery (LIB) represents one of the most technologically advanced forms of electrical energy storage, both for the high value of the energy density and for the versatility of the product in terms of charge and discharge rate. This battery was introduced on the market in 1990 by Sony Energy. Consumer electronics were the first to benefit from this technology and the application of rechargeable lithium-ion batteries to the so-called 3 C equipment (Cellular, Cameras, and Computers) has favored the increasingly development of compact, lightweight, and portable systems.[2] LIBs require low maintenance, an advantage that most other chemistries cannot claim. They do not have the annoying memory effect typical of nickel–cadmium batteries for which no programmed cycle is required to prolong battery life. Furthermore, self-discharge is less than half that of nickel–cadmium, making LIBs suitable for automotive applications as well. From this point of view, however, it must be considered that the autonomy of fully electric powered cars is still limited,[3] an autonomy that progressively decreases due to the loss of

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battery capacity during the repeated charging and discharging cycles. Furthermore, about stationary storage, nowadays the costs of LIBs are too high.[4] For the construction of storage systems for electromobility or for stationary energy storage, further technological progress and greater cost competitiveness are hence required. For this reason, great part of the activities carried out inside the ENEA project were mainly oriented towards materials for innovative LIBs with the aim of increasing energy density and reducing manufacturing costs.

The basis of the success of the Sony Energy battery was the replacement of lithium metal with petroleum coke, which is capable of reversibly interacting with lithium ions.[5] Researchers from Panasonic and Sanyo then replaced petroleum coke with graphite resulting in increased voltage and energy densities. Graphite, thanks to its laminar structure, can in fact intercalate lithium by inserting it between the graphene planes. Lithium is inserted into the graphite as an ion while the electrons are delocalized within the conduction band of the graphite, at a value of the potential slightly higher (a few tens of mV) than that of metallic lithium.[6] Compared to lithium metal, graphite has the disadvantage of having a lower specific capacity (about an order of magnitude), but its use solves most of the safety issue associated with lithium metal anodes.

Lithium metal batteries have been a real challenge in the past. Research on lithium metal batteries, which began around the 1950s, quickly led to the commercialization of the first primary (not rechargeable) batteries which were proposed on the market at the end of the 1960s.[7] Unsurprisingly, development of lithium metal rechargeable batteries has been slower. The main problems were related to the low cycling efficiency of lithium: only a part of the lithium involved in the charging process remained available for the subsequent discharge with a consequent decrease in the capacity of the system. Several tricks were proposed to solve this problem, and, through a combination of these, the Canadian company Moli Energy created a rechargeable lithium metal battery in the late 1980s. Unfortunately, NTT Docomo, the company that marketed the accumulators developed by Moli Energy, was forced to withdraw them from sale due to a flame vent episode that caused injury to the user.[8] Nonetheless, lithium metal batteries have great advantages over cutting-edge LIBs in terms of energy density and cost, which present huge opportunities for long-range, low-cost electric vehicles in the future. For these reasons, various activities on lithium metal batteries have been planned within the project. The activities involved methods for protecting the surface of lithium metal, the development of materials for lithium–oxygen batteries and the study of lithium–sulfur batteries.

Even though LIBs and lithium metal batteries promise further performance improvements, it must still be considered that their development for large-scale applications is limited by the scarcity of lithium on the earth's crust. In fact, lithium occurs naturally in many rocks and in some brines, it can still be considered a rare element because it constitutes only 0.002% of the earth's crust and appears only 33rd on the scale of relative abundances of the elements.[9]

On the contrary, sodium is very abundant; the earth's crust contains 2.6% sodium by weight, making it the sixth most abundant element on the Earth. As for the electrochemical characteristics, sodium has a very low redox potential ($E°$ (Na^+/Na) = −2.71 V compared to the standard hydrogen electrode, only 0.3 V higher than that of lithium) making the sodium-based rechargeable electrochemical cells very promising for high energy density energy storage applications.[10] Research activities on sodium batteries began around the 1960s and were directed towards the development of high temperature batteries and quickly led to the development of a sodium–sulfur battery operating at around 300 °C developed for automotive purposes.[11] At that time, a series of studies focusing on intercalation materials suitable for use as cathodes in low temperature sodium batteries began,[12,13] but the promising results obtained in the development of LIBs held back this research. However, it is undeniable that the development of sodium batteries operating at room temperature (RT) would represent a significant advantage over lithium batteries. For this reason, the study on sodium-ion batteries (SIBs) operating at RT was included in the project, with the final goal to replace LIBs in large scale applications.

A possible strategy to reduce the costs necessary to equip an energy production plant with a LIBs stationary storage system is to use batteries that have been already used and are no longer suitable for their first application. For example, the useful life of a LIB for electric cars is approximately 10–12 years. The residual capacity of the battery, when the battery is removed from the car, can still reach up to 80% of the nominal one.[14] This represents a significant percentage for other uses but is not suitable for a car. Therefore, such a battery can be used for powerless applications, such as to stabilize the grid interactions of photovoltaic systems and to reduce the overall residential demand from the grid.[15] Following this concept, a series of activities aimed at giving a second life to used cells have been included within the project. These activities involved the realization of a module and its management system. The module was also used to store energy coming from renewable sources in a car recharging system.

The Electric System Research is a program that provides for the wide spreading of the obtained results. For this reason, results dissemination was an integral part of the research project. Moreover, the activity on electricity storage has led to the participation in various international initiatives where it has been possible to illustrate the activities in progress and acquire information on the programs ongoing in other countries. The participation was also preparatory to the role of technical, scientific, and programmatic support played by ENEA towards the competent Ministries.

ENEA played an active role in carrying out the research activities. In addition to ENEA, twelve university research groups from ten departments located in seven universities participated in the project. The university research groups are listed in table 1. The research activities can be grouped into five lines of activity:

1. Innovative electrode materials for Li- and Na-ion batteries.
2. Electrolytic materials for Li- and Na-ion batteries.

Table 1. List of university departments involved in the project.

Department	University
Hydro-Eco Research Centre [a]	Sapienza University of Rome
Department of Chemical Sciences	University of Napoli Federico II
Physics Department	University of Rome Tor Vergata
Department of Basic and Applied Sciences for Engineering	Sapienza University of Rome
Department of Chemistry – School of Science and Technology	University of Camerino
Department of Applied Science and Technology	Politecnico di Torino
Department of Chemistry "Giacomo Ciamician"	Alma Mater Studiorum – University of Bologna
Department of Chemistry	Sapienza University of Rome
Department of Information Engineering	University of Pisa
Department of Industrial Engineering	University of Rome Tor Vergata

[a] The Hydro-Eco Research Centre involves four departments of the Faculties of Mathematical, Physical and Natural Sciences (Department of Chemistry) and Engineering (Department of Basic and Applied Sciences for Engineering; Department of Chemistry, Materials and Environment; Department of Mechanical and Aerospace Engineering) of Sapienza University of Rome.

3. Lithium metal batteries.
4. Second life.
5. Diffusion of the results.

2.1. Innovative electrode materials for Li- and Na-ion batteries

The research activities carried out on electrode materials mainly concerned anode materials and, to a lesser extent, cathode materials. Among anodic materials, hard carbons (HCs) have been extensively studied. The effect of the metal hydroxides (MeOH with Me = Na, K, Rb, Cs) in the HCs activation mechanism[16] and the use of various binders such as Na–carboxymethylcellulose (CMC), alginate (Alg), polyacrylic acid (PAA), and poly(vinylidene difluoride) (PVdF) was investigated.[17]

The effect of the cation size on the HCs activation process was explained considering that the alkali metal acts through a mechanism combined which on the one hand determines an increase in the porosity of the carbon and on the other one, an increase in the inter-atomic distance of the carbon structure. The electrochemical results showed that absolute capacity for the activated sample follow the trend KOH > CsOH > NaOH > RbOH. This result seems to confirm that the activation of HCs is influenced from both lattice dilatation and chemical-physical structure modification. Mixed effects can explain the best positive results obtained with KOH for which a higher porosity is recorded together with a good dilation of the lattice.[16]

Among the various binders, CMC-based electrode delivered the best performance in terms of discharge capacity. During the first cycle, all electrodes evidence a capacity on the order of 600–700 mAh g^{-1} and the corresponding Coulombic efficiencies of around 56%. During the second cycle, the discharge capacity of CMC-based electrode was 421 mAh g^{-1} at 0.2 C, while lower values of 360, 350, and 350 mAh g^{-1} were obtained for Alg-, PAA-, and PVDF-based electrodes, respectively. According to these results, the enhanced capacity of an electrode using CMC for LIBs can be attributed to improved mechanical and interfacial properties and uniform electrode morphology. When cycled at 2 C rate, CMC confirmed to be the best electrode binder showing the highest first cycle capacity. However, the PAA-based electrode showed enhanced cycling stability.[17]

Metal oxides were proposed as alternative anodes for LIBs and iron oxides were selected as potential candidate for the realization of high-capacity negative electrodes. A simple yet effective vanillin-templated synthesis together with a low-impact poly(acrylic acid)-based electrode processing allowed to obtain a low-cost and sustainable Fe_2O_3 anode material which exhibits remarkable rate performance, even in long-term cycling. The cells delivered capacity values up to 700 mAh g^{-1} under prolonged galvanostatic cycling at 500 mA g^{-1}, as well as excellent rate capability and high efficiency.[18] Composite anode material based on Fe_3O_4 and reduced graphene oxide was prepared by base-catalysed co-precipitation and sono-chemical dispersion. Electrochemical characterization highlights specific capacities higher than 1000 mAh g^{-1} at 1 C, while a capacity of 980 mAh g^{-1} was retained at 4 C, with outstanding cycling stability.[19]

Thanks to its high theoretical capacity, abundant availability and respect for the environment, silicon has been proposed as a possible alternative to graphite. Already in the previous three-year program this material had been studied even reaching the realization of a complete battery.[20] In this three-year plan, silicon nanocomposites (silicon on nanocarbon) and silicon nanowires were further investigated to solve the problems associated with the large volume change and the unstable formation of the solid electrolyte interphase (SEI).

A technique for producing multilayer carbon–silicon nano-composite electrodes was developed. Carbon nanostructures were produced by plasma-enhanced methane cracking processes while silicon nanospheres were deposited via a simply liquid dispersion technique. SEM analysis showed that the carbon substrates, after the functionalization process with silicon, maintained their mesostructure and shape. Electro-chemical analysis showed that, although silicon is well confined within the carbon structure, a decrease in the specific capacity was observed as the cycle progresses. Furthermore, a high irreversible capacity was observed in the first cycle which was related to the formation of the SEI. Upon cycling, the electrodes presented a stable capacity between 500 and 650 mAh g^{-1} and good reversibility.

Silicon nanowires were grown on copper[21] or carbon paper[22] substrate and the influence of growth parameters (silane gas pressure, temperature, and deposition time) on the morphology and crystalline structure of the product was evaluated. The electrochemical characterization showed that a large irreversible capacity affected the electrode during the first cycle and, to a lesser extent, during the second cycle. In subsequent cycles a good reversibility was observed even if the Coulombic efficiency did not exceed 95%, suggesting the formation of an unstable SEI film and a continuous decomposition of the electrolyte on the silicon surface.[21] Considerable loads of active material (2–5 mg cm^{-2}) and, consequently, high-capacity densities was obtained using carbon paper as the substrate. It has been observed that, a very slow first cycle (C/40) helps the formation of a stable SEI on the silicon surface and improves the performance of the cells. However, the cycle life was considered not entirely satisfactory: a dense silicon layer found underneath the nanowires could be responsible for the loose of electrical contact between the active material and the substrate upon cycling.[22]

Another research activity concerned the use of magnesium hydride as anode for LIBs. The study involved the grinding of the materials and the embrittlement with hydrogen to reduce the crystalline size. The electrochemical analysis showed that, after the first discharge process in which the electrode has exhibited a capacity of 1400 mAh g^{-1}, the capacity rapidly reduces to 300 mAh g^{-1} already in the second cycle and tends to further decrease in subsequent cycles. Three hypotheses have been formulated to explain this behaviour: (i) irreversible decomposition of the electrolyte with the formation of a passivation layer on the surface of the MgH_2, (ii) loss of electrical contact between the active material and the electrical conductor, and (iii) insufficient physical and electrical contact between LiH and Mg, which significantly hampers the kinetics of the conversion process.

Titanium oxide[23] and tin[24] were also tested as anodes for LIBs. Pulsed laser deposition was applied to TiO_2 target materials to produce thin films of TiO_2 nanoparticles on aluminium substrates. Compact and dense TiO_2 thin films composed of nanoparticles were obtained with both anatase and rutile phases. The as deposited films were found electrochemically inactive in lithium half cells. Post-deposition annealing (either in argon or air) at temperature of 500 °C promoted the rutile to anatase phase transition and boosted the electrochemical activity.[23]

A tin-graphite (Sn/C) composite anode containing also a glassy solid electrolyte (LiI–Li_3PS_4, LPS) was synthesized via a one-step, manual grinding. Potentiodynamic cycling with galvanostatic acceleration analysis and cyclic voltammetry of Sn/graphite|LPSI|Li cells demonstrate that electrochemical processes of graphite are promoted by integrating it with Sn. The improvement appears as increased battery capacity in galvanostatic charge/discharge cycling.[24]

As regards the cathode material, the interest was directed to lithium-rich cobalt free materials[25] or materials with low cobalt content.[26–28]

A Co-free over-lithiated material with a limited nickel content, of formula $Li_{1.25}Mn_{0.625}Ni_{0.125}O_2$, was synthetized by a facile solution combustion synthesis. The material was able to exchange reversibly a practical specific capacity at RT of 230 mAh g^{-1} at C/10 for almost 200 cycles. Also, the rate capability was good; the material discharged 118 mAh g^{-1} at 2 C.[25]

A strategy to reduce the content of cobalt of a typical Li-rich material by co-doping with lithium and aluminium was investigate. Through a rational balancing of aluminium and lithium content with respect to cobalt, an optimized material with of formula $Li_{1.28}Mn_{0.54}Ni_{0.13}Co_{0.02}Al_{0.03}O_2$ was obtained.[26] The material delivered 214 mA h g^{-1} during the first discharge cycle with a Coulombic efficiency of 81%. Furthermore, the material showed increasing discharge capacities upon cycling. An almost constant specific capacity value of about 200 mA h g^{-1} was exhibited from cycle 50 to cycle 200.

A series of innovative materials with general formula $Li_{1.2+x}Mn_{0.54}Ni_{0.13}Co_{0.13-x-y}Al_yO_2$ (where $0.03 \leq x \leq 0.08$ and $0.03 \leq y \leq 0.05$) capable to supply large reversible specific capacities (around 200 mAh g^{-1}), stable cycling performance, and reduced voltage decay was synthetized.[27] All the material showed a first cycle specific capacity higher than 200 mAh g^{-1} (Figure 1).

The material of formula $Li_{1.23}Mn_{0.54}Ni_{0.13}Co_{0.07}Al_{0.03}O_2$ exhibited a first cycle specific capacity of 226 mAh g^{-1} and, despite the significative reduction of cobalt, the capacity was still 225 mAh g^{-1} after 200 cycles. The simultaneous synthesis of reduced graphene oxide and lithium–manganese-rich material ($Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$) was demonstrated starting from end-of-life LIBs. Quantitative extraction of the target metals (Co, Ni, Mn) and oxidation of graphite to graphene oxide (GO) were simultaneously achieved using a $KMnO_4$ solution. A Mn-rich metal solution resulted after GO filtration. This solution was directly employed for the synthesis of $Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$ cathode material. It was found that some impurities in the material, such as silicate, sulphate, and copper, can improve the

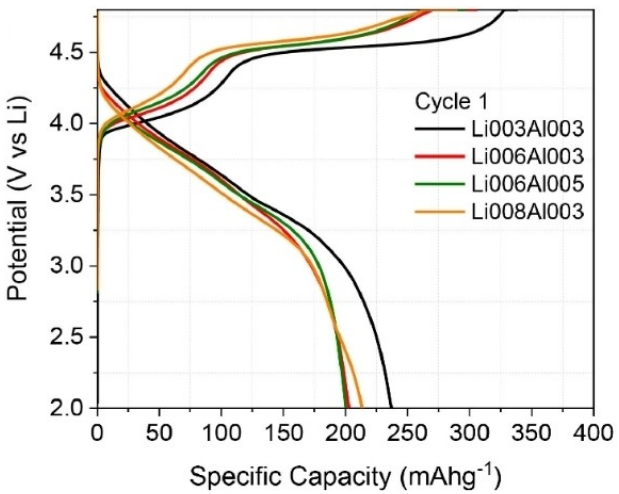

Figure 1. Voltage profiles as a function of the specific capacity during the first cycle for materials with general formula $Li_{1.2+x}Mn_{0.54}Ni_{0.13}Co_{0.13-x-y}Al_yO_2$ cycled at a current density of 37.7 mA g^{-1} (C/10). Reproduced from Ref. [27] Copyright (2022), with permission from Elsevier.

cathode performance both in terms of capacity retention and voltage fading. A second cycle capacity as high as 242 mAh g^{-1} was recorded. After 100 cycles, the capacity value decreases to 177 mAh g^{-1}, corresponding to a capacity retention of 73%. During the first 100 cycles, the potential associated with MnO_2 lithiation shifts downward from 3.3 to 2.9 V with a mean voltage decay of 4 mV per cycle.[28]

Layered oxides were synthesised by high temperature solid state synthesis. The effect on the structure and morphology of the material obtained was studied with X-ray diffraction, thermogravimetry and SEM techniques. Metal oxides were synthesised by mechano-chemistry and high temperature sintering. The study focused on lithium nickel manganese oxide doped with chromium, iron, or both. Various synthetic ways have been tested for the preparation of the cathode material of formula $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) in view of their possible use for the preparation of large amount of material. Finally, a synthetic method to produce LNMO in a batch of 1 kg was fine-tuned. The material obtained was electrochemically tested showing electrochemical properties equal to those obtained on a laboratory scale.

Parallel to the activities just described, anodes, cathodes and separators from plant origin were taken into consideration.

Self-supporting negative electrodes based on interconnected two-dimensional carbonized cotton fibres were prepared.[29] The reversible specific capacity at 1 C rate after 30 cycles was higher than 225 mAh g^{-1}. The electrode maintained a rather stable specific capacity values well more than 200 mAh g^{-1} up to 400 cycles.

Carbon derived from hazelnut shell has been obtained by hydrothermal processing of the bio-waste followed by thermal treatments and laser irradiation in liquid. When used as the anode of a LIB cell, the irradiated material showed a high specific capacity (1108, 682 and 578 mAh g^{-1} at cycles 1, 10 and 20, respectively), good capacity retention (52% at cycle 20 in respect to cycle 1), and relatively high first cycle Coulombic efficiency (56%).[30]

Furthermore, components of vegetable origin were tested as a binder[31–37] for both LIBs and SIBs. The use of pullulan as a binder was first demonstrated in a supercapacitor with carbon electrodes obtained from pepper-seeds waste[31,32] and then in a lithium metal battery using a LNMO-based cathode.[33] The cell performance was compared to that of cells assembled with PVdF. At C/10, the specific capacity of the cathode prepared with the pullulan was 127 mAh g^{-1}, slightly higher than that of PVdF (124 mAh g^{-1}) while the capacity retention at higher C-rates and under repeated cycling was similar.[33] The pullulan was also used as a binder for the production of cathodes based on $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC). The cathodes exhibited up to 135 mAh g^{-1} of composite material and 167 mAh g^{-1} of NMC, and excellent cycling stability over 500 cycles along with good capacity retention at high C-rates.[34] Electrodes prepared using pullulan or the bifunctional electronically conductive poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) demonstrated to be a valuable alternative to PVdF. Specifically with PEDOT:PSS a greater utilization of the active material was achieved compared to a similar PVdF-based electrode (Figure 2).[35]

It was also demonstrated the feasibility of a chitosan-based binder to produce freestanding electrodes for Na ion cells, without the use of organic solvents and current collectors in electrode processing[36] and sodium alginate as binder for lithium titanate-based electrodes.[37] Semisolid redox flow batteries simultaneously address the need for high energy density and design flexibility. For this kind of batteries, high electrical percolating network and elevated electrochemical stability of the flowable electrodes are required. For these reasons, the effect of the ion concentration on the electronic percolating network of carbonaceous slurries was studied.[38] It was found that the electrical percolation is more efficient when super-concentrated electrolytes are used. Indeed, the slurries with molal concentration equal to 3.0 mol kg^{-1} featured percolating resistances smaller than those of 0.5 mol kg^{-1} based slurries.

The fabrication of large-scale electrodes was carried out by rotogravures methods.[39] It was found that this technique did not allow to obtain high electrode loads. To overcome this problem, a multilayer process was adopted in which several layers were superimposed. The electrode performance was evaluated in a lithium metal cell. Commercial $LiFePO_4$ (LFP) was used as the active material. The electrodes showed good stability and rate capability; discharge capacities exceeding 100 mAh g^{-1} at 2 C rate were recorded. However, the electrode loads were found too low for practical applications. It was supposed that the load could be improved by increasing layer thickness and density. Electrode deposition techniques that avoid the use of volatile organic compounds have been developed. This allows not only to replace toxic substances such as N–methyl pyrrolidone with water, but also to easily recover the cathode powder after the use. LFP was used as the active material. The electrodes were prepared using water as process fluid and ethyl vinyl acetate as the binder. A LFP/

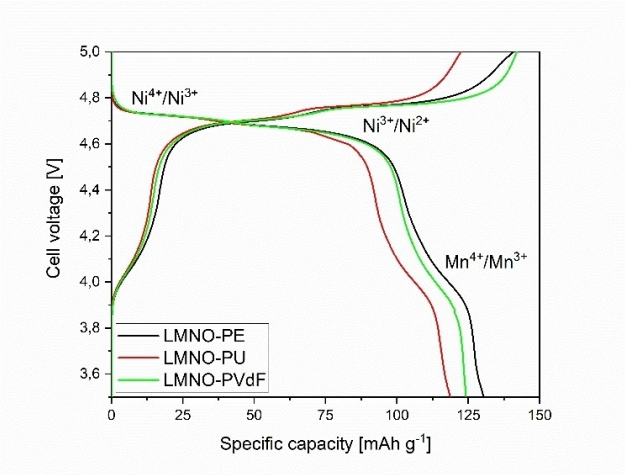

Figure 2. Voltage profiles as a function of time for the first charge/discharge cycle of the electrode prepared with PEDOT:PSS (LNMO–PE), pullulan (LNMO–PU)) or PVdF (LNMO–PVdf) as the binder. Reproduced from Ref. [35] Copyright (2022), with permission from The Authors.

graphite bipolar cell with a capacity of 50 mAh was assembled with these electrodes.

Theoretical studies were conducted to understand the Li- and Na-ion de-insertion/insertion mechanisms from/into the active materials.

The insertion of Li-ion into the lattice of the mixed olivine $LiCo_{1/3}Fe_{1/3}Mn_{1/3}PO$ was investigated through advanced structural characterization, based on *ex-situ* synchrotron radiation diffraction coupled with first-principles simulations on samples at different lithium contents. It was found that the mixing of the three transition-metal cations in the olivine lattice leads to a solid solution, providing the olivine lattice with the necessary flexibility to retain its single-phase structure during cell operation.[40]

As regards electrode materials for SIBs, theoretical studies have been carried out to highlight the structure-property relationships that are of interest for the sodium ion insertion and extraction processes in nanostructured electrodes. A first-principles study of the P2-type Mn-deficient layered oxide of formula $Na_xNi_{0.25}Mn_{0.68}O_2$ was carried out. The feature of the material was examined at the atomistic level to determine the O-redox activity at different sodiation stages, while concurrently providing new insights on the underlying mechanisms. Indeed, accurate electronic structure analysis revealed that de-sodiation is coupled to $Ni^{2+} \rightarrow Ni^{3+}$ oxidation and, when the state of charge goes up to 4.5 V, further oxidation to Ni^{4+} with a non-innocent contribution of O^{2-} takes place. Mn^{4+} does not participate to the redox reaction.[41]

The factors that directly affect the sodiation/de-sodiation processes have been identified at the electrode/electrolyte interface. *Ab-initio* computational simulations of the geometric and electronic properties of cathodes for SIBs were performed[42] and the atomic interaction between the surface of the ionic polymers and the sodium metal electrode was investigated.[43–45] Using a new surface slab model, the interaction between the layered $Na_{0.85}Li_{0.17}Ni_{0.21}Mn_{0.64}O_2$ (001) surface and the Na^+ ions was examined to identify the most favourable adsorption sites and the possible paths for the migration of the Na^+ ions on the electrode surface. The analysis of atomic partial charges and atomic magnetic moments revealed that Li has a purely structural role, while Ni and Mn actively participate in both redox processes and electronic conduction.[42]

Studies on TiO_2 anatase, which has been proposed as a promising anode material for Na-ion batteries, showed that the exposed crystal facets in different morphologies of nanostructured anatase can affect the electrochemical performance. The comparison of the energy barrier values, computed by means of the climbing image-nudge elastic band method, allowed to state that the (001) surface is the most effective termination for Na^+ insertion.[43] It was also found that field polarization affects Na^+ uptake as well as titania electronic features, promoting redox processes within Ti sublattice. These results highlight the high-energy (001) surface is the most active, for both directions of external fields, proving its activity to be exerted reversibly.[44]

To address the structural and electronic properties of heterointerfaces between the MoS_2 monolayers and graphene, a potential anode material for Na-ion batteries, two MoS_2 polymorphs were considered. It was showed that the best Na host site is found at the MoS_2 side of the interface, and the evaluation of the band structure revealed a proper n-type character of the graphene moiety, which is responsible for electric conduction. Analysis of structural features along the diffusion transition states allowed to identify the strong coordination of Na^+ with the exposed S atoms as the main feature hindering an effective diffusion.[45]

Following the route paved by Ru-based Li-rich cathode materials, a first-principles investigation of a Ru-doped Na_xTMO_2 (TM = Ru, Ni, and Mn) system and the related structural and electronic properties of interest for SIBs was investigated.[46]

Theoretical studies on SIBs have also confirmed with experimental one. Compounds of general formula $Na_x[Li_yNi_zMn_{(1-y-z)}]O_\delta$ have been synthesized, characterised, and used in the preparation of cathodes for sodium ion cells.[47] The $NaLi_{0.2}Ni_{0.25}Mn_{0.75}O_\delta$ was synthetized and electrochemically characterized in a sodium cell: the discharge-specific capacity increased with cycling, reaching at the end of the fifth cycle a capacity of 82 $mAh\,g^{-1}$. The electrode was then coupled with a negative electrode based on nanostructured tin deposited on reduced graphene oxide to form a full sodium-ion cell. The cell's power response was evaluated by discharging the SIB at different rates. At the lower discharge rate, the anode capacity approached the rated value (170 $mAh\,g^{-1}$, based on the capacity of the negative electrode). By increasing the discharge current, the capacity decreased but the decline was not so pronounced: the anode discharged about 80% of the rated capacity at 1 C rate and more than 50% at 5 C rate. The synthesis procedure was then scaled-up to produce about 1 kg of the material.

2.2. Electrolytic materials for Li- and Na-ion batteries

The effect of the addition of ionic liquid (IL) to lithium-ion electrolyte was studied. Commercial IL (1-butyl-1-methylpyrrolidinium hexafluorophosphate) was added to 1.0M $LiPF_6$ in ethylene carbonate–dimethyl carbonate (LP30). These mixtures were employed in high voltage Li/LNMO cells. The cells exhibited high specific capacity of about 110 $mAh\,g^{-1}$ over 200 cycles and improved Coulombic efficiency.[48]

Innovative electrolytes based on non-commercial cation N–methoxy ethyl–N-methyl–piperidinium were synthesised. The IL salified with bis(trifluoromethanesulfonyl)imide exhibited high ionic conductivity (2.4×10^{-3} $S\,cm^{-1}$ at RT), wide electrochemical stability window, and low interfacial resistance on lithium surfaces. A Li/LFP cell containing this electrolyte reached a specific capacity of 150 $mAh\,g^{-1}$ when cycled at C/10.[49] It was also salified with orthoborate salts, such as bis oxalate borate or (fluorine)oxalate borate and mixed with the commercial electrolyte LP71 (1M $LiPF_6$ in ethylene carbonate–dimethyl carbonate–diethyl carbonate) and used as the electrolyte in a Li/LNMO cell the cell. In this case the cell exhibited specific capacity of 120 $mAh\,g^{-1}$ at the 10th cycle with the capacity retention higher than 98.1% at the 100th cycle. Infrared spectra

of the cathode after cycling showed the presence of several peaks attributed to borate compounds. This confirmed that the orthoborate anions can form a durable and effective interface layer, allowing prolonged cyclability of high voltage lithium cells.[50]

Electrolyte formulations based on ILs and commercial electrolytes (LP30 or LP70) have been developed to produce gel polymer electrolytes[51,52] based on poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF–HFP), 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate, and 1-butyl-1-methylpyrrolidinium hexafluorophosphate. These gel polymer electrolytes showed improved inherent safety and can be used in high voltage lithium batteries. The overvoltage during galvanostatic stripping-deposition cycles of symmetrical Li/Li cells containing only the electrolyte and its mixtures with 30% and 50% IL are shown in Figure 3.

The GPE was used in lithium metal batteries having LNMO as a high voltage cathode. The battery demonstrated improved electrochemical performance with Coulombic efficiency above 99% and high specific capacity above 110 $mAh\,g^{-1}$ at C/5 throughout 150 cycles.[51] GPE composed of PVdF, a ternary solvent of ethylene carbonate:propylene carbonate:dimethyl carbonate, and orthoborate anions have been tested in a LIB battery employing Sn–C as the anode and LFP as the cathode. The cell exhibited the capacity of 160 $mAh\,g^{-1}$ in the first charge-discharge cycle, which is corresponding to 94% of the theoretical specific capacity of LFP and good capacity retention over 10 cycles, with high Coulombic efficiency (>95%). In following cycles, the cell maintained a good Coulombic efficiency (98.4% at 40th cycle) but a slow decay of the full-cell performances was observed.[52]

Solid electrolytes suitable for working at high voltage have been also developed and characterised.[24,53–55] A perspective on strategies and opportunities, particularly around the development of all-solid-state system configurations, can be found in Ref. [53] and [54].

A simple method of realizing all-solid-state lithium batteries employing a Sn/graphite composite anode and LPS glassy solid electrolyte was developed. The Sn/graphite|LPSI|Li cell exhibited a capacity of 400 $mAh\,g^{-1}$ in the 1st cycle at C/30, which was about 83% of the nominal capacity of the Sn/graphite composite electrode. Throughout the course of 30 cycles, the cell retained a capacity above 320 $mAh\,g^{-1}$ with a Coulombic efficiency of 98%.[24]

A hybrid solid polymer electrolytes based on poly(ethylene oxide) (PEO) polymer matrix encompassing NASICON-type $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ super Li-ion conducting ceramic was prepared. Cells based on this electrolyte showed high specific capacity (about 70% of the theoretical value retained at 2 *C* rate), limited fading, and excellent Coulombic efficiency (> 99.5%). Interfacial stability issues remain to be solved, chiefly linked to the reactivity of the ceramic component in contact with lithium metal.[55]

A polymer electrolyte based on PEO, tetra (ethylene glycol) dimethyl ether, and lithium salt cross-linked by UV irradiation was prepared (PEO_HPyr–VC).[56] Comprehensive analysis confirms that UV-induced cross-linking is an effective technique to suppress the crystallinity of the polymer matrix and reduce ion aggregation. As a result, improved Li^+ ion transport number (> 0.5) and ionic conductivity (> 0.1 $mS\,cm^{-1}$) at RT was measured. Finally, when used in a LFP/Li cell, the polymer electrolyte allows reversible operation with stable profile for hundreds of cycles upon galvanostatic test at RT. The cell delivered full capacity at 0.05 or 0.1 C rate and retained high-rate capabilities up to C/5 (Figure 4).

Composite separators for Li–sulphur batteries were obtained by electrospinning or drop-casting a polymer solution of PVdF containing graphene oxide on a commercial Celgard® polyolefin separator. The electrospun layer improved the wettability of the polyolefin separator and was beneficial to the growth of soft dendrite on Li anode. Furthermore, it had a positive effect on the polysulphide shuttle process overall improving the performance of Li–sulphur batteries.[57]

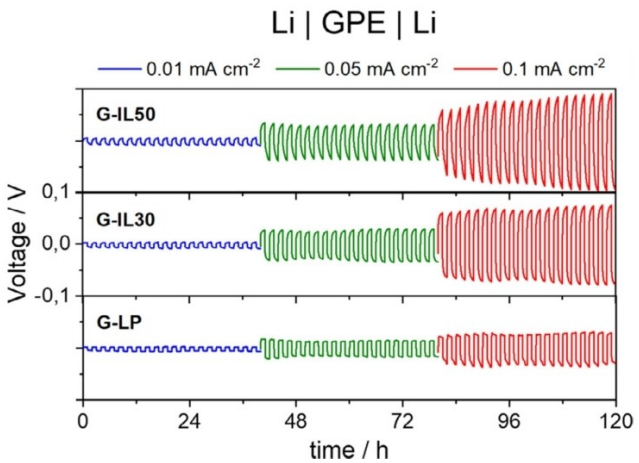

Figure 3. Overvoltage during the galvanostatic stripping-deposition cycles recorded at different currents of symmetrical Li/Li cells containing only the electrolyte (G–LP) and its mixtures with 30% (G–IL 30) and 50% (G–IL 50) of IL. Reproduced from Ref. [51] Copyright (2022), with permission from Elsevier.

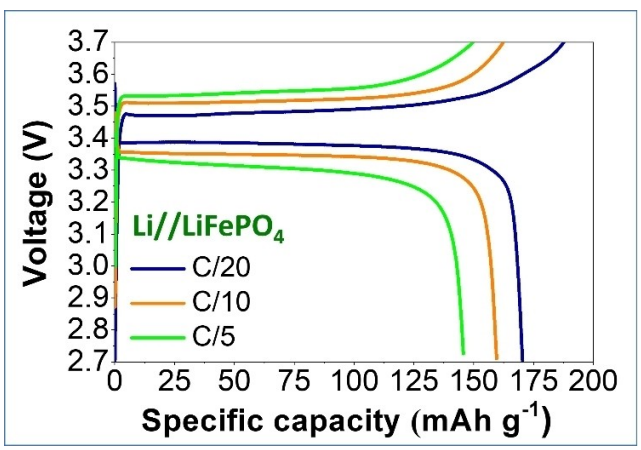

Figure 4. Voltage profiles vs. specific capacity of an all-solid-state Li/PEO_HPyr–VC/LFP cell at C/20, C/10, and C/5 rate. Reproduced from Ref. [56] Copyright (2022), with permission from the American Chemical Society.

Another membrane prepared by electrospinning based on polycaprolactone (PCL) were tested as separators for lithium batteries to evaluate their ion transport properties. Electrochemical results demonstrated that PCL nanofiber membranes can withstand high discharge currents and deliver high power. A lab scale cell was assembled sandwiching the PCL nanofiber membranes between a lithium metal anode and a LFP electrode as the cathode. The cell showed a specific capacity of about 150 $mAh\,g^{-1}$ when cycled with a constant current equal to C/10. The cell showed a good capacity retention with increasing rates, being able to provide 70% of the capacity exhibited at C/10 when discharged with a 50 times higher current.[58]

Solid and safe electrolytes with high conductivity and stable at high working voltage have been developed and characterised. An innovative crosslinked polymer electrolyte based on PEO encompassing protic ILs displayed high ionic conductivity, wide thermal, and good electrochemical stability. The polymer has proven to be suitable for use in energy storage devices. Initially, the polymer was used to make an all-solid-state double-layer electrochemical capacitor. Subsequently, its ability to be used as an electrolyte in a lithium metal cell with LFP cathodes was demonstrated, which provided an almost full capacity (i.e., 150 $mAh\,g^{-1}$ at C/20) and a highly reversible cycle at ambient conditions and different current rates.[59]

At the same time electrolytes for sodium-ion cells were prepared and characterized from chemical, physical and electrochemical point of view. The electrochemical stability of different sodium-conducting electrolyte families, based on several ILs was investigated through voltammetry techniques with the aim of evaluating their feasibility in Na-ion devices. All IL-based electrolytes were found to be electrochemically stable within the 0.1–4.5 V (vs. $Na^+/Na°$) voltage range. Preliminary electrochemical investigations have shown good compatibility between the electrolytes and both the hard carbon anodes and the $NaMnO_2$ cathodes.[60]

Aqueous and IL-based electrolytes were developed. The ILs consisted of the cations N–methyl–N-alkyl–piperidinium, trimethyl–butyl–ammonium and 1-ethyl-3-methyl–imidazolium, and by the anions bis (fluor–sulfonyl) imide and bis (trifluoromethyl sulfonyl) imide.[61] These innovative ILs showed potentially appealing characteristics as electrolytes for realizing safer and more reliable sodium battery systems. RT conductivities of interest for practical devices, i.e., largely overcoming 10^{-4} or $10^{-3}\,S\,cm^{-1}$, have been displayed. The 1-ethyl-3-methyl–imidazolium-based electrolytes exhibited the best ion transport properties, especially at low temperatures: at −20 °C from 10^{-4} to $10^{-3}\,S\,cm^{-1}$ are observed. The mixture consisting of 0.1 Na-bis (trifluoromethyl sulfonyl) imide and 0.9 IL was found to be thermally robust up to 275 °C. This peculiarity enables this sodium electrolyte to be used in battery systems operating at temperatures higher than 100 °C which are not allowed in standard organic solutions.

As regards the water-based electrolytes, both sodium or lithium salts and mixed lithium/sodium salts have been used. A two-steps method that modifies SiO_2 with acrylamide by grafting process to prepare a functional SiO_2 composite electrolyte with improved thermal stability was developed.[62]

SiO_2 particles were used as advanced fillers in cross-linked PEO based matrix to form three-dimensional cross-linked inorganic/organic composite electrolyte. The crystallinity of PEO in the resultant composite was greatly decreased, giving rise to high conductivity ($3.3\times10^{-4}\,S\,cm^{-1}$) and a Li-ion transference number of 0.60 at 60 °C. The Li/Li symmetrical cells prepared with the composite electrolyte cycled for more than 400 h at 60 °C and 550 h at 120 °C at a current density of 0.1 $mA\,cm^{-2}$.

Separator based on Nafion™ were also investigated to improve the adhesion with the cathode[63] or to build a sodium metal battery.[64] In this research, polyolefin separators were modified with Nafion™ solutions and their performance in contact with high-potential LNMO electrodes was investigated. The initial specific discharge capacity delivered by the best cell was 110 $mAh\,g^{-1}$ at C/3 rate and 93 $mAh\,g^{-1}$ at 1 C rate. The cell maintained a capacity higher than 90% over more than 80 cycles.[63] Sodiated Nafion™ membrane were tested as a single-ion conductor electrolyte for sodium metal batteries using $NaMnO_2$ as the positive electrode. The use of this membrane decreases the performance of the cell with respect to that of the liquid electrolyte by about 30%. On the other hand, the positive electrode fading upon cycling was reduced. After approximately 10 cycles, the capacity reversibly cycled in the cell prepared with the sodiated Nafion™ membrane stabilized between 60 and 70 $mA\,g^{-1}$ for the following 90 cycles whereas the liquid electrolyte benchmark cell performance fades monotonically.[64]

2.3. Lithium metal batteries

The protection of metallic lithium was carried out by means of two *ex situ* treatments: the first used polydimethylsiloxane (PDMS) and the second ammonium hexafluorophosphate (AHFF). Symmetrical Li/Li cells with PDMS-modified lithium electrodes showed good cycling stability and resistance values slightly higher than the reference cell. The higher resistance was probably due to the PDMS insulating layer formed on the lithium surface. This difference decreased with cycling, probably due to the formation of a passivation film on the lithium surface in the reference cell and to the stabilization and homogenization of the PDMS layer. Cells containing AHFF showed good stability for over 500 cycles with resistance values like those found in the reference cell. XRD measurements on the lithium electrodes immersed for ten days in LP30 containing AHFF showed the appearance of signals that can be attributable to lithium nitride, probably formed on the surface of the lithium by reaction between the metallic lithium and the ammonium additive.

Studies on Li–oxygen and Li–sulphur batteries were carried out. The disproportionation reaction of superoxide anions in the presence of H^+ and Li^+ cations was investigated with high quality multiconfigurational ab-initio methods.[65] The thermodynamic and kinetic data of the reaction have been drawn from an accurate theoretical model where the electronic structure of the reactant and products was treated at the necessary level of theory. It was found that the H^+ catalysed $O_2^- + O_2^-$ dispropor-

tionation follows a very efficient thermodynamic and kinetic reaction path leading to neutral $^3O_2$, $^1O_2$ species and peroxide anions. On the contrary, the Li^+ catalysis promotes only the release of $^3O_2$ whereas the $^1O_2$ formation is energetically unfeasible at RT.

The use of hybrid membranes was proposed to improve the performance of Li metal anode and sulphur cathode.[57] Li–sulphur cells assembled with KJB- and Super P-based electrodes showed excellent electrochemical performances in terms of specific capacity and cell resistance. The Super P-based electrodes showed an initial specific capacity of about 1350 mAh g^{-1} at the first cycle and then undergo a continuous and gradual decrease down to about 900 mAh g^{-1} at the tenth cycle. The capacity loss decreases in subsequent cycles and the specific capacity evaluated at the 60th cycle was around 825 mAh g^{-1}. The KJB based electrodes showed a higher first-cycle specific capacity. Also, in this case a capacity reduction upon cycling was observed. After 10 cycles the specific capacity was reduced to about 1200 mAh g^{-1}.[66]

Activated hard carbons, obtained from the pyrolysis of various waste biomasses, were prepared, and characterised as the active material for the fabrication of electrodes for lithium sulphur batteries.[67] A cell with a 1 cm^2 electrode containing approximately 4.5 mg of sulphur cycled for sixty cycles while maintaining a specific capacity of 1000 mAh g^{-1} (Figure 5).

2.4. Second life

This activity focused on the improvements of mathematical models able to predict the state of health of the batteries, on the realization of a second-life module, and on the testing of the module. At the same time, studies were conducted to equip an electric vehicle recharging station with second life batteries. Experimental tests have been carried out to verify the ability of a previously developed mathematical model to estimate the life span of a battery (at the cell level) based on the incidence of different stress factors. A new approach was developed to estimate the remaining battery life using an inverse Gaussian model. This model has proved to be useful as it adequately considers the degradation phenomena acting on the battery.[68] A recursive Bayesian statistical inference approach has been elaborated for estimating the battery capacity fading, under the widely adopted exponential decay model.[69]

A preliminary design of a flexible test station for second-life battery modules was investigated.[70] The station was designed to accelerate the investigation on the second-life battery issues. The station is highly flexible because it is allocated in a 19-inch rack architecture that allows seamless board swap and replacement. Indeed, the battery cells and the electronic control boards can easily and quickly be replaced by extracting the specific rack drawers and inserting new ones with different features.

The hardware and software architecture of a Battery Management System was developed and validated an open-hardware low-cost battery maintenance tool architecture.[71] Figure 6 shows the general architecture of the tool for a battery with N series-connected cells.

It consists of some blocks, among which are the control and measurement unit, the diverter relay-matrix, and the management unit. The tool is very simple and can be used with common laboratory instruments. The tool is based on a relay-matrix and a battery monitor integrated circuit. It can completely characterize and optimize the state of a battery independently of the battery management system and gives a figure of the individual aging of the battery cells. The work was focused on the architecture and the experimental validation of a 16-cells battery maintenance tool prototype. The results

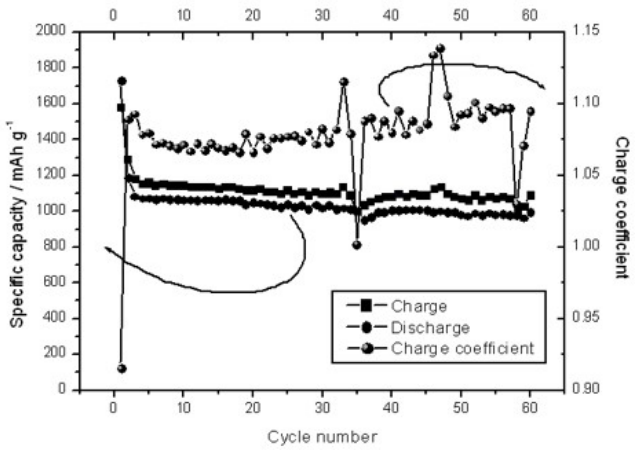

Figure 5. Specific charge and discharge capacity and charge coefficient as a function of the number of cycles for a Li–sulphur cell using a 1.0 M solution of lithium bis (trifluoro methane) sulfone imide, in a mixture of dioxolane/dimethoxy ethane at 50% by volume and containing 0.1 M lithium nitrate, as electrolyte. Reproduced from Ref. [67] Copyright (2022), with permission from The Authors.

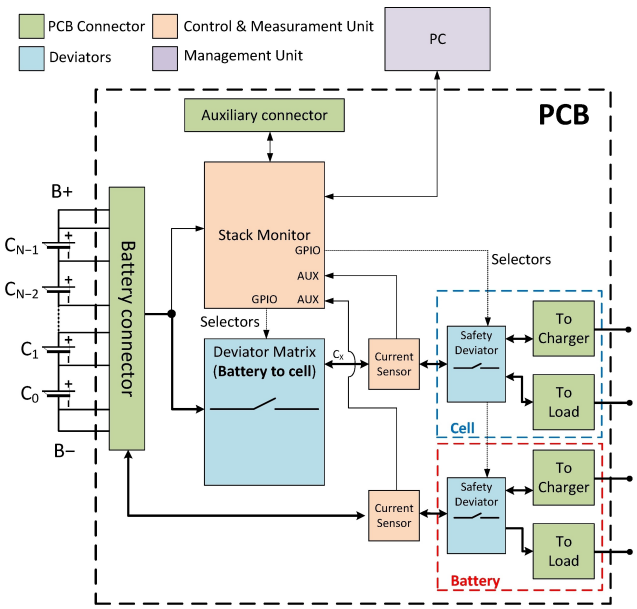

Figure 6. General architecture of the proposed maintenance tool for a battery composed of N series-connected cells. Reproduced from Ref. [71] Copyright (2021), with permission from The Authors.

demonstrated that utilizing the tool brings the battery in the best possible state and identifies the degradation of the cells in terms of capacity and resistance. According with the open access philosophy the tool hardware and software source files can be freely downloaded at https://github.com/batterylabunipi/MaintenanceToolForLightElectricVehicles.[72]

Finally, a stationary storage system based on second-life batteries was designed for an electric vehicle charging station to be implemented at the ENEA Casaccia research centre.[73] To implement an optimal design methodology for the electric vehicle charging station, the PV peak power, the electric energy storage capacity with retired electric vehicle batteries and the number of charging stations to be to install were defined. Two different charging strategies were proposed and compared to quantify the influence of the control approach on the final configuration of the charging station. Furthermore, in the production of the input data, the energy demand and the uncertainties related to the production from renewable energy sources were considered. The results suggested that an optimal control strategy allows a greater reduction of carbon dioxide emissions as it allows to size the storage capacity of batteries and photovoltaics to achieve carbon neutrality during the recharge of electric vehicles.

2.5. Diffusion of the results

ENEA and the beneficiary university partners have actively participated in various international initiatives and collaborations. Numerous documents of roadmap, implementation plans, and white papers have been produced in the working groups of the SET plan, the ETIP platforms, the Battery 2030 + initiative and the EERA and EBA alliances. The results of the activities were collected in 109 technical reports and disseminated through 56 peer-reviewed scientific publications and 132 presentations at national and international conferences.

Two patents were also deposited to protect the results of potential industrial interest.[74,75] The first invention claims the preparation of a thin film cathode electrode for lithium sulphur batteries. During the first cycle the electrode, used as the cathode of a Li–sulphur cell, showed a specific capacity equal to 1550 $mAh\,g^{-1}$, close to the theoretical value (1588 $mAh\,g^{-1}$, calculated for the Li_2S_8 compound). In the subsequent charge not all the capacity is recovered and a rapid decline in capacity, which reaches around 900 $mAh\,g^{-1}$ after the first six cycles, was observed. From the seventh cycle onwards, the capacity remains stable around this value. The Coulombic efficiency was 98.5 % while the energy efficiency was slightly higher than 90 %.

The second patent concerns the development of carbon–silicon hybrid electrodes. The patented electrodes consist of one or more layers in which the carbon is made up of 1D or 0D nanostructures obtained through CVD, while silicon (always nanostructured) fills the empty spaces between the carbon nanostructures. The claimed structures have been achieved with carbon nano walls and silicon nanoparticles.

3. Conclusion

The research program carried out by ENEA in the three-year period 2019–2021 gave the opportunity to explore the entire battery value chain, starting from the synthesis of the materials and arriving at the production of complete batteries, without neglecting the reuse of exhausted batteries. Both lithium-ion batteries and more innovative systems such as sodium-ion, Li–sulphur or Li–air batteries have been studied. To obtain these results, the contribution of the universities that collaborated in the project was invaluable. The high number of technical reports, publications and conference participations testify to the goodness of the obtained results.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: battery · electrochemistry · energy storage · research project

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