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Overview of ENEA's Projects on lithium batteries

F. Alessandrini, M. Conte*, S. Passerini, P.P. Prosini
ENEA, Advanced Energy Technology Division, C.R. Casaccia, Via Anguillarese 301, Rome 00060, Italy

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Abstract

The increasing need of high performance batteries in various small-scale and large-scale applications (portable electronics, notebooks, palmtops, cellular phones, electric vehicles, UPS, load levelling) in Italy is motivating the R&D efforts of various public and private organizations. Research of lithium batteries in Italy goes back to the beginning of the technological development of primary and secondary lithium systems with national know-how spread in various academic and public institutions with a few private stakeholders. In the field of lithium polymer batteries, ENEA has been dedicating significant efforts in almost two decades to promote and carry out basic R&D and pre-industrial development projects. In recent years, three major national projects have been performed and coordinated by ENEA in co-operation with some universities, governmental research organizations and industry. In these projects novel polymer electrolytes with ceramic additives, low cost manganese oxide-based composite cathodes, environmentally friendly process for polymer electrolyte, fabrication processes of components and cells have been investigated and developed in order to fulfill long-term needs of cost-effective and highly performant lithium polymer batteries.

Keywords: Lithium polymer batteries; Lithium-metal; Lithium-ion; Polymer electrolytes; Composite cathodes; Fabrication process

1. Introduction

The use of electrochemical batteries in Italy is increasingly required in a variety of applications ranging from small scale (cellular phones, notebooks, consumer products) up to large-scale (electrical and hybrid vehicles, load levelling, renewable energy). The development of new batteries for conventional and new applications is demanding in Italy by several technical, economical, industrial and environmental reasons. The larger applications and lower energy consumption require higher technical performances. Reduced environmental impacts ask for cleaner materials and processes with ease of recycling; and rapid introduction in the national economy and industry, due to the strong dependence of imported batteries may rely on available expertise and scientific and industrial know-how.

Since mid-1980s ENEA, the Italian National Agency for New Technology, Energy and the Environment, has been promoting research and development (R&D) programs on innovative and advanced batteries with improved performances (specific power and energy, cyclability, low maintenance and lower environmental impacts) and costs. At beginning of 1990's a research-oriented exploratory program was concluded, during which various batteries were analyzed and some proprietary results were obtained, particularly on polymer electrolytes with ceramic fillers for lithium-metal batteries. Based on those interesting results, new activities on lithium batteries have been defined and started. Three R&D projects on lithium polymer batteries for electric vehicles and consumer applications, partially funded by Italian Ministries, aimed at investigating basic phenomena, researching and developing materials, analyzing and optimizing processes and pre-industrial lithium polymer batteries. This paper highlights main objectives and updated results of these projects.

2. The ALPE Project

In the framework of a Program Agreement with the Ministry of Industry, ENEA started in 1994 a national integrated project on lithium-metal batteries with polymeric components. The project, named ALPE (Accumulatori al Litio Per Elettrotrazione: Lithium Accumulators for Electric Traction), involved, along with ENEA, two Universities (Bologna and Rome) and an industry (Arcotronics Italia), world leader in equipment production. The goal of the first phase of ALPE Project, completed in 1999, has been the

* Corresponding author. Tel.: +39-0630484829; fax: +39-0603486306.
E-mail address: conte@casaccia.enea.it (M. Conte).

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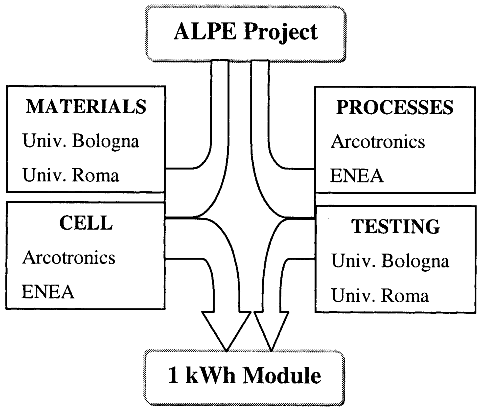

Fig. 1. ALPE Project structure and main R&D tasks.

R&D of innovative materials and processes for lithium-metal batteries with polymer electrolyte aimed at electric vehicle applications. The technical objectives of this phase of the project have been of precompetitive nature, good energy performance (>100 Wh/kg), acceptable cyclability (>300 cycles), limited self-discharge (<1% per day), low-cost and environmentally benign materials and processes [1–3]. The construction of planar cells and small-scale modules (of about 1 kWh) has been used to verify the basic phenomena, the materials selection and the preparation technologies. Fig. 1 shows the structure and the roles of the participants. The cell is basically composed by a lithium-metal anode on a copper current collector, a polymer electrolyte (including a lithium salt, PEO and ceramic fillers) and a composite cathode (mainly made of manganese oxide-based insertion compounds) on an aluminum current collector. The cell works at a temperature of about 90°C. Various electrolytes and cathode materials have been developed with the main scope to have solvent-free or environmentally friendly processes and high performances.

2.1. University of Bologna — Department of Chemistry

The University of Bologna focused the research work on the preparation processes for polymer electrolytes and composite cathodes (based on $LiMn_2O_4$) in order to get rid of the solvent problem. Solvent-free and solvent trapping solutions were analyzed with an in-depth experimental work. Four processes were then selected for the composite cathodes with good results obtained for the casting and hot pressing in terms of chemical and electrochemical behavior. The electrolytes were prepared by chemical crosslinking of a PEO-based material (PEO–PEGDME–$LiCF_3SO_3$–$\gamma LiAlO_2$) and by plasticizing another PEO-based compound (PEG–PEGDME–$LiCF_3SO_3$–$\gamma LiAlO_2$). The results were very interesting for electric vehicle applications, because of the high coulombic efficiency of the lithium stripping-deposition process at the metal anode (94–96%) and good stability of the actual capacity under cycling tests at C/3 and at 94°C [4,5].

2.2. University of Rome "La Sapienza" — Department of Chemistry

The Department of Chemistry has been developing polymer electrolytes with high ionic conductivity (higher than 10^{-4} S/cm at 80°C) and limited passivation phenomena at the lithium metal anode. A variety of composite polymer electrolytes have been developed and used in prototype cells. Most electrolytes have been based on PEO and a proprietary composition with ceramic fillers [6]. Several plastic-like and dry PEO-based composite electrolytes have been produced for testing with extremely promising performances for lithium metal systems operating at about 90°C, but also for lithium ion batteries working at room temperature [7–9]. More recently, nanometre-sized ceramic powders have been added to PEO-based electrolytes and, acting as solid plasticisers, have improved the ionic conductivity at temperature lower than 60°C (around 10^{-4} S/cm at 50°C and 10^{-5} S/cm at 30°C have been obtained) [10].

2.2.1. University of Rome "La Sapienza" — Department of Chemical Engineering, Materials and Metallurgy

This department has been involved only at the end of the project to investigate new insertion cathode materials based on manganese oxides able to operate at high temperature and voltages. The research was concentrated on lithiated manganese dioxides in alternative to spinel types, confirming the problems of such materials at certain voltage and temperature.

2.3. Arcotronics Italia

Arcotronics has designed, set up and used for sample preparation a complete small-scale pilot production plant. The built pilot line starts from extruded compounds for both cathodic and electrolytic films, which are calendered (Fig. 2) and then a lamination phase. The plant is composed by seven different equipment performing the following operations: (1) calendering of extruded components; (2) lamination of sets of components and complete cells; (3) cell assembly; (4) tab ultrasonic welding; (5) cell and stack sealing. A stack of 10 cells (10 Ah) is assembled by parallel connection with ultrasonic welding. Inserting the stack in a soft envelope thermally welded then produces a final "softpack".

2.4. ENEA

ENEA was involved in material selection, cell design, process development and scale up. A large dry room has been built for such work. The final cell design was of double-anode type, a cathode is inserted between two anodes and separated by polymer electrolytes. Based on this design, the production process was jointly developed with Arcotronics. Main results, integrated with those of universities, are

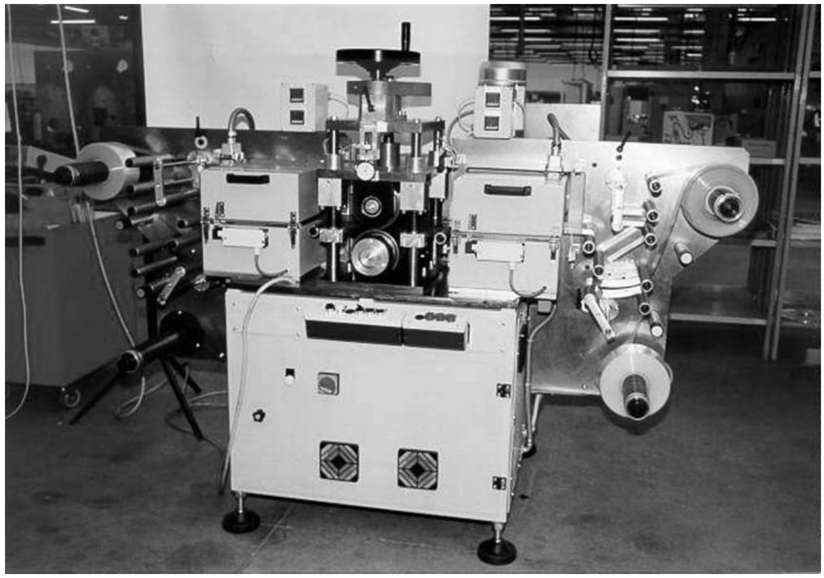

Fig. 2. Calendering machine for the preparation of polymer electrolytes and composite cathodes.

1. a good selection of solvent-free electrolytes with ionic conductivity interesting also for lithium-ion batteries,
2. an optimal behavior of the anode-polymer electrolyte interface with an efficiency of lithium insertion and stripping exceeding 98% (see Fig. 3) [11],
3. an easy-to-built design with limited environmental impact during production and use, a flexible pilot line for small scale production of cells and "softpack".

Some technical barriers still remain to be overcome, cathode capacity fading with limited cyclability, engineering of the module to control thermal and safety aspects [12,13].

3. Ongoing projects

Two new product-oriented projects on lithium batteries have been defined in 1998 and officially started in September 1999. Both projects are partially funded by the Ministry of Scientific and Technological Research (MURST) and are regulated by a Program Agreement between MURST and ENEA. These cost-shared projects are aimed to stimulate the collaboration between public and private institutions in order to accelerate the introduction of high-risk technologies. The project "Rechargeable lithium batteries with polymeric components for consumer products" is aimed at developing plastic-like polymer electrolyte lithium-ion

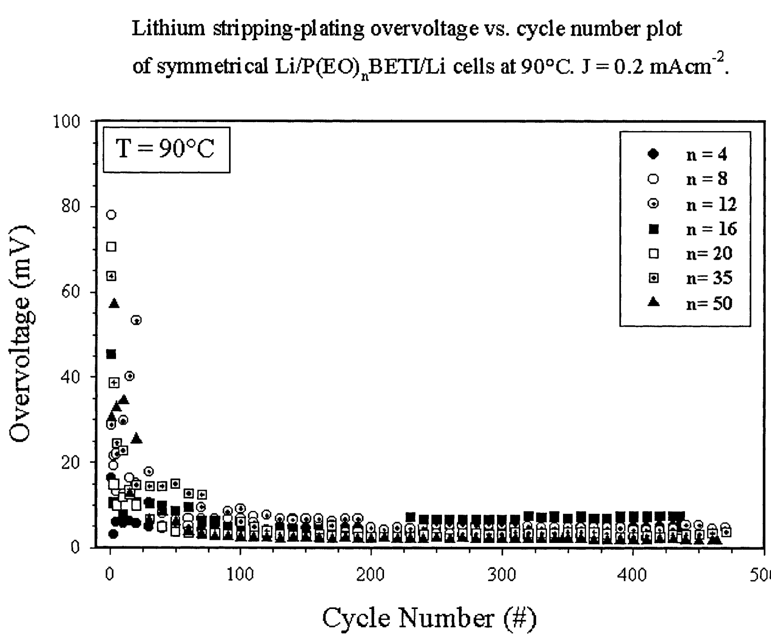

Fig. 3. Lithium stripping-plating over voltage vs. cycle number.

batteries in planar configurations. The technical objectives are to research and develop pre-industrial prototypes with more than 110 Wh/kg (250 Wh/L) at about 4 V and a cycle life in excess of 500 cycles.

The project ''Lithium Batteries with polymeric components for electric vehicles'' is the second phase of the ALPE project. In fact, the polymer lithium-metal system will be improved in terms of performance and safety. The goal is a 20% increase in basic technical performances with respect to the first phase and the introduction of thermal and safety management systems in a fully monitored case.

Apart from ENEA, 12 public and private organizations are involved in the projects, combining large experience in lithium battery electrochemistry, materials development, thin film and battery production, modeling, and battery application in electric vehicles.

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