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The Italian contribution to battery science and technology

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Abstract

The activities in the battery field currently in progress in Italian academic and industrial laboratories will be briefly reviewed. After reporting the key achievements obtained in lead-acid batteries, the presentation will be focused on systems of more recent development with particular attention to the lithium batteries. Interestingly, there is in Italy quite an intense research and development activity on these new-concept batteries which are now the power sources of choice for popular electronic devices, e.g. cellular phones, and in prospect valid systems for powering electric vehicles. Basic research is carried out in various university and government centers with the aim of characterizing new lithium ion electrode and electrolyte materials. This intense research is backed by substantial development activity since few Italian industries are presently engaged in the production of lithium batteries of different size and characteristics. Italy is then well established in battery R&D, confirming the country's historical involvement in the field since Volta's pile invention in 1800.

Keywords: Batteries; Lead-acid; Lithium; Italian contribution

1. Introduction

The discovery of the electric pile, announced in 1800 by Alessandro Volta, opened the route for the establishment of the present battery technology. Shortly after Volta, Leclanché introduced the zinc–carbon cell, followed in 1859 by Gaston Planté with the lead-acid battery and in 1899 by Waldemar Jungner with the nickel–cadmium battery. A part from some structural modification, the Leclanché concept is the operating base of the common zinc ''dry'' batteries which are sold throughout the world at a several million units rate. Even more impressive is the continuous success of the lead-acid system which, in addition to its wide use in the automobile sector, is still the object of intense research and development as demonstrated among other events, by the relevance of the Conference to which this special issue is devoted. Also the nickel–cadmium is a quite popular power sources, especially for low value electronics.

However, this market domination has been in part interrupted in the most recent years due to the progress of the sophisticated consumer electronics and to the increasing concern in the air quality in urban areas. The energy and the power content, as well as the degree of toxicity, of nickel–cadmium batteries are not adequate for operating modern and popular portable devices, such as note books and, particularly, cellular phones. Similarly, lead-acid batteries are too heavy and too bulky to be considered appropriate for powering zero-emission electric vehicles [1].

Accordingly, new electrochemical power sources are emerging and among these advanced systems, lithium batteries are the most successful, commercial-wise for the consumer electronic market and in prospect for the electric vehicle sector.

These recent developments have triggered an intense, renewed activity in the battery community with particular attention focused on the new systems with the aim of continuously improving their performance, however without neglecting conventional batteries for further establishing their role in the still large market sector where they are dominating. The Italian contribution for the progress of this activity in the battery science and technology will be briefly reviewed in this paper.

2. Lead-acid batteries

As already mentioned, although lead-acid is an old concept, consistent activity both on development and on research is still in progress in industrial and academic laboratories. The involvement of Italian industry is reported in other papers of this issue, so that it will not be mentioned

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Table 1
Italian groups involved in lithium ion battery R&D

Institution	Topic	Sponsor
Department of Chemistry, University of Rome "La Sapienza"	New cathodes materials: $LiNi_yCo_{1-y}O_2$; iron phosphates; new anode materials: lithium alloys, inter-metallic compounds. Lithium polymer electrolytes; composite lithium conducting membranes	MIUR[a], CNR[b]
Faculty of Pharmacy, University of Bologna	Manganese spinel cathode materials. Active carbon anodes	MIUR[a], CNR[b]
Department of Chemistry, University of Camerino	Large surface area carbon anodes; lithium-rich graphites	MIUR[a], CNR[b]
Department of Chemistry, University of Pavia	Lithium polymer electrolytes	MIUR[a], CNR[b]
Department of Materials Science & Chemical Eng. Polytechnic of Turin	New cathodes materials; substituted iron phosphates	MIUR[a]
Faculty of Pharmacy, University of Chieti	Iron phosphate cathodes; nano-composite polymer electrolytes.	MIUR[a]
Center for Electrochemistry of Interfaces, Rome	Substituted manganese spinel cathodes	CNR[b]
ENEA, Casaccia, Rome	Iron phosphate cathodes; polymer electrolytes; fabrication and test of lithium ion battery prototypes	MIUR[a]

[a] Italian Ministry for University and Research.
[b] Italian National Research Council.

here. Research on lead-acid battery materials is systematically carried out in Government and University centers. Particularly active in the field is a group at the Polytechnic of Turin where investigation is carried out on the electrochemical behavior of expanders in the negative plates and on the influence of electrolyte additives on the behavior of electrochemically formed lead-dioxide [2].

3. Lithium ion batteries

Rechargeable lithium batteries are presently the power sources of choice for consumer electronics. The structure of these batteries involves non-conventional electrode and electrolyte materials. Most commonly, the anode consists of a compound capable of accepting and releasing lithium ions within its lattice, such as graphite or carbon. The cathode is a compound originally containing lithium in its lattice, e.g. of the $LiMO_2$ (M = Co or Ni) or of the $LiMn_2O_4$ type. Similarly to the anode, this compound is capable of releasing lithium ions and of accepting them back. By combining these two electrode materials in an electrolyte formed by a solution of a lithium salt in an aprotic organic solvent mixture [3], one obtains batteries where the electrochemical process involves the cyclic transfer of lithium ions from the lithium-source cathode to the lithium-sink anode, according to the overall process:

$$LiMO_2 + C \Leftrightarrow Li_{(1-x)}MO_2 + Li_xC \quad (1)$$

Hence the name "lithium ion" batteries. In the most common cases M = Co, $x = 6$ and the open circuit voltage, OCV = 3.8 V at 25 °C [4].

The anode and cathode materials are mixed with a binder (generally PVdF) and a conductive additive (generally carbon) and laminated on a thin copper or aluminum, current collector. A separator felt is sandwiched between the electrode films and the entire assembly is spiral wounded or corrugated in order to form cylindrical or prismatic battery configurations. The electrolyte is then added to soak the separator and the battery is finally sealed in a compact, high energy density structure.

Lithium ion batteries are rapidly assuming a leading role in the consumer electronics market where they are progressively and consistently replacing the bulkier and polluting nickel–cadmium batteries and even the second generation nickel-metal hydride batteries. In 2001 the production of lithium ion batteries amounted to 542 millions of units with a corresponding value of 2.2 billions of dollars; in 2002 the production is estimated to rise to 656 millions of units for 2.4 billions of dollars market [5]. This commercial booming is accompanied by intense research activity mainly directed to: (i) the development of new cathode materials being less expensive than $LiCoO_2$, (ii) the characterization of new anode materials, having a specific capacity greater than graphite and (iii) to the replacement of the liquid-soaked separator with a lithium conducting membrane in order to obtain a flexible-shaped, light-structure, polymer battery configuration.

Few lithium ion battery research programs carried out in the framework of government sponsored projects are in progress in Italian laboratories. Some of them are listed in Table 1. This intense academic research is backed by substantial development activity since few Italian industries are presently engaged in the production of lithium batteries of different size and characteristics. Table 2 summarizes this industrial effort.

Table 2
Industrial activity in lithium ion battery R&D

Industry	Activity
Eldor corporation SpA Orsenigo (Como)	Production of lithium ion batteries
Ion energy resources, SpA Bazzano (Bologna)	Production of lithium ion polymer batteries
Arcotronics Italia SpA Sasso Marconi	Design and production of battery assembling machines
Ferrania SpA Cairo Montenotte (Savona)	Fabrication of electrode and electrolyte films

4. Lithium polymer batteries

Although ideal power sources for consumer electronics, lithium ion batteries are not yet in production for electric vehicle application, although prototypes are under tests. The major concern is safety. More promising, long-term EV systems are the lithium polymer batteries. In these batteries the anode is commonly a lithium metal foil and the cathode is a reversible lithium intercalation compound of similar type to that used in the lithium ion systems, e.g. V_2O_5. The electrolyte is a lithium conducting membrane formed by combining a lithium salt with a high molecular weight, Li-coordinating polymer, e.g. poly(ethylene oxide), PEO [3]. The electrochemical cycling process is the lithium stripping-deposition at the anode and the lithium insertion–extraction at the cathode:

$$x\mathrm{Li} + \mathrm{V_2O_5} \Leftrightarrow \mathrm{Li}_x\mathrm{V_2O_5} \quad (2)$$

to which is associated an average OCV of 3 V at room temperature.

The lithium intercalation cathode is blended with the polymer electrolyte and with carbon in order to form a plastic composite which is spread on an aluminum current collector. Complete lithium polymer cells are formed by laminating the electrode and the electrolyte components together to obtain a bendable, thin, plastic and compact structure [6]. This battery laminate can be easily manufactured by automatic processes. Another key advantage of the lithium polymer concept is associated to its all-solid-state configuration which facilitates the achievement of a rugged, leak-proof and modular design geometry. Also, the absence of free liquids allows the batteries to be packaged in light weight plastic containers unlike the common lithium ion batteries which require metallic casing [4]. This feature, combined with the high specific capacity of the lithium metal anode, confers on the lithium polymer battery energy density values even higher than those associated with lithium ion batteries, see Fig. 1.

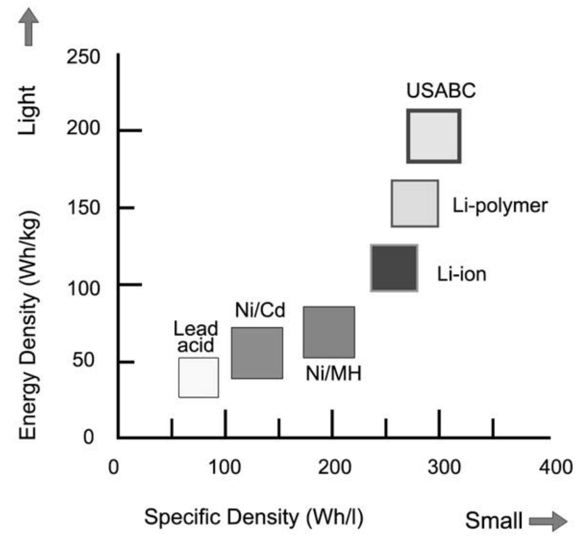

Fig. 1. Energy density (Wh/kg) vs. specific density (Wh/l) for portable batteries. The energy target fixed by the United States Advanced Battery Consortium, USABC, for optimum EV performance is also reported.

These specific advantages have promoted the ongoing of various R&D projects aimed at the production of lithium polymer batteries of practical importance. Among these is of interest an Italian project named "ALPE" focused on the development of a lithium polymer battery using a specifically developed, ceramic-added, composite polymer electrolyte [7]. Although not yet completed, this project has achieved results which are very promising in suggesting that lithium polymer batteries may indeed be considered among the most promising long-range systems for EV application.

5. Conclusion

Although of very recent development, lithium batteries are now established power sources for consumer electronics

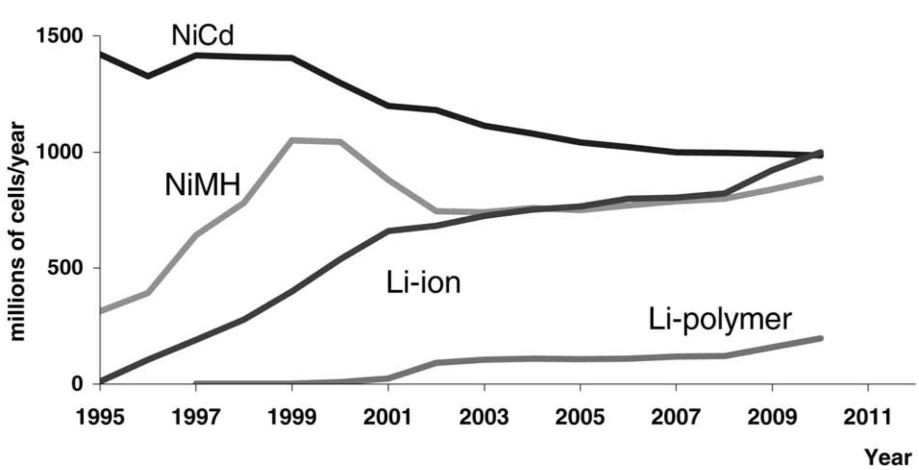

Fig. 2. Market forecast for portable batteries.

and in prospect, very promising electric vehicle powering systems. Continuous R&D has led to continuous progress in the energy content and in the reliability of these batteries to such a level that the modern prototypes are progressively and consistently replacing the bulkier and polluting nickel–cadmium batteries and even the second generation nickel-metal hydride batteries in the world market, see Fig. 2. Italian academic laboratories have contributed to this effort with a series of government sponsored research projects. Also this research activity has promoted practical development since few Italian industries are presently engaged in the production of lithium batteries of different size and characteristics.

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