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Industrial awareness of lithium batteries in the world, during the past two years

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Abstract

The different requirements of lithium battery systems, as well as the structures of different lithium secondary systems, have been reviewed. The main research and development programs in the world are listed, in order to try to understand better the future directions for lithium systems development. © 1998 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

This work has been carried out in the context of electric vehicle applications. We have attempted to draw a rough panoramic view of the actual situation of lithium batteries technologies in the world, with a view to gaining a better understanding of the present and future actors in the field. As lithium technology is still under development for most of its possible applications, the actors are generally involved in the following research and development areas: battery structure and composition optimization, manufacturing, use and arrangement, and recycling.

In this paper, we shall first review the main different kinds of lithium battery technologies (that could be suitable as electric vehicle traction batteries), and then the main national and trans-national R&D programs, in Europe, in the USA and in Japan. We shall then indicate the directions which seem to be actually taken and the most striking outstanding features. For this, we have focused on literature, congress proceedings, and US patents, all of them published within the last 2 years. We shall try to evaluate each step of the battery life (battery design, manufacturing and recycling).

2. Different uses for lithium technologies

Several kinds of lithium battery technologies have appeared, as well as several configurations. We can distinguish between primary and secondary batteries, and among secondary batteries, we can consider portable batteries, and traction or storage batteries, these differences in applications resulting in differences in structure and composition.

The most widespread technologies for primary batteries using lithium metal as anodes are commonly based on the use of manganese, copper or sulfur oxides as cathodes, soluble or solid, with aprotic electrolytes and lithium-based solute additives for electrolyte conductivity enhancement. The shape of cells may be button type, cylindrical or prismatic.

A thorough knowledge and a confirmed experience of the manufacturing and use of lithium primary cells may be a good basis for the development of secondary cells, providing an idea of the constraints existing on the choice, compatibilities and behaviours of the different components and additives.

Lithium secondary batteries are generally used in applications requiring high energy densities and high voltages. They are outstanding candidates for all portable applications like cellular phones, notebooks, or small computers, and the demand for them is presently in tremendous growth, particularly in Japan, where several battery manufacturers make them at an industrial level. Common points exist between portable applications and bigger devices for

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home energy levelling, particularly the high cyclability (even if it is not practically the same order of magnitude, around 1000 for portable, and closer to 3000 for stationary), even though sizes and capacities are different in both cases, and if weight is less crucial in stationary devices.

The energetic characteristics of lithium secondary systems might make them quite attractive as electric vehicle traction batteries, the biggest differences between portable and traction applications lying mainly in size and consequently the thermal or safety behaviour of the batteries.

The above differences and common points give rough directions for systems optimization. It is clear that if one system could lead to high energy density, high cyclability, and still remain of small size, it could be of great interest in many fields of life and industry.

Some minor differences may play a part in the resulting structure and composition of lithium secondary batteries, such as, for example, the need for low costs, high safety, the types of mission profiles or the particular power demand levels.

Other applications of lithium batteries, that concern military systems that require high energy density but not necessarily high cyclability, low costs or small sizes will not be dealt with here.

3. Different compositions of lithium secondary batteries

Many particular factors may influence the configurations of lithium secondary batteries [1], depending on the requirements set by users, as mentioned in Fig. 1. However, setting aside requirements, lithium secondary systems have been developed in several directions, that appeared to diverge for a certain time, and that now seem to be converging once more.

We can distinguish between different kinds of lithium systems, related to several criteria, as listed in Table 1: on the composition of the negative electrode, of the positive electrode, on the physical state and composition of the electrolyte, or on some other criteria.

A major difference arose, in the 1980s, between what has been called lithium-ion (or lithium–carbon, or rocking-chair system), and lithium-polymer (-electrolyte)

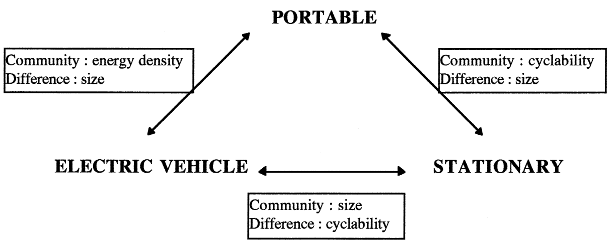

Fig. 1. Lithium battery systems applications and main requirements.

Table 1
Criteria on differences between lithium secondary systems

●Criterion on negative electrode composition:
Pure lithium
Carbon–lithium, graphite–lithium
Lithium alloy
Other alloy
●Criterion on electrolyte state:
Liquid electrolyte
Polymer-solid electrolyte
Gelified electrolyte
●Criterion on positive electrode:
Intercalation cathode ($LiCoO_2$, $LiNiO_2$, $LiMnO_2$, V_2O_5, ...)
Polymer cathode
●Criterion on lithium based additive in electrolyte
● ...

batteries, the difference lying mainly in the physical state of the electrolyte (liquid for lithium-carbon, and solid for lithium-polymer), and in the negative electrode composition (carbon with intercalation of lithium ions, as opppsed to pure lithium in the initial lithium-polymer systems).

Both systems, lithium–carbon and lithium-polymer, were developed separately in different directions, until about 1992. Research was mainly directed to the improvement of the drawbacks of each system:

- For lithium-ion systems:
  - new materials of intercalation for the negative and the positive electrodes
  - new electrolytes and conductive salts
  - safety improvement
  - cost reduction
  - cyclability
- For lithium-polymer systems:
  - improvement of the conductivity of the electrolyte and additive salt
  - test of new materials for the positive and the negative electrodes
  - cyclability

The distinction between the two systems lost part of its meaning in 1992, when Bellcore (Bell Communications Research) laid patents showing the possibility for making cells using both solid polymer electrolyte and carbon as negative electrode, involving at the same time the intercalation phenomenon of lithium ions in the carbon electrode, and their transport through a salt in the solid electrolyte, thus combining the safety aspect of the lithium-polymer system and with the high potential energy density of the lithium-ion. Since this time, this ‘hybrid’ concept has been widely developed, particularly in Japan, and now it would be necessary to specify if ‘lithium-polymer’ is developed with carbon as negative or with pure lithium, or if ‘lithium-ion’ has a solid or liquid electrolyte. Unfortu-

Table 2
USABC funded programs in the US

Partners	Program duration and funds	Objectives
W.R. Grace (USA)	3 years (Beginning: 1992); $24.5 million	Develop lithium-polymer batteries
Saft America–Argonne Nat. Lab. (USA)	3 years (Beginning: 1992); $17.3 million	Develop LiAl/FeS2 batteries
3M (USA)–Hydro-Quebec (Canada)–Argonne Nat. Lab. (USA)	2 years (Beginning: 1993); $32.9 million	Develop lithium-polymer batteries
Varta (Germany) – Duracell (USA)	2 years (Beginning: 1995); $18.0 million	Develop lithium-ion batteries for electric vehicles
SRI International (USA)	1/2 years (Beginning: 1996); $0.8 million	Develop lithium-ion technology
Saft America	1/2 year (Beginning: 1996); $1.4 million	Develop lithium-ion batteries
3M (USA) – Hydro-Québec (Canada)	2 years (Beginning: 1996); $27.4 million	Manufacture lithium-polymer batteries for electric vehicles
Varta (Germany) – Duracell (USA)	2 years (Beginning: 1997); $14.5 million	Develop lithium-ion batteries for electric vehicles

nately, only few manufacturers give this kind of information.

Another system, the hot lithium–aluminium/iron sulfide (or disulfide), has been developed by the Argonne National Laboratory in the United States since the 1960's. Its running temperature is around 450 to 500°C. Even if potentially suitable for electric vehicle applications, because of its performances, this system does not offer the required safety guarantees (problems of corrosion at high temperatures).

Other systems using pure lithium as negative electrode have been mainly developed for military applications (high energy density) but offer low interest for EV applications, because of poor cyclability.

4. R & D programs

Many programs concerning secondary lithium batteries have been or are funded worldwide, by national or continental authorities, in the United States, in Japan or in Europe. We shall list the most important of them hereafter and deal with the different policies on lithium battery research and development in the different continents.

4.1. In the United States

The United States Advanced Battery Consortium (USABC) has already funded several big programs on lithium batteries, in order to power electric vehicles (Table 2). For years, the USABC has been funding only hot lithium batteries and lithium-polymer technologies, and it is only very recently, in 1995, that the USABC began to get interested in the lithium-ion system, allocating some funds to SRI, to Saft America, and to Varta and Duracell. The last contract Varta and Duracell have signed with the USABC is aimed at production ability, safety, life time and cost improvement of the lithium-ion battery.

Hot lithium systems have been particularly developed in the USA by the Argonne National Laboratory, since the 1960s, and by Saft America. This battery could have satisfied the USABC requirements in some respects, but needs further development.

The USABC has been investing a lot in lithium-polymer, as it has been claimed for years, in the United States, that it could reach much higher performances than the lithium-ion system. As the differences between the two systems have been diminishing, and as both systems have been improved, the USABC now begins to evaluate lithium-ion.

The total amount of money invested in lithium battery research by the USABC reaches $136.8 million, of which only part is really provided by USABC, the other part being supported by the battery companies themselves.

Table 3
LIBES objectives for lithium systems development

	High cyclability batteries	High energy batteries
Energy density		
Wh/kg	120	180
Wh/lit.	240	360
Lifetime	3500 cycles	500 cycles
Energy efficiency	90%	85%
Prototypes capacity	20 kWh	30 kWh
Companies involved	Hitachi	Asahi–Toshiba
	Mitsubishi Electric	Japan Storage
	Sanyo	Matsushita
	Yuasa	Nippon Denso

4.2. In Japan

In Japan, the most famous program concerning lithium batteries is the LIBES, that began in 1992, and should last for 10 years. The total Government funding reaches ¥14 billion (about US$118 million). This program gathers several big Japanese battery manufacturers, all specialised in batteries and lithium systems. Only SONY, one of the most advanced lithium-ion Japanese battery companies, has not been involved. The LIBES has structured research in two directions: those batteries that could offer good cyclability, and those that could offer good energy density, as these two features seemed conflicting. We can see in Table 3 the target values for these two systems, and the companies involved. Some other companies, like OSAKA GAS, CRIEPI, MITSUBISHI Petrochemical, are involved in the LIBES materials research too. Each company had a precise task in the development of batteries [2].

4.3. In Europa

Several programs, Joule or Brite-Euram, gathering European companies, for lithium batteries development, have been or are funded by the European Community [3] (Table 4).

The European Community has funded eight Joule programs concerning the development of lithium batteries, for a total amount of 12 338 kECU (about $14 million). We can see that, as in the USA, many programs concern the lithium-polymer technology, only one being dedicated to lithium-ion with liquid electrolyte.

Even if an important difference seems to appear in the level of the funds dedicated to lithium systems between Japan, the US and Europe, it must be remembered that some more national programs, not listed here, are helped by some of the European Governments.

5. Manufacturing and commercialization of lithium batteries

If we first have a look at the Japanese industry of primary lithium batteries, we can notice that output has

Table 4
European funded lithium batteries programs (Joule)

Partners	Duration and alloc. funds	Objective
VARTA (D)–HARWELL (UK)–Univ. Roma–Univ. Warsaw–Bulgarian Acad. Sc.	2 years (Beginning: 1993); 852 kECU	Lithium-ion polymer electrolyte of 2 kWh
DANIONICS (Dan)–Univ. St Andrews– Univ. Southampton–Univ. Uppsala	2 years (Beginning: 1993); 570 kECU	Develop lithium-polymer modules
DANIONICS (Dan)–Univ. St Andrews– Univ. Southampton–TU Delft		Develop lithium-polymer batteries
CEA (F)–CNRS (F)–EDF (F)–BOLLORÉ (F)–SADACEM (B)	3 years (Beginning: 1993); 560 kECU	Develop positive electrodes for lithium-polymer systems
Sonnenschein (D)–DANIONICS (Dan)–ISITEM Nantes (F)	2 years (Beginning: 1994); 500 kECU	Develop lithium-ion technology with polymer electrolyte
SAFT (F)–VARTA (D)–SOLVAY (B)–AAR (F)–EUCAR	3 years (Beginning: 1996); 6000 kECU	Develop lithium-ion batteries with liquid electrolyte for electric vehicles
Sonnenschein(D)–DANIONICS (Dan)–ISITEM (F)–AAR (F)–TU Delft–UK Univ.	x years (Beginning: 1996); 1900 kECU	Develop lithium-polymer batteries
DANIONICS (Dan)–TOBIAS JENSEN (Dan)–STENOVIST (Sw)–DB (D)	x years (Beginning: 1996); 1306 kECU	Develop lithium-polymer batteries for electric vehicles

Table 5
Monthly production of lithium-ion secondary portable batteries

	Million units manufactured per month	Date of forecasts
Asahi–Toshiba	1.6	mid-1996
Fujifilm	1.5	1998
Hitachi–Maxell	6	July 1997
Japan Storage	3	April 1997
Matsushita	20	1999
Matsushita US	1.5	1997
Moli Energy Canada	10	2000
Nippon Moli	2	January 1998
Sanyo	5	September 1996
Sony	10	March 1997
	20	1999

drastically increased from 1988, when it was 234 million units, to 1992, when it reached 451 million units, representing more than 38% of the total Japanese production of primary batteries [4].

The production of secondary portable batteries (of capacities ranging between 0.5 and 2 Ah) is increasing at a much higher rate, companies announcing every month that the output will be doubled soon, and that new production lines are to be built. We give hereunder the production of several big Japanese companies, as well as the dates forecast for these, as published in the newspapers during the first six months of 1997:

It appears that in 1996, the Japanese battery industry produced 120 million lithium based portable units. It should be 3 times more in 2000.

All the companies listed in Table 5, even if they do not all belong to the LIBES, have already been working a lot in the field of research and development concerning lithium secondary batteries, laying patents and sometimes funding their own studies.

We must emphasize that Japan is the only place in the world where the growth in lithium portable battery manufacturing is so significant. Some other companies in the world, like Saft or Varta, already make and commercialize lithium primary batteries since the 1990s, and since very recently, portable secondary batteries, but today in much smaller quantities than in Japan. The same phenomenon is happening in the United States, with a lower increase than in Japan.

Concerning lithium secondary batteries that could be EV suitable, only very few manufacturers really produce prototypes. In Japan, Sony makes lithium batteries for Nissan electric and hybrid vehicle applications, according to a special agreement. In Canada, Hydro-Quebec will manufacture big EV batteries next year, that will be reserved for USABC members' tests. In Europe, Saft and Varta have to manufacture EV size lithium-ion batteries in the frame of their Joule program with EUCAR, for bench tests.

So that today, lithium-ion batteries for EVs are not commercially available, unless by special agreement with battery manufacturers.

6. Recent and possible future developments in the lithium battery industry

Several areas have been developed in research and development on lithium systems. We have listed the main ones, as well as the companies known for their progresses in these areas, and the most striking events (Table 6). This progress may concern secondary portable as well as EV or stationary applications. If a company is not listed in a special area, it does not mean that this company has done nothing, but that we have found nothing about its activities. We did not list all the universities participating in these researches, although many of them do, in Japan, in the United States and in Europe.

Much work has already been done on the improvement of the different components of lithium ambient temperature systems.

Concerning the positive electrodes, many elements have been studied, as possible intercalation compounds: cobalt, nickel, manganese oxides, as well as many combinations of these elements, and use of additives in the positives. Vanadium oxides and titanium sulfide combinations have been studied alone or mixed as carbon composites. Recently, some other elements have been introduced as positives, like gallium by Sumitomo [5], or copper by Hitachi [6].

The negative electrodes have been tested in different forms: pure lithium, generally with polymer electrolytes, or carbon-based. When carbon-based, many kinds of carbons; graphites, pitches, fibers of different sizes and combinations, have been tried, as well as many pretreatments for these fibers or mixes [7–11]. Fuji patented new compositions for negatives, replacing the carbon by composite materials of mixes between metals of groups IIIA, IVA or VA of the Mendeleyev Table (B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Sb, Bi), with oxide, sulfide, selenide or telluride (of group VIA), underlining that the best results were observed with tin oxide composites [12]. Hitachi suggested the use of composites of lithium–lead–carbon [13]. Osaka University has studied negatives made of carbon composites mixed with conducting polymers [14].

The electrolytes have been the object of much work too; on their composition and on the nature of the salts to be dissolved in them for conductivity enhancement. Moreover the electrolytes have to be aprotic, in order to avoid explosions with lithium. They might be liquid organic, polymer organic or gelified. Recently, Nagoya University found a new kind of electrolyte, that is inorganic and aprotic. Conductive salts have been widely tested too, and several lithium-ion liquid electrolyte manufacturers seem to prefer $LiPF_6$.

Table 6
Companies' involvement in lithium battery R&D

	Europe	US–Canada	Japan
Positive electrodes	AAR (F), Bolloré Technol, (F), CNRS (F), EDF (F), Saft (F), TU Graz (A). Univ. Sofia (Bu), Univ. Uppsala (S), Varta (D)	Argonne NL, Bellcore, Hydro-Quebec, Dalhousie Univ.	Aichi Steels, Asahi–Toshiba, Hitachi–Maxell, Japan Storage, Matsushita, Mitsubishi, Mitsui, Moli Energy, Nippondenso, Sony
Negative electrodes	AAR (F), Bolloré Technol, (F), Carbone Lorraine (F), CNRS (F), EDF (F), Saft (F), TU Graz (Au), Varta (D)	Bellcore, Livermore NL–Berkeley, Hydro-Quebec, Dalhousie Univ.	Asahi–Toshiba, Fuji, Hitachi–Maxell, Japan Storage, Matsushita, Mitsubishi, Moly Energy, Nippondenso Nippon Steel, Sanyo, Sony
Electrolytes	AAR (F), Bolloré Technol. (F), CNRS (F), EDF (F), Elf Atochem (F), Saft (F), Varta (D)	Arizona Univ., Hydro-Quebec, 3M, Dalhousie Univ.	Asahi–Toshiba, Fuji, Hitachi–Maxell, Japan Storage, Matsushita, Mitsubishi, Mitsui, Moli Energy, Nippondenso, Sony, Yuasa
Manufacturing	Bolloré Technol. (F), Saft (F), Tadiran (Is), Varta (D)	Bellcore, Hydro-Quebec, Dalhousie Univ., Valence	Asahi–Toshiba, Hitachi–Maxell, Japan Storage, Matsushita, Mitsubishi, Moli Energy, Nippondenso, Sony
Recycling		Greatbatch, Bellcore, National Technical Systems	Canon, Hitachi–Maxell, Miyiazaki Univ.

Concerning possible structures, Yardney has recently patented a lithium based bipolar battery [15].

7. Conclusions

Lithium battery technologies are still at a research and development stage, and the first EV suitable prototypes are actually, or will soon be, under test.

Many points have still to be improved for EV powering applications, like costs, cyclability, and safety. One of the biggest difficulties comes from the fact that these three points have to be optimized at the same time.

Anyhow, much has already been done since the beginning of lithium batteries, even if it is a very young technology, and it seems that further scientific advances, like on conducting polymers, or new micro-visualization processes, will be helpful. We can see either that some interesting trends have recently been observed and should allow some new advances. Moreover, the interest in these technologies is great worldwide, and the level of money invested is high. So, we could hope to see some applications to EVs... at the beginning of the next century...?

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