

PROGRESS IN AND FUTURE DEVELOPMENT OF AMBIENT TEMPERATURE LITHIUM BATTERIES

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Summary

A brief overview of the progress and the future development of lithium batteries is presented. The primary systems have reached a very advanced stage of development and no substantial changes are foreseen in the near future. The secondary systems on the contrary are still open to diversified research activities and the most relevant of these are outlined here.

Primary lithium batteries

Lithium batteries may be cited as a rare example of a very fast developing technology. In fact, less than 20 years have passed from early laboratory studies to commercial production.

Such impressive, fast progress has been largely promoted by the electronic evolution which has favoured the massive production of various devices of increasingly smaller size. The long-term power requirements of this portable electronic instrumentation cannot be satisfactorily fulfilled by conventional dry cells and thus batteries with greater energy density ($W h/cm^3$) are continually required.

Lithium batteries appear to be the most suitable power source to meet this vast requirement. In fact, long-life, solid-state lithium batteries are now predominantly used in cardiac pacemakers; high-energy organic electrolyte lithium batteries are preferred for electronic watches and pocket calculators, and high-current, inorganic electrolyte lithium batteries are selected for military applications.

However, even if the technology of these batteries is quite advanced and satisfactory for today's applications, the constantly increasing sophistication and diversification of consumer and military electronic devices leads to the prediction that improved types of lithium batteries will soon be required.

For instance, Li/I_2 solid-state batteries are presently used to power cardiac pacemakers. The electrolyte of these batteries is lithium iodide, LiI , formed *in situ* as a result of direct contact between a lithium anode and a poly(2-vinyl pyridine)-iodine charge transfer complex cathode [1]. Lithium

iodide is a very poorly conductive solid electrolyte. Consequently, the batteries presently available, having a high internal resistance, are only capable of supplying low output current regimes. While this performance is still adequate for the actual pacemakers, it may not be sufficient for future generation devices, where higher power requirements for dual chamber and programmable pacing may be expected.

Therefore, if one wishes to retain a solid-state power source in the pacemaker (this type of power source is, in fact, particularly convenient in implanted devices because of its unique characteristics of reliability and longevity), a new solid electrolyte, having higher conductivity and comparable thermodynamic and chemical properties, should be used as an alternative to lithium iodide.

Since such an electrolyte is not yet known, consistent effort must be directed to the characterization of improved lithium ion solid conductors. Particular attention in this respect is presently being devoted to polyphase electrolytes of the $\text{Li} \cdot \text{Al}_2\text{O}_3$ type [2]. Systematic and careful research should also be directed to glassy lithium electrolytes, where highly disordered structures and thus fast ion transfer are expected to take place.

A larger variety of prototypes is already available amongst the organic electrolyte lithium batteries. These batteries may be broadly subdivided into two groups, one operating at high voltages, *i.e.*, around 3 V, and one at low voltages, *i.e.*, around 1.5 V.

A wide selection of high-voltage lithium batteries is actually under production using advanced and sophisticated procedures. Typical examples are the Li/MnO_2 system, produced in a large variety of sizes and capacities and aimed at a vast consumer market, the $\text{Li}/(\text{CF})_n$ system, again produced in various configurations for a similar range of applications, the $\text{Li}/\text{Ag}_2\text{CrO}_4$ system, mainly directed at the pacemaker market, and the soluble cathode Li/SO_2 system, produced only in large cylindrical sizes and mainly for the military market*.

These 3 V batteries perform satisfactorily, having good voltage regulation, rate capability, low temperature behaviour and overall energy density. Therefore, no substantial improvement appears to be necessary in the near future.

No comparable variety of prototypes is however available in the low-voltage group which, by contrast, is of particular technological interest since the 1.5 V lithium batteries may be directly interchanged with conventional zinc dry cells, with immediate advantages in longevity and energy density.

Only two types of these so called 'voltage compatible' lithium batteries have reached the commercial stage. They are the Li/CuO [3] and the Li/FeS [4] systems respectively.

*Details on the design and performance of these batteries may be found in the Technical Bulletins of the producing Companies and in various reviews recently dedicated to their characteristics. A very comprehensive review has been presented by P. Bro at the *Lithium Battery Technology and Application Seminar*, Florida Atlantic University, Boca Raton, Florida, USA, March, 1983.

There is, then, a need for development in this sector, which calls for the research and characterization of new cathodic materials to couple with lithium for the production of batteries having good voltage regulation, around 1.5 V, and high energy density. A promising selection could be metal oxides and metal chalcogenides.

The inorganic electrolyte lithium/thionyl chloride, Li/SOCl_2 , and lithium sulphuryl chloride, $\text{Li}/\text{SO}_2\text{Cl}_2$, batteries are very important systems in that they provide very high energy contents. These batteries also are now produced commercially, particularly directed at the military market.

Two aspects of batteries of this type need particular attention and further consideration. They are voltage delay, and safety, the first being associated with the elimination of the passivation film which grows on the lithium electrode on standing in inorganic electrolytes, and the second with the aggression of the solvents.

Even if both aspects are common to all lithium batteries, they are particularly severe in the case of inorganic electrolyte systems. Here, in fact, the voltage delay effect may seriously limit the low-temperature performance and serious hazards may result from cell abuse (short circuit, overdischarge, etc.).

To control these problems, careful consideration should be devoted to the nature and the composition of the inorganic electrolyte (additives, relative concentration, and so forth), to limit the growth of the passivation film, and to engineering design to assure safety under any operational condition, be it programmed or accidental.

Another area, again common to all lithium batteries, which deserves further attention is the disposal of both manufacturing and user wastes. This is a real problem to which little consideration has been so far given, probably because the actual consumption of lithium batteries is still limited. However, the situation is likely to change quite considerably in the future and thus a safe disposal procedure should soon be defined and generally recommended.

Secondary lithium batteries

The state of development of secondary lithium batteries is not so advanced as that of primary systems. Only one type of rechargeable lithium battery has so far been proposed for the consumer market. This battery, produced in a low-capacity version [5], was based on an intercalation cathode, TiS_2 , *i.e.*, an electrode which allows the reversible insertion of lithium within its structure [6].

Effectively, there are no theoretical obstacles to the realization of a rechargeable lithium battery: lithium can, in fact, be efficiently deposited from organic electrolytes at the negative and easily driven in and out of the matrix of intercalation positive electrodes. What, in practice, limits the performance of these batteries, including the one cited above, is the poor

cyclability of the lithium electrode. Lithium is, in fact, attacked by the electrolyte, with the formation of passivated areas on its surface. These areas are electronically isolated from the bulk and thus no longer available for subsequent dissolution. The effect is cumulative and progressively reduces the charge-discharge efficiency to unacceptable values.

Therefore, if the passivation phenomena are beneficial in primary systems, in so much as they protect the electrode from further attack, thus assuring its stability, they are, instead, catastrophic in secondary systems. Consequently, a large fraction of present effort in the field is directed to a solution of the problem of the cyclability of the lithium electrode in organic electrolytes. The following three main approaches are recommended.

- (i) The research and characterization of 'optimized' organic electrolytes;
- (ii) the research and characterization of 'alternative', non-metallic lithium electrodes;
- (iii) the research and the characterization of 'new' battery materials.

Since lithium passivation is unavoidable in organic electrolytes and, furthermore, serves to assure the electrode stability, the first approach considers the selection of suitable electrolytes which may induce the formation of a 'controlled' passivation layer, the nature and morphology of which are such as to favour the cyclability, whilst still maintaining the general protective action. Promising results in this direction have been obtained using solvents kinetically stable toward lithium, such as substituted solvents, *e.g.*, 2-methyltetrahydrofuran [7] and mixed solvents, *e.g.*, diethylenethertetrahydrofuran [8].

The second approach considers the use of a non-metallic electrode having a lesser tendency to passivation by the electrolyte solution than the pure metal. In this fashion, lithium could, for instance be replaced by a highly intercalated lithium electrode. Obviously, the activity of lithium in this electrode is less than unity and thus its potential less than that of pure Li metal; however, if the intercalation reaction is fast and reversible, the electrode may be used more efficiently for a long cycle life battery.

The highly intercalated electrode may be regarded as a lithium sink which, when coupled with a 'virgin' intercalation compound, allows the reversible and multiple transfer of lithium from one side of the cell to the other.

To be competitive, however, these 'rocking chair' lithium batteries must maintain a reasonably high operational voltage and offer high rate capability and high energy density [9]. To achieve these conditions, the intercalate negative electrode must have the following properties:

- (i) high lithium activity and small voltage variation during the electrochemical intercalation and deintercalation processes (to ensure high operational cell voltages);
- (ii) low weight and high number of lithium equivalents per mole (to ensure high specific capacity and energy density);
- (iii) high reversibility and fast kinetics (to ensure high cycling rates).

These requirements are not simultaneously met by the majority of the known insertion electrodes. Therefore, consistent research is needed in this

area to define the most appropriate compound(s). Preliminary results indicate transition metal oxides as a promising class of materials [9].

Finally, the most interesting effort for the development of a good, rechargeable lithium battery is undoubtedly that directed to the discovery and characterization of new electrode and electrolyte systems. Such a fascinating approach is being followed by various laboratories and some interesting preliminary suggestions have already been proposed, especially in the area of polymeric materials.

Polymer lithium electrolytes, based on the combination of lithium salts with polyethylenoxide (PEO), have been developed and characterized [10]. The main advantages of these electrolytes are in the ease of fabrication as thin films and the low cost. Inexpensive, thin-film lithium batteries are obviously welcome and this reflects the current interest in these polymeric electrolytes. However, the types so far known suffer from low lithium ion conductivity which does not allow their use in ambient temperature batteries, even in the thin film configuration. Consequently, consistent effort is presently directed to the enhancement of the conductivity of the known polymer electrolytes, as well as to the characterization of less-resistive new electrolytes.

Great interest also lies in polymeric electrodes, especially after the recent announcement that electrochemically-doped polyacetylene could be considered as a revolutionary electrode material for high-energy lithium batteries [11, 12]. Effectively, polyacetylene may be *n* and *p* doped in organic electrolytes such as LiClO_4 in propylene carbonate, with the consequent insertion of ClO_4^- and Li^+ ions respectively, and these electrochemical processes allow the realization of polymeric electrode lithium batteries. Further studies [13] however, have shown that the initial claims for the effective application of these batteries were over-enthusiastic. In fact, the coulombic efficiency and the rate of the electrochemical processes are effectively low, and the charge retention of the doped polyacetylene is very poor.

Even if these aspects seem to exclude its immediate application, polyacetylene and, more generally, the class of polymeric electrodes, remain of great importance for the advancement of secondary lithium battery technology. Systematic and intense research should, then, be devoted to these materials, with particular attention being given to the role of the morphology of the polymer and to the nature and composition of the electrolyte on the electrochemical characteristics of polyacetylene. Obviously, the research on alternative polymers to polyacetylene capable of offering faster and more reversible electrochemical reactions remains the main goal in this area.

Conclusions

Even if lithium batteries are in a very advanced technological and development stage, there are still sectors which need further attention and research.

Various primary lithium batteries are now commercially available with very satisfactory performance and no substantial technical changes are foreseen in the near future. Sectors in this area which may deserve the immediate attention of academic and industrial research laboratories are mainly the following:

- (i) characterization of improved, highly conductive lithium solid electrolytes for the development of high-rate lithium solid-state batteries;
- (ii) evaluation of the properties of suitable cathode materials to achieve new values of voltage compatible with lithium organic electrolyte batteries;
- (iii) safety and disposal of lithium batteries in general.

Secondary lithium cells are more open to research as no system has yet reached a stable commercial stage, mainly because of the poor cyclability of the lithium metal electrode. The major approaches which seem to be promising for the solution of the problem are the following:

- (i) use of selected organic electrolytes;
- (ii) use of alternative, non-metallic lithium electrodes.

If these goals can be satisfactorily attained, lithium batteries with long cycle life could be effectively realized. However, the low conductivity of the common organic electrolytes and the low diffusion rate of lithium ions in and out of the intercalation electrodes, would necessarily confine these batteries to low regime ranges.

A real breakthrough in the field can only be obtained with the discovery of 'revolutionary', new electrode and electrolyte materials. Some preliminary results, obtained with polymeric compounds, show that this concept is not purely idealistic, and it may be achieved if adequate research is continuously devoted to the area.

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