ALL-SOLID-STATE BATTERIES

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Summary

Recent work on rechargeable, all-solid-state alkali–metal batteries has advanced the technology to a point where applications through the whole battery product range can be envisaged. From electric vehicle traction batteries, through rechargeable batteries for consumer appliances and power tools, down to miniature rechargeable cells on electronic chips, the solid-state cells now being developed may revolutionize the product range of the battery industry.

Introduction

Solid-state batteries are widely used as power sources for heart pacemakers. The most frequently used type comprises a lithium anode and an iodine–polyvinylpyridine complex as the cathode. The lithium iodide electrolyte formed during cell discharge has relatively low ionic conductivity but the low current requirements for this application can be adequately met and the relatively high volumetric energy density is advantageous.

Nevertheless, the two disadvantages of low ionic conductivity of solid electrolytes and poor interfacial contact between solid electrolytes and solid electrodes has encouraged a general concensus that, in spite of the attractions of low discharge rate and easy sealing, all-solid-state batteries will find application only in specialist, low-current applications such as pacemakers.

In this survey, we highlight the change in perspective gained as a result of recent work at Harwell and elsewhere. Our work as part of a programme aimed ultimately at improved vehicle traction batteries, has involved the fabrication and testing of all-solid-state cells using polymer-based electrolytes. The results to date show that batteries of this type may be cost-effective, not only, eventually, in vehicle traction applications, but also in smaller rechargeable power units for consumer products, power tools and portable electronic devices, and even as micro-power sources on integrated circuits. The materials and fabrication technology for these applications will be very similar and may significantly change battery fabrication technology.

Battery development to date

Most traditional battery applications still utilize battery types evolved over the past century or more. Lead–acid batteries are still almost exclusively used for traction and SLI applications for vehicles as well as for other smaller scale uses such as reserve supplies or as power sources for miners' lamps and safety equipment.

Zinc–manganese dioxide based cells still dominate primary battery applications. Indeed, notable advances in primary battery technology in recent years relate as much to advances with these cells, for example the use of electrolytic MnO_2 and alkaline gel electrolytes, as to the development of new cell types. In spite of many attempts, however, such cells cannot be used with confidence in rechargeable applications.

The third traditional battery type in relatively wide use is the rechargeable alkaline battery. However, only nickel–cadmium and, in a very few special cases, nickel–hydrogen cells have found significant commercial application and materials costs will continue to be a barrier to increased market penetration. It is a common feature of all the traditional batteries that they use aqueous or gelled electrolytes and that the most electro-positive metal which can be used as an electrode for rechargeable applications is zinc.

Alkali–metal rechargeable batteries

The high energy densities that can, in principle, be achieved with batteries based on alkali metal couples have long been realized but technical development has been hampered by inadequate properties of the materials or by incompatibilities between materials. The best known applications to date involve primary cells such as power the heart pacemaker or high-rate cells with non-aqueous-solvent electrolytes such as Li/SO_2 or lithium/thionyl chloride.

For rechargeable applications, the lithium–sulphur couple is very attractive, having an extremely high theoretical energy density of 2600 W h/kg. This is very difficult to realise directly, however, and development work has concentrated on a cell with solid Li(Al) and FeS electrodes and a molten salt electrolyte. Having to operate at over 400 °C, such a cell still poses severe problems of materials compatibility. Even if the technical problems are solved, the energy density may not be much more than 100 W h/kg in practice, much less than originally hoped for, although still twice that projected for the lead–acid battery in the long term.

The discovery of high sodium-ion conductivity in sodium beta alumina in the mid 1960s was a tremendous boost both to scientific and technological research and development, and also to hopes of a real breakthrough in the development of high energy density rechargeable batteries. The chemistry of beta alumina and related materials has proved extremely rich and interesting and many other sodium- and lithium-ion conducting solid elec-

trolytes have since been described both in crystalline and amorphous forms. Work on electrode materials has also flourished since the discovery of lithium insertion into TiS_2. This material, and the oxide V_6O_{13} are currently widely used as insertion-type cathodes in scientific and technical studies.

Very soon after the discovery of beta alumina, work commenced on development of the sodium–sulphur battery, initially at Ford but soon followed up in many other centres. The use of cheap materials, and the promise of realisable energy densities well above 100 W h/kg made the system apparently very attractive for motive power applications and also for load levelling. However, although initial difficulties with seals and corrosion seem largely to have been overcome, sodium–sulphur batteries are still not commercially available.

The high temperatures of operation of the sodium–sulphur battery, above 300 °C, and the Li(Al)FeS battery mean that there is no simple learning curve which can be followed to improve the technology prior to large-scale application, either in fleets of electric vehicles or for load levelling. These are essentially the only markets, and the stringent cost and performance targets for these applications must, therefore, be satisfied with the very first sales. The compatibility and durability requirements for large rechargeable batteries needing many hundreds of deep discharge cycles seem as difficult to solve for these batteries as for the more traditional battery systems also promoted with vigour in the 1970s for electric vehicle traction as a consequence of the fuel price rises in that decade. The most attractive of these is possibly the nickel–zinc battery, with projected realisable energy densities up to 90 W h/kg, although the cost of this system will always be a problem. Difficult materials problems such as dendrite formation and electrode slumping also remain. These, together with the apparently disappearing prospective markets for large numbers of new electric vehicles, at least in the near future, seem to be removing the justification for large research and development programmes, not only for nickel–zinc but also for other systems such as nickel–iron, zinc–air and zinc–chlorine. The prevailing view now seems to be that electric vehicle penetration will proceed at a very moderate rate on the basis of slow improvements in lead–acid batteries and appropriate vehicle and power-train design. An up-swing in scientific and technical research and development on lead–acid batteries and PbO_2 can be anticipated.

New materials for batteries

As a result of the interest in advanced battery materials stimulated, on the one hand, by the discovery of beta alumina and the development of the sodium–sulphur battery, and, on the other hand, by the energy crises of the 1970s, many new electrolytes for lithium and sodium conduction, and also new electrode materials have been discovered. The electrolytes include framework oxides such as LISICON ($Li_{14}Zn(GeO_4)_4$), lithium nitride (Li_3N),

composite materials such as $LiI(Al_2O_3)$, and glassy materials based on oxide or sulphide hosts. Several of the complex oxides are not thermodynamically stable against metallic lithium, although Li_3N, $LiI(Al_2O_3)$ and several glasses are.

In general, the conductivities of lithium-ion solid electrolytes are an order of magnitude or more worse than the best sodium-ion conducting materials such as beta alumina and NASICON $(Na_{(1+x)}Zr_2(P_{(3-x)}Si_x)O_{12})$. This is assumed to be a reflection of the greater ability of Li^+ to polarize towards low-coordination arrays of anions than Na^+, so leading to a higher activation energy for Li^+ conduction in spite of its smaller size. In contrast, although Na^+ insertion into electronically conducting electrodes such as TiS_2 is well established, the larger Na^+ ion encourages the formation of intermediate staged compounds, often with lattice reconstruction, with the result that lithium insertion rather than sodium insertion electrodes are preferable for battery applications in general. From the point of view of electrode behaviour, the smaller lithium ion is also more readily able to insert into framework materials such as V_6O_{13}. The lack of insertion electrodes for sodium is a continuing disadvantage in the development of ambient or moderate temperature sodium-based batteries.

The lack of high conductivity lithium solid electrolytes, at least at moderate temperatures, encouraged a 'traditional' approach to the development of a high energy density lithium battery utilizing an insertion cathode. Much work has been done on systems having lithium anodes, TiS_2 or analogous cathode materials, and a liquid electrolyte, consisting of a polar organic liquid containing a dissolved lithium salt. Once again, however, in spite of great expectations, fundamental problems persist with this type of cell for rechargeable applications, notably concerned with the rechargeability of the lithium anode and subsequent capacity loss on cycling.

In spite of large research and development programmes into batteries as diverse as Li(Al)/FeS, Na/S and Li/TiS$_2$, notably to develop systems for advanced power sources, and also, in spite of the considerable scientific and technical research carried on in related areas, almost the only alkali battery systems in the market place are primary cells. In addition to heart pacemaker batteries, systems presently available include Li/MnO_2 organic electrolyte button cells, and Li/SO_2 and $Li/SOCl_2$ high energy density cells originally developed for military applications. For the latter two systems, sealing, self-passivation and, particularly, safety may pose difficulties for widespread commercial application. Interesting developments continue to be made in lithium primary battery technology, for example, the thin cells now in use with instant cameras and portable miniature televisions. However, in spite of the work and enthusiasm of the last decade or so there has seemed, until recently, very little prospect either of alkali–metal secondary systems entering the markets presently dominated by primaries, or of their entering new markets or existing ones presently catered for by nickel–cadmium or lead–acid.

Progress with polymers

In 1978, Harwell initiated a programme which, in the U.K., was partly sponsored by the DoI, to investigate materials more objectively for advanced alkali–metal rechargeable batteries. The work was shared between Harwell, universities in the U.K. and R. and D. establishments in Denmark, and the 'Anglo/Danish Battery Programme' as it became known was 50% sponsored by the CEC. The scientific basis of the work at the time was described in a review article in *Nature* [1] and the rationale for the work, which was addressed at the use of batteries for energy conservation and storage in electric vehicle traction and load levelling applications, was also reviewed [2]. In addition to the technical programme, a detailed market assessment and feasibility study was carried out which provided a very useful basis for future technical planning [3].

The technical objective of the programme was to examine the properties and behaviour of several promising solid electrolytes and insertion electrodes described in the literature to obtain a realistic assessment of their properties, the problems in their use in batteries and their compatability with other materials in cells. Hence a more realistic determination of which materials might be technologically useful for electric vehicle batteries of the future could be made. It was hoped, thereby, to obtain a fairly hard-headed assessment of whether alkali metal batteries could be developed to realise their potential energy density advantages and to identify which materials could best be chosen for future cell development studies. A temperature range of 100 - 200 °C was considered acceptable for such a first-generation electric vehicle battery.

Phase I of this programme ended in 1980 [4, 5]. The work was successful and clear choices of materials for further work and for incorporation in test cells were available. A Phase II programme now concerned primarily with cell testing and evaluation rather than with materials research started in 1980 and will continue until early 1984. The prospective at the beginning of Phase II has been described [6].

All-solid-state cells were seen as the only practical way forward for ambient and moderate temperature cells, given the persisting difficulties with organic liquid electrolyte batteries. The cells in the Phase II programme utilize a lithium or lithium-alloy anode and an insertion cathode. V_6O_{13} and TiS_2 have both been evaluated, although the former is presently preferred because it can be prepared in fine particulate form and does not suffer from the morphological difficulties of TiS_2. Although the Phase I programme studied in depth the very interesting ceramic lithium-ion-conducting electrolytes Li_3N [7, 8] and $LiI(Al_2O_3)$ [9, 10], the choice of this type of cell was made more realistic by the discovery of polymer-based solid electrolytes by Armand and co-workers in France [11]. Some polar organic materials such as poly(ethylene oxide) will take alkali salts into solution and manifest rapid alkali-ion conductivity. Although absolute conductivities of such polymer-based materials are not in general so high as those of crystalline solid

electrolytes, plastic materials may be made into thin pinhole-free sheets with sufficient conductance for use in cells and batteries. Equally importantly, the plasticity of polymers overcomes the other major problem with solid-state battery systems, that of maintaining good interfacial contact.

Prospects for solid-state rechargeable batteries

The technical feasibility of such batteries has been established during the last two years, initially on small area cells and, more recently, using cells with areas up to 500 cm^2. It has been demonstrated that cells may be cycled under deep discharge (over 90%) to over 100 cycles while maintaining over 50% theoretical capacity (based on $Li_8V_6O_{13}$). Operating temperatures are in the range 100 - 140 °C and current densities up to 1 mA cm^{-2} are achieved. The progress to date has recently been reviewed [10].

Techniques for continuous fabrication of electrolyte and electrolyte-containing composite cathode films have been developed (Figs. 1 and 2).

Fig. 1. The fabrication of an all-solid-state composite cathode using a continuous-casting, solvent-evaporation technique.
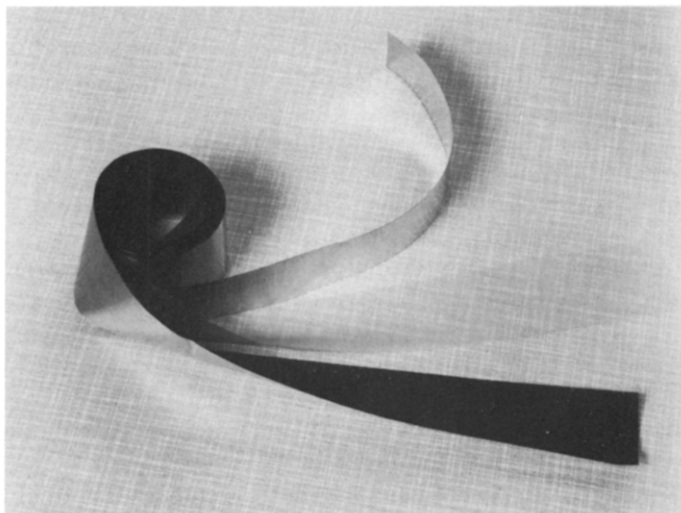
Fig. 2. The components of an all-solid-state rechargeable cell utilizing a poly(ethylene oxide)-based electrolyte.

Typical electrolyte and cathode thicknesses are 35 and 70 μm. Developments in the fabrication technology and the results from cell testing have allowed realistic predictions to be made of ultimate battery performance and of materials costs.

For electric vehicle batteries, it is estimated that the selling price may be within the present range for lead–acid batteries. The outstanding feature of the solid-state battery, however, as presently projected, is in the extremely high energy densities which may be achieved. A volumetric energy density of around 525 W h/l and a gravimetric energy density of around 425 W h/kg are considered feasible. These figures include bipolar connectors, busbars and cell casing. Although they would be degraded by the lagging required to maintain the temperature at 120 °C, by heaters to bring the cell to operating temperature, and by provision for cooling at high discharge rates, these are such attractive energy densities that some degradation would be quite acceptable. For electric vehicle application, the temperature is almost ideal, being low enough not to pose serious materials or heat conservation problems and high enough to be independent of ambient temperature and not to require cooling in summer conditions. Moreover, the energy/peak power ratio (about 1.6) is also appropriate to this application. The improvement in gravimetric energy density over that of lead–acid is so enormous that it opens up considerable scope for innovative engineering in vehicle design. It is this, rather than cheaper batteries, which will lead to a cost-competitive electric vehicle.

Many questions remain to be answered by further research and development. From the point of view of battery operations, prime objectives are to build and study series-connected stacks and to solve the problems which may

occur in the cycling and thermal management of such stacks. Improvements in materials would also be useful, particularly with respect to the ionic conductivity of the electrolytes, the ionic and electronic conductivity of cathode materials, fabrication methods and cost.

Nevertheless, the all-solid-state battery concept currently under study is intrinsically very attractive. Bipolar series-connected units made of thick-film components are the basic building blocks. The all-solid-state system is inherently leak-proof and safe, and the fabrication technology of such thick-film cells lends itself not only, ultimately, to large electric vehicle batteries but also to rechargeable systems of smaller sizes right down to micro-power sources on electronic devices. Considerations of large-scale manufacturing technology are presently at an early stage and much development work still needs to be done, but the products presently made by the packaging, photographic film and other industries give confidence that fabrication technology appropriate to these batteries can be developed.

We, therefore, have the prospect of all-solid-state rechargeable thick-film lithium batteries being developed, using similar fabrication technology as for large vehicular power units, for power tools, consumer products, toys, domestic appliances, flashlights and so on with significant performance or cost advantages over present day Ni–Cd or lead–acid rechargeable systems. The market potential for batteries for easy-to-use cordless appliances, where mains power is currently used, for example with vacuum cleaners, power tools or lawn mowers, and for relatively cheap rechargeable batteries in place of, to the consumer, expensive primary cells, is very attractive. For many applications at room temperature, higher conductivity electrolytes, in particular, must be developed but there is some confidence that appropriate materials research in this field will be successful.

Initial applications of these cells will probably be found in special high-cost hostile environments in the 100 - 200 °C range where their operation is presently at an optimum but where most present-day batteries will not function. The technology will probably advance beyond that through application of single-cell batteries in low power room-temperature applications, possibly even, initially, as primary batteries or as cells requiring recharge only a few times. Cells having flashlight capability have already been technically demonstrated in prototype form in the Harwell work. Technical development will then proceed to larger multicell batteries, initially for use with consumer products, toys and tools but leading, ultimately, to electric vehicle power sources.

Solid-state cells should provide many benefits in 'exotic' applications such as satellite power, power for submersibles or for remote-controlled vehicles under water, in mines or other 'difficult' environments. Solid-state cells also have great attractions as power sources for electronic devices, whether in 'conventional' form for appliances such as mobile telephones, or in miniature form for 'on-chip' applications. Micro-power sources integrated with the circuits they power are as exciting a development prospect in many ways as the development of large units for electric vehicle traction.

Although the materials fabrication and compatibility problems will be rather different, the solid-state concepts now under development offer exciting prospects for this field also.

Acknowledgements

References

1 B. C. Tofield, R. M. Dell and J. Jensen, Advanced batteries, *Nature, 276* (1978) 217 - 220.
2 B. C. Tofield, The current state of battery research, *Electr. Rev., 204* (1) (1979) 29 - 32 (1979); Battery research diversifies to meet the future, *Electr. Rev., 204* (4) (1979) 29 - 31; Battery research spans the Continent, *Electr. Rev., 204* (16) (1979) 38 - 40.
3 J. Jensen, P. McGeehin and R. M. Dell, *Electric Batteries for Energy Storage and Conservation*, Odense University Press, Odense, Denmark, 1979.
4 B. C. Tofield, Materials research and development for advanced batteries, in *New Ways to Save Energy, Proc. Int. Seminar, Brussels, 23 - 25 October, 1979*, Reidel, Dordrecht, The Netherlands, 1980, pp. 579 - 599.
5 J. Jensen, Battery application and assessment studies, in *New Ways to Save Energy, Proc. Int. Seminar, Brussels, 23 - 25 October, 1979*, Reidel, Dordrecht, The Netherlands, 1980, pp. 600 - 609.
6 A. Hooper, Towards the solid-state rechargeable battery, *Electr. Rev., 209* (21) (1981) 27 - 31.
7 U. v. Alpen, A. Rabenau and G. H. Talat, Ionic conductivity in Li_3N single crystals, *Appl. Phys. Lett., 30* (1977) 621 - 623.
8 A. Hooper, T. Lapp and S. Skaarup, Studies of hydrogen doped lithium nitride, *Mater. Res. Bull., 14* (1979) 1617 - 1622.
9 C. C. Liang, A. V. Joshi and N. E. Hamilton, Solid-state storage batteries, *J. Appl. Electrochem., 8* (1978) 445 - 454.
10 A. Hooper, lithium iodide-based solid electrolytes, *J. Power Sources, 9* (1983) 161 - 166.
11 M. B. Armand, J. M. Chabagno and M. J. Duclot, Poly-ethers as solid electrolytes, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, North-Holland, New York, Amsterdam, Oxford, 1979, pp. 131 - 136.
12 J. M. North and A. Hooper, Fabrication and performance of all-solid-state polymer electrolyte-based rechargeable lithium cells, Proc. 4th International Conference on Solid State Ionics, Grenoble, 4 - 7 July, 1983, *Solid State Ionics*, to be published.