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Short communication

Recent developments and likely advances in lithium-ion batteries

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Abstract

Advances in lithium-ion battery technology since the last International Power Sources Symposium in Amsterdam in September 2003 are reviewed.

Cost and safety are still seen as important factors limiting further expansion of application of lithium-ion batteries.

Lithium bis-oxalato borate electolyte salt and lithium iron phosphate cathode material are being actively investigated.

Keywords: Lithium-ion; Batteries; Bis-Oxalatoborate; Iron phosphate; Battery safety

1. Introduction

This paper is a successor in the series presented at the last International Power Sources Symposium in Amsterdam in September 2003 [1] and at the preceding symposium in Manchester in April 2001 [2]. As in these papers, the aim is not to review every paper which has been published on lithium-ion batteries, as this would be a vast undertaking, but instead to focus on those papers of which the authors are aware which concentrate on the most significant aspects.

It is a relatively short time since the last symposium, so major advances in that time would not be expected, particularly as significant steps forward were reported at the last meeting. These included the possible introduction of a new electrolyte salt (lithium bis-oxalato borate, LiBOB) and a new cathode material lithium iron phosphate, $LiFePO_4$, or variants with other transition metals. Developments and applications of both of these are in progress.

The major emphasis at the last meeting was on the great success of lithium-ion batteries for small scale applications such as portable telephones and computers but on its present limitations for larger scale applications, such as electric vehicles, for which it is technically suited. The limitations were seen as cost and safety, rather than performance as such, except possibly for military [3] or space [4] applications where high energy and high power are needed over a wide operating temperature range, e.g. the US military would like lithium-ion batteries to approach the energy density of lithium primary ones [5].

At Manchester in 2001, lithium-ion battery performance in terms of energy density was predicted to have a limit of about 250 Wh kg^{-1} [2]. A more detailed analysis of battery construction presented at the Amsterdam meeting produced a similar figure [6].

2. Anode materials

Anode materials continue to attract attention with the aim of developing a material capable of absorbing lithium reversibly with a higher capacity than carbon. Many metal alloys have been studied in the past [1] but cracking of the alloy on cycling has always been a problem. This is reduced if nano-sized particles, e.g. of tin, are used [7]. Nanocomposite $Li_4Ti_5O_{12}$ has been tested as an anode material for high rate batteries [3].

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Carbon fibre anodes, instead of carbon (e.g. graphite) powder stuck on to copper backing have been tested for improved overcharge safety [8].

Most interest has been in lithium-ion batteries but lithium metal polymer batteries have also been described [9,10].

3. Electrolyte development

The new electrolyte salt, LiBOB ($LiB(C_2O_4)_2$) was discussed at the last symposium and is now attracting considerable interest because of its ease of manufacture from cheap, readily-available starting materials, and its reasonable conductivity in battery solvents. In line with the conclusion at the last symposium that cost is now a major factor, the potential lower cost of this material is important. Its properties have been extensively described [11]. Its main technical advantage is that it is less acidic than the present electrolyte salt, lithium hexafluorophosphate ($LiPF_6$), and so is more stable when used with lithium manganese oxide, 'manganese spinel' cathode material [12]. The chemistry of electrolyte salts is being actively investigated, particularly with reference to variants on LiBOB (see, e.g. [13–15]). Conductivities of various electrolytes, including those containing LiBOB, have been investigated [16]. Solutions containing LiBOB are less conductive than those containing $LiPF_6$ and may not be suitable at low temperatures, due to low solubility. This is more significant for military applications.

Polymer electrolytes are now well established [1]. Using these electrolytes and a pouch cell construction, energy densities of 200–230 Wh kg^{-1} has been reported [17], close to the estimated limits for lithium-ion battery chemistries [1,6]. Solid electrolytes with a cathode system which generates sulphur dioxide have also been proposed [18]. Dry polymers of a rubbery nature with no liquid or gel component but with an incorporated lithium salt can operate at 40–60 °C [9]. Nitrogen-containing conductive polymers are also being investigated [19,20].

The solid state lithium phosphorus oxynitride (LIPON) electrolyte, which was developed by Bates and co-workers at Oak Ridge National Laboratory, has been known for several years. Commercial cells based on this technology are now reported to have achieved 300 Wh kg^{-1} [21].

Lithium-ion batteries are usually described as suitable for operation up to 60 °C. The stability of lithium-ion battery electrolytes containing $LiPF_6$ has been investigated at temperatures up to 100 °C. Electrolyte decomposition was found which could be retarded by addition of Lewis base additives [22].

Another possibility for electrolytes is the use of ionic liquids [19], such as tetra-alkyl ammonium $N(SO_2CF_3)_2^-$ species which have potential windows <0 to >5 V. Solutions with lithium trifluorosulphonimide show conductivities in the 10^{-4} to 10^{-5} S cm^{-1} range, with higher values at higher temperatures [19]. Ionic liquids are non-flammable, stable to >300 °C and are non-toxic. However, they are in the early stages of development at the present.

4. Cathode materials

At the last symposium, the usage of mixed cobalt/nickel lithiated oxides to replace lithium cobalt oxide as the standard cathode material for lithium-ion batteries was predicted. Active research continues, e.g. on lithium mixed cobalt/nickel/manganese oxides [12]. The use of lithium nickel/cobalt/aluminium oxide as cathode material in lithium-ion batteries for hybrid electric vehicles (HEV) has been reported [23]. A related system is layered $Li_x(MnNi)O_2$, preferably with $x > 1$. These species do not de-oxygenate when charged, reducing fire and explosion risks, and produce extraordinary capacities over the range 2.5–4.6 V. Energy outputs are >1 Wh g^{-1}, but the potential limits point to ionic liquid electrolytes and >40 °C operation enhances performance, e.g. a substantial departure from current technology is needed [19]. Multi-phased Al-doped spinels offer unprecedented high rate performance, especially suitable for hybrid vehicle batteries, but a non-acidic electrolyte is still required for long cycle life [24].

Another development, possibly more significant in the long run, could be the adoption of lithium iron phosphate (or other lithium transition metal phosphates) to replace lithium cobalt oxide as the cathode material. This material has the advantage of possibly lower cost and improved safety. For these reasons, it is now attracting commercial interest (see, e.g. [17,25]). However, low conductivity is a technical disadvantage, though high rate operation has been reported [26]. Partial substitution of iron by other atoms (doping), coating with carbon or Fe_2P could greatly increase the conductivity [27]. Other lithium metal phosphates have been investigated but high polarisation was thought to eliminate pure $LiMnPO_4$ even though it has a higher voltage than $LiFePO_4$ [28]. Metals other than Fe or Mn seem less attractive as they are more expensive and toxic though various vanadium compounds are being actively investigated. For high rate applications, nanocomposite $LiFePO_4$ has been tested [3]. Phosphate cathode materials have been reviewed [29].

A different chemistry for lithium rechargeable batteries is the lithium/sulphur system. Energy densities of 300–350 Wh kg^{-1} are reported and development is continuing [30]. Other work on the lithium–sulphur system will be reported at this symposium [31].

Vanadium oxide cathode materials are used in the lithium metal polymer battery [9,10].

5. Battery safety

Battery safety is a matter of crucial importance to the lithium battery industry. The massive sales of lithium-ion batteries depend on consumer confidence in these batteries and this has been achieved. However, for larger size batteries, e.g. for electric vehicles, the safety problems for the large batteries required are greater than for the small batteries used in telephones or computers. Charging lithium-ion batteries to above 4.6 V $cell^{-1}$ when using lithium metal oxide cathodes and flammable liquid electrolyte cathodes can lead to unsafe events [1], possibly due to lithium deposition or to oxidation of solvents at these high potentials. Lithium iron phosphate may be safer as complete oxidation of this material occurs at a lower voltage (3.4 V), and the oxidation product of lithium iron phosphate is the stable material, ferric phosphate, according to the reaction:

$$LiFePO_4 + 6C \rightarrow LiC_6 + FePO_4$$

LiBOB has been seen as a safe battery electrolyte for large scale lithium-ion batteries [32]. The thermal stability of 18,650 cells with LiBOB electrolyte has been investigated but reaction of the charged positive electrode occurred at 40 °C lower than for $LiPF_6$ electrolyte [33].

In order to achieve battery safety without relying solely on external electronics, internal electronics within the cell have been used to provide overcharge and short circuit protection [5].

6. Battery cost

Cost was emphasised at the last symposium as the major challenge for lithium ion-batteries in the future. LiBOB could be cheaper than $LiPF_6$ as a battery electrolyte salt and moreover could enable the cheaper lithium manganese oxide spinel, $LiMn_2O_4$, to be used instead of the expensive lithium cobalt oxide, $LiCoO_2$. Lithium iron phosphate could be a cheaper cathode material. It has been estimated that use of lithium iron phosphate as cathode material could reduce the cathode cost from 50% to 10% of the battery cost [17].

If new cathode materials, such as phosphates, are intrinsically safer than lithium cobalt oxide, then it might be possible to save on the sophisticated electronics which are currently needed to ensure lithium-ion battery safety, though this would need thorough investigation.

7. Battery applications

The high power capabilities of lithium-ion batteries make them useful in combination with other power sources, such as zinc-air batteries [34,35] or fuel cells [36,37]. The high energy content of Zn-air primary batteries makes them possible battery chargers for Li-ion portable batteries.

For Autonomous Undersea Vehicles and Unmanned Vehicles, high energy contents of 195 Wh kg^{-1} and 300 Wh l^{-1} have been achieved [23].

Hybrid electric vehicles are now commercially available using nickel-metal hydride batteries. Lithium-ion batteries have the potential for higher energy density, higher power density and longer calendar and cycle life. High power lithium-ion batteries have been developed for this application [23].

Lithium metal polymer rechargeable batteries have been developed for telecommunications applications [9,10].

8. Conclusions

In the relatively short time since the last International Power Sources Symposium, progress on lithium-ion batteries has been generally incremental with considerable interest in the new lithium electrolyte salt (LiBOB) and in the new cathode material, lithium iron phosphate ($LiFePO_4$). Developing technologies include layered LiMnNi oxides, ionic liquids and N-containing polymer electrolytes.

The conclusions at the last symposium that cost and safety are the main factors limiting the usage of lithium-ion batteries in larger sizes, such as for electric vehicles, remain.

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