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Recent developments and future prospects for lithium rechargeable batteries[☆]

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Abstract

Possible future developments of lithium rechargeable batteries are discussed. Lithium ion liquid electrolyte batteries are now well established, with energy densities of up to around 150 Wh kg^{-1} . There are prospects of increases in the energy density to perhaps $200\text{--}250 \text{ Wh kg}^{-1}$ by using new cathode materials (lithium nickel cobalt oxide) and light weight construction. High power cells make it possible for these batteries to find new uses, e.g. in military applications. Some new materials could reduce the cost, which might make lithium rechargeable batteries economic for electric vehicles.

Keywords: Lithium ion rechargeable batteries; Lithium oxides

1. Introduction

Since the introduction of lithium ion batteries by SONY [1], the market for these has grown to around 400 million cells per year [2] for premium consumer applications, such as camcorders, portable telephones and computers. 95% of these batteries are made in Japan [2]. The vast majority of them use the same basic chemistry as announced by SONY, which is a carbon negative electrode into which lithium intercalates and a lithium cobalt oxide, LiCoO_2 , positive electrode. The voltage range is 2.5–4.2 V, with a nominal voltage of 3.6 V. This paper gives a personal assessment of recent developments since the 1999 International Power Sources Symposium and of likely improvements to the lithium ion system. It does not attempt to give an exhaustive review of the subject, as that has been done recently [3], but rather gives the author's opinions of those developments which are significant and have the potential for industrial exploitation. It describes recent developments and new ideas for all aspects of lithium ion batteries: anode, electrolyte, cathode and construction and is not limited to purely chemical aspects.

2. Anode development

Existing lithium ion batteries use carbon in various forms, such as graphite, hard carbon and microspheres, as the negative electrode. The use of carbon as a negative defines the lithium ion system, with lithium intercalation into the carbon obviating the use of lithium metal as a negative electrode with the hazards resulting from possible uneven lithium plating and dendrite formation. However, a new electrolyte system has been developed in which, it is reported, lithium can be plated safely [4]. The use of a negative electrode has been avoided completely in the FORTU battery, which is a metal-free system, in which lithium is produced within the battery on charging from the cathode system that uses lithium cobalt oxide [5]. This system uses a sulfur dioxide electrolyte (see below). The advantages of this system arise from the electrolyte, as the cathode is the same as the standard SONY system. However, avoiding the use of an intercalating carbon negative electrode reduces the weight.

Research on tin compounds as negative electrodes to replace the carbon continues, following the announcement by FUJI [6] of lithium ion batteries using this system.

3. Electrolyte development

Electrolytes based on organic carbonate mixtures have become the standard for lithium ion batteries. The main

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developments recently have been investigations of different mixtures of propylene, ethylene, diethyl, dimethyl and ethyl methyl carbonates to obtain the best low temperature performance. Performance down to about -20°C is possible with various mixtures of the above compounds. This is adequate for domestic applications. To get lower temperature performance (which is needed for some military applications) with organic electrolyte systems, other organic compounds, such as acetates, need to be added to the carbonate mixtures [7].

An alternative approach to good low temperature performance is to use completely different electrolytes. This is achieved in the FORTU battery. This uses the standard lithium cobalt oxide cathode material, but the electrolyte is liquid sulfur dioxide with lithium tetrachloroaluminate (LiAlCl_4) as the electrolyte salt. This solution has a freezing point below -80°C and a conductivity at room temperature of about 10 times that of organic electrolytes. Hence, this system has high power capability. The good low temperature performance and high power capability are important for military applications.

Apart from liquid electrolytes, polymer electrolytes are now developing rapidly, particularly those of the gelled electrolyte type. As with the liquid electrolyte cells, production is concentrated in Japan [8]. Performance of liquid and gelled electrolyte cells can be compared for cells of the same construction (envelope or packet cells, see below) made by the same manufacturer (GS-MELCOTECH) [9]. Performance was remarkably similar. Pure polymer electrolytes have been investigated extensively [10], but still suffer from the problems of low conductivity and poor low temperature performance. Hence, the only application has been for uses in above-ambient temperatures [11].

4. Cathode materials

The standard cathode material remains lithium cobalt oxide, LiCoO_2 , for the vast majority of lithium ion batteries. Its advantages of reliable performance and long cycle life outweigh its disadvantages of only moderate capacity (130 mAh g^{-1}), high cost of cobalt metal and moderate toxicity. The lithium cobalt nickel oxide ($\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$) cathode material was already known at the time of the last International Power Sources Symposium [12]. This material has potential advantages of significantly higher electrochemical capacity (180 mAh g^{-1}) and also should have the advantage of lower cost as 80% of the cobalt in LiCoO_2 has been replaced by nickel. However, metal prices are volatile and cost advantages cannot be estimated on a long-term basis. The technical problem which has limited its widespread use so far has been the poor capacity retention on cycling, as reported at the last Symposium. However, it has been discovered recently that addition of small amounts of aluminium significantly improves capacity retention

[13,14] so lithium cobalt nickel oxide is likely to replace lithium cobalt oxide.

Lithium manganese oxide spinel (LiMn_2O_4) continues to attract attention because of the lower price and toxicity advantages of manganese over cobalt. However, notwithstanding large amounts of work, the fundamental problems with this material remain, which are low electrochemical capacity (110 mAh g^{-1}), instability during storage in the charged state and limited cycle life. These may be related to the greater sensitivity of manganese compounds than cobalt ones to hydrolysis by acidic impurities in the electrolyte arising from the lithium hexafluorophosphate electrolyte salt. As major work has failed to eliminate these problems, it seems that they are insuperable, and widespread use of manganese oxide spinel seems unlikely. Another approach has been to try to develop a manganese analogue of the lithium cobalt oxide with the formula LiMnO_2 [15]. This had been reported before the last Symposium but, although this material showed a high initial capacity, capacity was lost on cycling as the material reverted to the spinel. Another form of LiMnO_2 has since been made [16]. Possibly this will find application as the lower cost and toxicity of manganese in comparison with cobalt would give it a significant advantage provided that a long cycle life could be obtained and that at least 50% of the manganese could be cycled, as this is roughly the proportion of the cobalt which can be reversibly cycled in lithium cobalt oxide.

Higher voltage cathodes have also been investigated such as LiCoMnO_4 and related compounds [17]. Application of these is likely to have to await electrolytes which are stable at these high voltages.

An alternative and imaginative cathode system, which was reported at the Symposium back in 1997 [18], was the metal oxide/lithium sulfite system. Various transition metal oxides are being investigated under a European Union CRAFT programme 'LIBEVA'.

Rechargeable lithium/sulfur dioxide liquid cathode batteries have been investigated for many years but have never reached commercial production because of safety concerns. A new approach from Battery Engineering Inc. [19] has been to make a lithium ion/sulfur dioxide rechargeable cell but with a lithium foil negative to act as a source of lithium. On discharge, the lithium reacts to form the normal discharge product for a lithium/sulfur dioxide primary battery, namely lithium dithionite, $\text{Li}_2\text{S}_2\text{O}_4$, which can then be cycled as a source of lithium ions. A variant on the rechargeable lithium/sulfur dioxide battery uses a copper chloride cathode, rather than just using the electrolyte as a liquid cathode. This system has been known for many years but has suffered the same safety problems as the lithium/sulfur dioxide rechargeable cell. Recent advances are reported to have avoided these problems [20].

Apart from the major efforts on oxides as cathode materials, some work has been reported on sulfides. These have the advantages of much higher capacity, e.g. 400 mAh g^{-1} for Li_2FeS_2 , cf. 130 mAh g^{-1} for LiCoO_2 . However, the

voltages are much less (1.8 V for Li_2FeS_2 , 3.6 V (nominal) for LiCoO_2), though the higher electrochemical capacities should more than compensate for this. One factor limiting the use of lithiated transition metal sulfides has been the inconvenient, slow, high temperature solid state syntheses of these materials [21]. New syntheses have been developed which avoid this problem [22].

5. Battery construction

Batteries are now widely available in both cylindrical and prismatic formats. Cells are also available using a flat spiral wind construction [23]. To save weight, light-weight packaging can be used and some techniques were reported at the last Symposium [24]. Recently, lithium ion batteries containing either liquid or gelled electrolytes have been announced using light-weight packaging [9]. Energy densities using either electrolyte were similar at about 160–170 Wh kg^{-1} .

6. Battery performance

Energy densities of about 140–150 Wh kg^{-1} are now available in cells using metal cans, with higher values of 160–170 Wh kg^{-1} in cells with light-weight packaging [9]. There are prospects for higher energy density batteries.

1. By the use of lithium cobalt nickel oxide cathode material instead of lithium cobalt oxide. This raises Coulombic capacity from around 130 to around 180 mAh g^{-1} , an increase of nearly 40%.
2. Light weight packaging. This gives an increase of around 20%.
3. Lithium-free batteries (e.g. SO_2 electrolyte/ LiCoO_2 cathode) for which around 200 Wh kg^{-1} is claimed.
4. New cathodes, e.g. sulfur compounds.

These improvements, individually or collectively, suggest that further significant increases in energy density for lithium rechargeable batteries are possible, with perhaps 200–250 Wh kg^{-1} being possible in the foreseeable future. This reflects roughly a doubling of the energy density that was available a few years ago when 100–110 Wh kg^{-1} was the norm. These energy densities bring the energy density of lithium ion batteries up to seven or eight times that available from lead–acid, which is around 30 Wh kg^{-1} .

The energy density available from a battery is not the only criterion to judge its performance. Power can be more important. As with any battery, the power available from lithium ion cells depends not only on the chemistry but also on the design. Some lithium ion batteries have been designed specifically for high power [25]. High power cells had power ratings of around 800 W kg^{-1} (continuous) or 1400 W kg^{-1} on 18 s pulses. These are high values and

indicate that lithium ion batteries can be high power devices. However, a high power design will affect the energy density, with high power batteries having energy densities of only around 80–100 Wh kg^{-1} , in contrast to high energy batteries which achieve around 140 Wh kg^{-1} .

Performance must be judged not only in relation to battery size or weight, but also in relation to cost. Partial replacement of the expensive cobalt in lithium cobalt oxide by nickel should reduce cathode material cost. Manganese compounds would be cheaper still. Sulfur compounds, for either cathode or electrolyte (sulfur dioxide) would further reduce cost.

7. New applications for lithium ion batteries

Existing applications for lithium ion batteries are for the premium applications for the consumer market, originally for camcorders, now more widely for portable telephones and computers. Lithium ion batteries for electric vehicles have been extensively investigated, but the cost needs to be reduced significantly. Lithium ion batteries are now being investigated for numerous military applications such as underwater applications [25], aircraft main batteries [26], space [27], and batteries for portable electronic equipment [28].

8. Conclusions

Since the introduction of lithium ion batteries nearly 10 years ago, their production has expanded enormously. The performance has improved significantly in the last couple of years, with prospect for further improvements due to different construction and new cathode materials (lithium nickel cobalt oxide). Gelled electrolyte batteries are now coming into production.

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