

Recent developments and likely advances in lithium rechargeable batteries

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Abstract

Developments in lithium rechargeable batteries since the last International Power Sources Symposium in Manchester in 2001 are described. The major developments are that, as expected, lithium cobalt oxide cathode material is being replaced by lithium cobalt/nickel oxide and polymer electrolyte batteries are now coming into production. Likely future developments are new cathode and electrolyte materials to reduce cost and to improve safety.

Some research has been reported on sodium-ion batteries.

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1. Introduction

Production of lithium-ion batteries continues to expand in line with increasing demand from the electronics industry, e.g. for portable telephones and computers. Production is now around 800 million cells per year, with 450 million being cylindrical cells, 250 million being prismatic and 100 million polymer [1]. About 75% of production comes from Japan [2]. Active research is continuing in all aspects of batteries, e.g. anodes, cathodes, electrolytes, construction. The major factors limiting wider application of lithium-ion batteries remain cost and safety. New developments are taking place to address these limitations.

This paper will follow the previous paper at the last International Power Sources Symposium at Manchester [3] in reviewing those aspects of lithium-ion batteries which appear to be of the most significance to the author but will not attempt exhaustive coverage of the subject. It will concentrate on those developments which were already starting to take place by the time of the Manchester symposium and new developments reported since then.

The paper will concentrate on lithium-ion batteries, as these are a major industry and rapidly developing but will also include brief reference to sodium-ion batteries, which have attracted a small amount of research attention recently.

2. Anode development

Carbon remains the pre-eminent anode material for lithium-ion batteries because of its good performance. However, lithium titanium oxides have been reported to offer longer cycle life, albeit at the expense of a much lower voltage. Cells using this technology are now in production [4].

Tin compounds continue to be investigated as lithium-absorbing materials for lithium-ion batteries [5].

Sodium-ion batteries have been shown to be technically possible and have the potential advantage that sodium compounds are cheaper than lithium ones [6]. A sodium-ion cell using a sodium cobalt oxide $\text{Na}_{0.7}\text{CoO}_2$ cathode, analogous to a lithium-ion cell has been successfully cycled [7]. Sodium could be successfully intercalated into hard carbon or petroleum coke. However, the chemistry of sodium is significantly different from lithium, particularly in the solubility of sodium salts in organic solvents. Few sodium salts are soluble in the commonly used lithium-ion battery electrolyte solvents (organic carbonates) and the only sodium salt which seems to be soluble is sodium perchlorate, which may not be stable in long term cycling.

3. Electrolyte development

Polymer gelled electrolytes are now available, with production rapidly increasing. Most production is in the Far East, with typical cell sizes being around 500 mAh, suitable for the portable telephone market.

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Pure polymer batteries are becoming available but, because their operating temperature still remains around 80–100 °C, they are limited to applications such as electric vehicles or emergency back-up power supplies for telecommunications installations [8,9].

One factor which increases the cost of lithium-ion batteries is the cost of the electrolyte salt, lithium hexafluorophosphate, LiPF_6 . This salt has the advantage of high conductivity and compatibility with the usual cathode materials, lithium cobalt/nickel oxides. However, it is expensive to make in the high purity needed and it is also prone to hydrolysis, forming the highly toxic hydrofluoric acid, HF [10]. A new electrolyte salt which has been reported is lithium bis-oxalato borate [11,12]. This is easily made from readily available, cheap starting materials and has adequate conductivity. It is not prone to hydrolysis releasing acidic impurities, as is LiPF_6 , so it is stable to lithium manganese oxide, manganese spinel, LiMn_2O_4 . Laboratory studies indicate better high temperature (50–70 °C) cycling performance than LiPF_6 , presumably due to its greater stability to hydrolysis [10]. Other related boron and phosphorus compounds have also been reported for this application [13,14]. These include alkyl and aryl, including fluorinated aryls, chelato borates and oxalato borates. Chelato complexes of phosphorus have also been reported. Other investigators have studied another class of electrolyte salts which are also potentially cheaper than LiPF_6 , based on imidazolium compounds [15].

4. Cathode development

The original cathode material for lithium-ion batteries, lithium cobalt oxide, LiCoO_2 , is now being replaced by a mixed lithium cobalt/nickel oxide, with the approximate composition $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$, though small amounts of other metals, e.g. aluminium, are needed to stabilise it. The advantages are that nickel is cheaper than cobalt and that a higher capacity (180 mAh, cf. 137 mAh) is achieved as only 1/2 of the lithium reacts in the pure lithium cobalt oxide, while 2/3 of the lithium can react in the mixed lithium nickel/cobalt oxide. The reason for this is that different phases are formed when the two materials are oxidised (charged) [16]. Many papers are being published on lithiated metal oxides, where the metal contains cobalt, nickel, manganese and sometimes other elements.

One material which has attracted considerable interest recently is lithium iron phosphate, LiFePO_4 as it has a moderate capacity (around 130 mAh/g or about 80% of theoretical) with a steady voltage (around 3.4 V) [17]. When carbon was intimately mixed with the cathode material, capacities close to 100% theoretical at rates up to 5 C were achieved [18]. The main advantage however is that it does not use expensive and somewhat toxic metals (nickel or cobalt) but instead uses the cheap and non-toxic metal, iron. Lithium iron and other transition metal phosphates, LiFePO_4 ,

LiCoPO_4 , $\text{LiV}_2(\text{PO}_4)_3$, LiVPO_4F are now being investigated [19].

Manganese spinel, LiMn_2O_4 , continues to be investigated as a cathode material but its low capacity (110 mAh/g) remains a disadvantage though the low cost and toxicity of manganese compared with nickel or cobalt are advantages. The relative capacities of manganese and cobalt can be compared in equivalent commercial cells in 18,650 size for which the capacities are 1.4 Ah for manganese and 2.2 Ah for cobalt [20]. The cycle life for manganese spinel is only moderate in standard lithium-ion battery electrolytes, due to hydrolysis by traces of HF. However, it may be possible to avoid this problem by using a non-acidic electrolyte salt, such as lithium bis-oxalato borate [13].

Lithium iron sulphide, Li_2FeS_2 , was suggested as a possible cathode material at the last Symposium [3]. Further work on this is reported at a separate paper at this Symposium [21]. It has also been suggested for use in solid electrolyte (sulphide glass) batteries [22]. Lithium/sulphur cells, in which lithium polysulphides take part, are being investigated [23].

5. Battery construction and design improvements

Batteries are normally supplied in cylindrical cans or in prismatic construction, though envelope (or pouch) cells can also be made, both for polymer and liquid electrolytes [3]. The battery cells are then assembled into a battery pack which must be incorporated into the equipment which it is powering. This approach neglects the possibility of integrating the battery into the equipment itself. This has been investigated for specialist applications: space [24] and unmanned air vehicles [25]. The space battery uses a rigid carbon composite anode to provide structural strength in the battery. For the unmanned air vehicles application, the Telcordia plastic lithium-ion battery technology is used but, as this battery is intrinsically flexible, it is stiffened by adding structural materials either inside or outside the plastic bag, which contains the battery.

Another different type of battery is the microbattery. This uses the lithium cobalt oxide cathode material, lithium phosphorus oxynitride (LIPON) solid electrolyte and a lithium anode. The batteries are constructed by evaporation or vapour deposition (sputtering) of the materials. The batteries are very thin, with the active components only micrometres thick. Very high capacities and currents for the size can be obtained. These batteries are now commercially available [26]. Because of its good charge retention, this battery can also be used as a long life primary battery.

Although not of fundamental scientific interest, it is worth noting that incremental design improvements have achieved significant advances in battery performance in the 10 years since their introduction with the capacity of 18,650 lithium-ion cells increasing from 0.96 to 2.4 Ah between 1992 and 2003 [2].

6. Battery cost

Battery cost, along with battery safety, are the factors limiting more widespread usage of lithium-ion batteries. Eighty percent of the cost of lithium-ion batteries is the cost of materials [27]. The most expensive materials are specialised carbon for the anode, electrolyte solvents, electrolyte salts, cathode materials and separator. Liquid electrolyte lithium-ion cells need highly purified electrolyte solvents. At the last Symposium, sulphur dioxide was suggested as a possible electrolyte solvent as it is cheap and has a wide operating temperature range [1]. However, the FORTU battery still seems to be the only battery using this electrolyte. Considerable research has been published on potentially cheaper new electrolyte salts, such as lithium bis-oxalato borate and related salts (Section 3). It will be interesting to see whether these find application in commercial cells.

As expected at the last Symposium [3], lithium nickel/cobalt oxide is replacing lithium cobalt oxide as the standard cathode materials, due to its lower metal cost and higher capacity. In the longer term, lithium iron phosphate appears to offer considerable advantages in terms of a high and steady voltage (3.4 V) but more particularly in terms of cost, as the transition metal used is iron which is cheap and non-toxic, unlike nickel and cobalt which are used at present. Sodium-ion batteries might be cheaper than lithium-ion ones, as sodium compounds are usually cheaper than lithium ones, but considerable further development is needed before sodium-ion batteries could become practical.

7. Battery safety

The voltage of lithium-ion cells needs to be controlled so that the battery voltage does not exceed 4.6 V [28,29] to ensure safety. One design technique which has been reported to improve safety is to use a carbon-carbon composite anode with sufficient capacity to absorb lithium generated on overcharging [27]. This avoids lithium metal being deposited on the anode during charging, with possible adverse safety effects.

Apart from cost, another factor potentially limiting lithium-ion battery application, particularly for large sizes, is safety. Lithium-ion batteries contain flammable organic electrolytes and, under certain abuse conditions (uncontrolled charging above 4.6 V), flame and smoke may result [28]. Hence lithium-ion cells need electronic control to avoid such abuse conditions. An alternative approach is to add fire retardant additives to the cells. Organic phosphates are known fire retardant additives and cells using these have been tested [30].

A polymer cell using a polyacrylonitrile gel has been reported to be stable up to 172 °C even when the cell was fully charged, indicating that the gel had fire retardant properties [31].

8. Battery calendar life

Ever since their introduction, it has been known that lithium-ion cells have a very high cycle life as the first description of them reported 1200 cycles [32]. At low depth of discharge, hundreds of thousands of cycles are possible [33]. However, in addition to a long cycle life, a long calendar life is also important for applications such as electric vehicles or satellites [33]. Standby power sources [34] also need long calendar life. Capacity loss over time depends on temperature and cell voltage, which is related to state-of-charge. The mechanisms of capacity loss include increase in impedance over time, causing loss of power, loss of lithium due to SEI (solid-electrolyte-interface) build up and degradation of the positive electrode. Loss of lithium is a parabolic function, with capacity loss decreasing with time, while positive electrode degradation causes a linear loss of capacity and impedance growth. Increasing temperature increases rate of capacity loss, according to the Arrhenius law. Capacity loss is greater at high states of charge, so batteries are stored below full charge. These relationships allow the prediction of calendar lives for lithium-ion batteries, e.g. for satellite applications, 8–15 years were predicted [33].

9. Battery applications

Lithium rechargeable battery applications in electric vehicles have been described [35–38]. Successful applications of lithium-ion batteries were reported by three vehicle manufacturers [35–37,39] and lithium metal polymer batteries have also been tested [38,40]. These papers indicate that lithium rechargeable batteries can be successfully used to power electric vehicles. Cost and safety are the limiting factors.

Lithium-ion batteries are now finding application in Space [41–43]. This includes satellites [40,41] and a large (190 Ah) battery for the Space Shuttle [43].

Another potential application for lithium polymer batteries is for vehicle starting using a 42 V, 27 Ah battery [44].

10. Conclusions

Lithium rechargeable batteries are still at an active state of development. Gelled electrolyte polymer batteries are in mass production and some new polymer electrolyte systems are being developed. Lithium iron phosphate has the potential to provide a cheap and non-toxic cathode material for lithium-ion batteries, with particular application in electric vehicles. Lithium-ion batteries have shown their technical capability in electric vehicles, though cost and safety remain problems. Sodium-ion batteries have been briefly investigated.

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