New Batteries are on the Charge

Energy Storage Materials, Cathy Darroch

The standard lithium ion battery has been the leading energy storage material since the mid 1990s, but a "changing of the guard" may soon occur. A new breed of lithium ion batteries are being investigated, with the hopes of producing batteries that are cheaper, less toxic and electrochemically superior. One recent development in lithium battery materials has been the conductive lithium phosphor-olivines compound that could become a replacement cathode in lithium batteries.

The lithium ion battery has competition from rechargeable batteries based on lead-acid, reusable alkaline, nickel cadmium (NiCd), nickel metal hydrides and sodium-sulphur or lithium-sulphur systems. Lithium ion batteries are market forerunners due to their compact size, high energy density and power source stability to above 500 cycles (Wakihara, 2001).

It is common to measure the performance of rechargeable batteries by their energy density (or capacity) and their life expectancy (in terms of cycles). The following points outline why lithium ion batteries are the market leaders (Garland and Jamieson, no date, Buchmann, 2001 and Wakihara, 2001).

- Conventional nickel batteries have a lower discharge voltage than Li-ion batteries and also experience a detrimental memory effect.
- NiCd batteries are toxic.
- Nickel metal hydrides have a reduced cycle life.
- Rechargeable alkaline batteries have a very short life (50% capacity after 50 cycles)
- The sulphur systems have a very high capacity at high temperatures, which cannot be easily utilised.
- Lead-acid batteries are durable and inexpensive, but they are toxic and have a low energy density.

The many current applications of lithium ion batteries guarantee that there is interest in developing new materials. These applications include power sources for portable consumer devices such as video cameras, mobile phones and laptops. These current uses combined with possible future applications through material advances, means that there are many research groups and industry members actively searching for superior materials.

Figure 1 A Nokia 8260 Lithium Ion Battery (Buynshop.com, 2003)

Structure and Properties:

A lithium battery is comprised of three main components - a cathode, an anode and the electrolyte. The cathode material is a lithium metal oxide, whilst the standard material for the anode is carbon. The electrolyte material can be an organic liquid containing dissolved electrolyte salts or a polymer electrolyte. Research is being carried out on all three components of the lithium ion battery, but this article focuses on cathode material innovations.

The desired characteristics of cathode materials are:

- A high discharge voltage
- A high energy capacity
- A long cycle life and
- A high power density.

It is also desired that the materials be easy to handle, stable chemically, non-toxic and low in cost.

A lithium ion rechargeable battery (refer to Figure 2) is known as a rocking chair battery due to the two-way motion of the lithium ions. The lithium ions are transported between the anode and the cathode through the electrolyte. During charging the lithium ions undergo deintercalation from the cathode into the electrolyte, simultaneously lithium ions intercalate from the electrolyte into the anode (Wakihara, 2001). Intercalation is the process of inserting lithium ions into the structure of the electrodes. During discharge the intercalation and deintercalation reverse. The shift in charge, due to Li^+ movement during charging and discharging is compensated by electron flow through the external circuit.

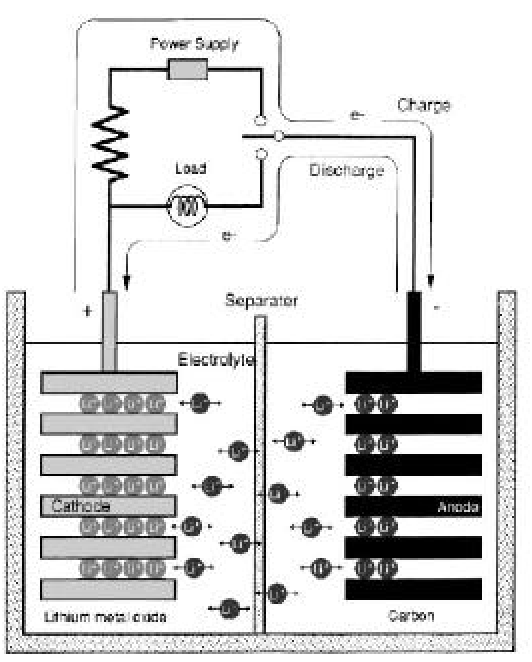

Figure 2 The theory of the lithium ion battery (Wakihara, 2001)

New Lithium Batteries

Steve Bewlay, a PhD researcher with the Institute of Superconducting and Electronic Materials (ISEM) at the University of Wollongong, is exploring some of these new battery materials. He finds the "undeniable practicality" of rechargeable energy storage materials a motivator in his work. The work at the ISEM in Wollongong is broad but a recent shift in focus has caused Steve to concentrate on the lithium iron phosphate system. These new cathode materials are desirable for replacing or minimising cobalt in the material, whilst maintaining electrochemical properties.

Cobalt is one of the primary constituents of standard cathodes for lithium batteries. Cobalt has a low abundance and hence a high cost, metals such as manganese could provide a cheaper alternative. Cobalt is also a heavy metal that can cause cumulative poisoning in animals and humans. Cobalt itself is not water soluble, but intermediates formed from a reaction with the electrolyte may be soluble, leading to its toxicity when disposed of incorrectly. Lithium cobaltate batteries also have an extra cost associated with a necessary protection circuit to ensure safety. Thus, there is a significant drive in industry, and in research, to develop batteries with materials that are non-toxic and less expensive.

The Sony Corporation commercialised the first lithium ion battery in 1991 (Buchmann, 2001). The lithium cobaltate ($LiCoO_2$) cathode used has a layered structure as seen in Figure 3. This structure has a good conductivity of lithium ions and electrons. The lithium ions can intercalate or deintercalate between the layers. Lithium cobaltate batteries have an energy density of 140 Wh/kg and a life expectancy of 300 cycles, with 50% capacity after 500 cycles (Buchmann, 2001). The life expectancy of a battery, according to Steve Bewlay of the ISEM, is the "number of cycles before the voltage or capacity decays too low to be practically useful". This may be observed in mobile phone battery life. The voltage and capacity gradually decrease with the number of charging cycles, eventually causing a recharged battery to discharge after only a few hours instead of after many days. Unfortunately, this process gives the battery a finite life span. Therefore new cathode materials with an increased cycle life are also desired.

Possible alternatives to lithium cobaltate include $LiNiO_2$, a solid solution of $LiCoO_2$ and $LiNiO_2$, $LiMn_2O_4$, $LiM_yMn_{2-y}O_4$ (where M is another metal atom) and other oxides, as well as olivine-structured compounds such as $LiFePO_4$. It is important to have an overview of the new cathode materials available in order to appreciate the advances made in specific compounds.

$LiNiO_2$ is a layered compound that has been investigated as a possible cathode material. This compound has the same structure as the lithium cobaltate compound, but due to its poor thermal stability it undergoes a structural change on heating, to cubic spinel. This structure acts to reduce the mobility of the lithium ions, which causes an undesired reduction in its conductivity (Wakihara, 2001). Therefore, $LiNiO_2$ is not currently practical as a battery material.

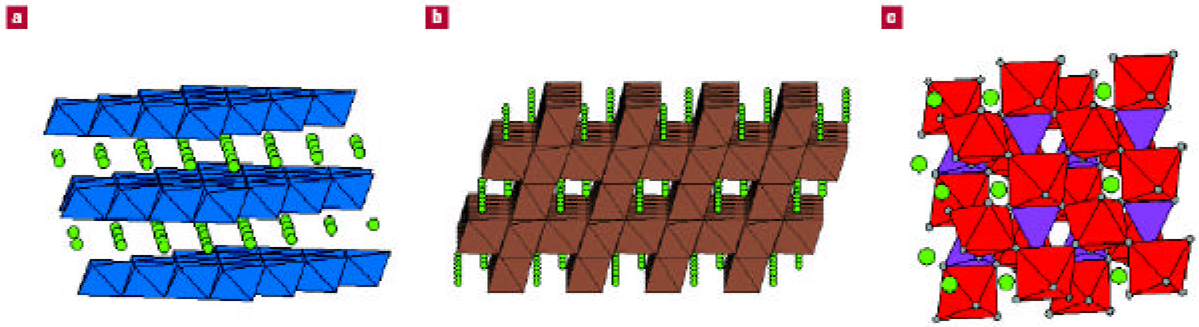

Figure 3 Structures of different cathode materials for lithium ion batteries: a) $LiCoO_2$ layered structure, b) $LiMn_2O_4$ spinel structure and c) $LiFePO_4$ olivine structure. The green circles are lithium ions, Li^+ (Thackerey, 2002)

$LiNiO_2$ and $LiCoO_2$ can form a solid solution as studied originally by Saadoune and Delmas (1992). Nickel partially substitutes for cobalt in the compound. The energy density was seen to increase to 150Wh/kg for $LiCo_yNi_{1-y}O_2$, although a decrease in the discharge voltage occurs (Wakihara, 2001). This solid solution is likely to become a next-generation cathode for lithium ion batteries.

The lithium manganese oxide system undergoes structure change to a spinel system upon cycling (refer to Figure 3). The resulting capacity fade can be improved by partial substitution with cobalt (Wakihara, 2001). Lithium manganese cobalt oxide compounds have been produced by Armstrong et. al. (1996 and 1998) with the general formula $Li_x(Mn_{1-x}Co_x)O_2$. These compounds are difficult to prepare and have a poor cycle life, but have a high initial capacity. Thus, these compounds are not at the forefront of the new generation of lithium battery cathode materials.

The cycle fading of the lithium manganese oxide ($LiMn_2O_4$) system is prominent. The compound has an initial capacity of 120mAh/kg, but by the 100^{th} cycle the capacity has fallen to about 60% (Wakihara, 2001). Metal substituted lithium manganese oxide compounds have also been investigated as cathode materials. They have the general formula $LiM_yMn_{2-y}O_4$, the metal (M) can be chromium, aluminium or nickel. The tested cells with substituted $LiMn_2O_4$ exhibit better cycle characteristics than undoped $LiMn_2O_4$ (Wakihara, 2001). Both these oxides are environmentally benign and cost-effective. Although the practicality of these compounds may be affected by an increase in capacity fade associated with a temperature range of 50-70°C. The possible applications of these two oxides include large-scale batteries for energy storage applications as well as miniature batteries for consumer use.

Lithium transition metal phosphates are emerging as materials of interest for rechargeable lithium batteries due to their low material cost, high energy density, safety and non-toxicity. These compounds have good lithium ion mobility, but have extremely low electron conductivity. Interest in $LiFePO_4$ in particular is high, as recent research into the compound by Chung, Bloking and Chiang (2002) has demonstrated a dramatic increase in conductivity. Through structure control, conductivities were seen to increase by a factor of ~10^8. Leaving vacancies or gaps in positions otherwise occupied by lithium or iron and doping the material with ions higher in valence than Li+ achieved this. Figure 3 depicts the olivine structure of $LiFePO_4$. This breakthrough has caused other research groups to investigate $LiFePO_4$ as a cathode material.

The ISEM covers many areas of interest in the field of cathode materials for lithium ion batteries. Unfortunately, limitations do exist, so not all research possibilities may be investigated. The ISEM Energy Storage Materials team often leave aside projects to investigate new breakthroughs discovered by other research teams. Steve Bewlay of the ISEM has recently switched his research focus to the developing area of electronically conductive phospho-olivines. As the focus switch has only occurred lately, he has not yet tested all the properties of the $LiFePO_4$ samples produced. However, Steve has discovered a new manufacturing technique, which simplifies and speeds up the making of the cathode powder.

The conventional method of manufacture of $LiFePO_4$ involves the use of solid-state reactions to achieve a powder suitable for the production of cathodes (Padhi, Nanjundaswamy and Goodenough, 1997). The process involves eight steps: the dry pre-mix containing exact amounts of precursors is ball milled for 7 hours, then separated from the milling media. A pre-sinter occurs for 10 hours under flowing argon gas, followed by a regrinding step. The powder is then made into pellets, by using a hydraulic press and sintered for 24 hours under flowing inert gas. The pellets are then re-ground and the cathode material powder finally separated from the milling media. This technique is costly as it consumes a large amount of inert gas and energy.

The new method for the production of $LiFePO_4$ developed by Steve and the team at the ISEM involves spray pyrolysis (Bewlay, 2002). This technique requires only four steps and is comparatively faster and energy efficient. The dry pre-mix is dissolved in de-ionised water, with added Nitric Acid to aid dissolution. The solution is then sprayed at high temperature generating a fine uniform powder. The powder is then sintered for only 3 to 12 hours under flowing argon gas. A short light grind then follows to achieve a powder suitable for the production of the cathode. The powder produced by Steve maintains phase-purity and gives the same composition as by the conventional method.

Another technique used by others for the manufacture of cathode powder involves the use of sol-gel techniques. The technique used to make the actual cathode is dependant upon the type and size of battery required.

Phospho-Olivine Lithium Batteries are Charging Forward

The original research team investigating $LiFePO_4$ has an advantage over the research competition in terms of time and momentum. However, research from other groups, such as the ISEM Energy Storage Materials team, could make important new discoveries and improvements in material properties and manufacturing techniques. The new manufacturing technique of the cathode material, discovered by Steve Bewlay et al, could be significant for future applications as the method is suitable for mass-production and is energy and cost efficient. Therefore the research at the ISEM is important to the development of $LiFePO_4$ as a cathode material.

The electronically conductive phospho-olivine materials could be used for applications demanding safe, high power, rechargeable lithium batteries (Chung, Bloking and Chiang, 2002). The applications could include power sources for hybrid and electric vehicles, and implantable medical devices as well as back-up power. Therefore, a wide range of new applications is possible for lithium batteries, causing the research on $LiFePO_4$ to be of great interest to industry.

A new breakthrough in electrically conductive phosphor-olivines has caused great interest in the research world. The Institute of Superconducting and Electronic Materials are part of this new research and have already discovered a new manufacture technique for the cathode powder. It is important to review the other areas of cathode research in order to put the $LiFePO_4$ breakthrough into context. The cathode materials discussed here are not the only new materials being investigated for lithium battery cathodes. The large field of research is indicative of the tremendous interest in lithium batteries due to their many uses and “undeniable practicality”.

Further Interest?
The Institute of Superconducting and Electronic Materials (ISEM) at the University of Wollongong also is investigating other cathode materials which include $LiMn_xX_yO_2$ (X=Co,Cr,Zn,Mo), $LiMn_xCo_yNi_{1-x-y}O_2$, $LiNi_xCo_yMg_zTi_zO_2$ and $LiCo_xNi_yO_2$. Research, past and present, at the ISEM also includes intermetallic compounds and carbon nanotubes for lithium ion battery anodes, polymer electrolytes and work on nickel metal hydrides. Further information and contacts may be found at the URL: http://www.uow.edu.au/eng/research/ISEM/

Acknowledgements

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