Future cathode materials for lithium rechargeable batteries

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Abstract

Lithium rechargeable batteries are now well established as power sources for portable equipment, such as portable telephones or computers. Future applications include electric vehicles. However before they can be used for this, or other price-sensitive applications, new cathode materials of much lower cost are needed. Possible cathode materials are reviewed. Crown Copyright © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium-ion batteries are now well known since their introduction by Sony [1]. Small sizes of lithium-ion cells are now manufactured at a rate of tens of millions per month. Most of these cells use the lithium carbon/lithium cobalt oxide chemistry. The success of this system is indicated by the scale of manufacture. However there is still research ongoing to develop improved chemistries. Most of this effort is concentrated on new cathode materials. The reasons for this are that cobalt is expensive and is somewhat toxic. A cheaper material is needed before lithium-ion cells can penetrate new markets, in particular that of electric vehicles. Furthermore the electrochemical capacity of lithium cobalt oxide is relatively low.

The chemistry of lithium-ion cells has recently been reviewed extensively [2] and it is not intended to attempt to repeat that here but rather to report results obtained by the authors over a wide range of cathode materials. The materials most extensively studied recently are lithium cobalt, nickel and manganese oxides or mixed oxides. This paper will compare theoretical energy densities available from different materials and will compare these with what has been experimentally achieved.

2. Theoretical energies

The cathode materials which are being widely investigated at the moment for lithium-ion batteries are lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$), lithium manganese oxide spinel ($LiMn_2O_4$) and mixed lithium cobalt nickel oxide ($LiNi_{0.8}Co_{0.2}O_2$). Recently another lithium manganese oxide ($LiMnO_2$) has attracted some attention [3]. In addition a new cathode material developed by one of us [4] is included. The theoretical specific densities and the assumed reactions are described in Table 1.

According to these simplified calculations, lithiated metal oxides of the formula $LiMO_2$, where M is Co, Ni, Mn, or a mixture, have energy densities of around 1000 W h kg^{-1} of cathode active material. The lithium manganese oxide spinel will have a much lower energy density because only one lithium atom is being cycled for two manganese atoms, in contrast to the theoretical 1:1 ratio for $LiMO_2$. Hence the recent interest in $LiMnO_2$, though $LiMn_2O_4$ is a much better established material.

The actual energy density in a battery will be lower because of the necessity to add conducting carbon to the cathode to improve conductivity and a binder to enable cathode components to be made. These calculations compare cathodes only, as the electrolyte and anode will be similar for different cathodes. Iron could also be consid-

Table 1
Theoretical specific capacities and energies for various cathode reactions

	Capacity (mA h g^{-1} cathode)	Average voltage	Specific density (W h kg^{-1} cathode)
$LiCoO_2 \rightarrow Li + CoO_2$	274	3.6	986
$LiNiO_2 \rightarrow Li + NiO_2$	275	3.6	990
$LiMn_2O_4 \rightarrow Li + Mn_2O_4$	148	3.8	562
$LiNi_{0.8}Co_{0.2}O_2 \rightarrow Li + Ni_{0.8}Co_{0.2}O_2$	274	3.6	986
$LiMnO_2 \rightarrow Li + MnO_2$	286	3.2	914
$2VO_2 \cdot Li_2SO_3 \rightarrow Li + 2VO_2LiSO_3$	206	3.5	722

ered in $LiMO_2$ but experience shows that $LiFeO_2$ cannot be recharged in lithium secondary cells.

3. Experimental results

Different cathode materials have been tested in laboratory cells, as described previously [5]. Cathodes were cycled against lithium metal so that the performance of the cathode material could be determined without being limited by the performance of a carbon anode. The capacity of the lithium was in large excess to that of the cathode. In real batteries, a lithium-ion system would be used. The aim of the present work is mainly to compare the energy densities of different systems so only a small number of cycles are illustrated. Using a lithium metal anode, high cycle life would not be expected. A standard electrolyte (ethylene carbonate (EC)/diethyl carbonate (DEC)/lithium hexafluorophosphate ($LiPF_6$)) was used. Cathode coatings were made using a doctor blade system to coat the cathode composite (oxide, carbon and binder) on to an aluminium backing. PVDF (polyvinylidene fluoride) was used as binder. The cathode materials were obtained from commercial sources except for the $LiMnO_2$ which was made at Reading University by reacting manganese oxyhydroxide (MnOOH) with lithium butyl.

Fig. 1 shows the capacity obtained from cycling lithium cobalt oxide. The results are as expected from commercial cell performance, i.e., the capacity is around 160 mA h g^{-1}, roughly 58% of theoretical. The voltage cycling range was 2.5–4.2 V, typical of those used for commercial cells. Fig. 2 shows the effect of different voltage limits for charging. The capacity is very low (only about 50 mA h g^{-1} of $LiCoO_2$) at 4.0 V but this rises rapidly with increase in upper voltage limit when, at about 4.7 V, the capacity is over 200 mA h g^{-1}. To limit electrolyte decomposition, this experiment used only one cycle at each voltage. Higher capacities could be obtained if the electrolyte were stable to repeated cycling above the normal limit of 4.2 V. A more stable electrolyte is the solid state LIPON electrolyte [6] which can be used up to 5 V [7]. Cycling of $LiCoO_2$ microbatteries showed a similar increase in capacity with increase in voltage (see Fig. 3).

Fig. 4 shows cycling of lithium nickel cobalt oxide. This material has recently become available from commercial sources and is attracting considerable interest. The sample tested here showed higher capacity (180 mA h g^{-1}, 66% of theoretical) than for the lithium cobalt oxide, but the capacity fell on cycling, unlike the pure cobalt oxide. Whether this is a general feature of this material, or whether it relates to our coating technique or to the particular source of supply remains to be seen. Little extra capacity appeared to be available at higher voltages (see Fig. 5).

Figs. 6 and 7 show cycling of lithium manganese oxide of slightly different stoichiometry. Cells were cycled from 3.5 to 4.2 V, as little capacity is obtained below 3.5 V. The capacity was steady at around 110 mA h g^{-1}, 74% of theoretical, typical for this material. Notwithstanding the higher percentage of theoretical capacity obtained, the
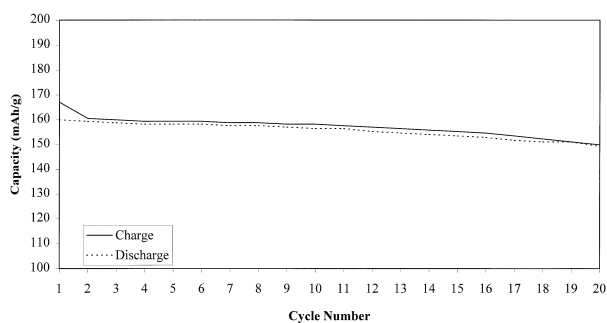

Fig. 1. Cycling performance of a Li/$LiCoO_2$ cell at the $C/4$ rate over the voltage range 2.5 to 4.2 V. Cycle number against specific capacity of cathode.
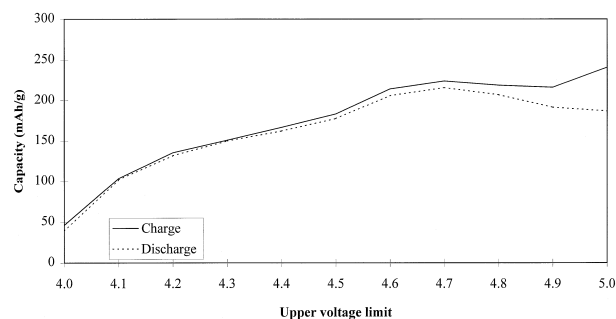

Fig. 2. Effect of upper voltage limit on the capacity of a Li/$LiCoO_2$ cell at the $C/5$ rate. End-of-discharge voltage: 2.5 V. Voltage limit against specific capacity of cathode.
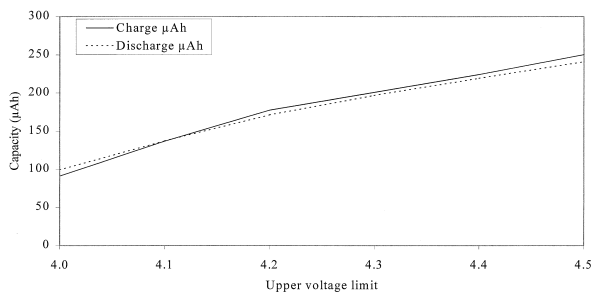
Fig. 3. Effect of upper voltage limit on the capacity of a $Li/LiCoO_2$ cell using solid electrolyte.
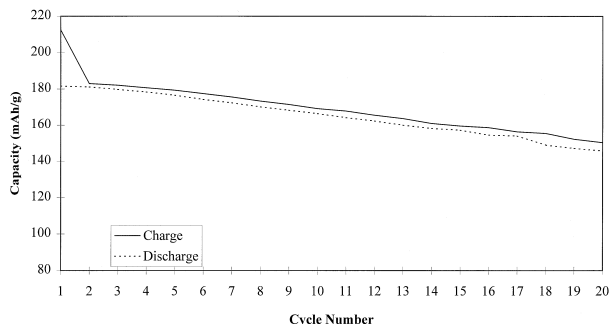

Fig. 4. Cycling performance of a $LiNi_{0.8}Co_{0.2}O_2$ cell at the $C/4$ rate over the voltage range 2.5 to 4.2 V. Cycle number against specific capacity of cathode.
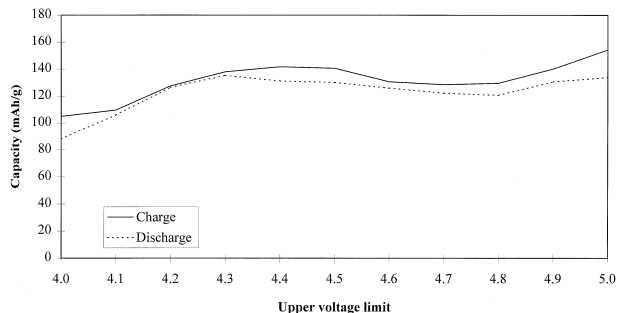

Fig. 5. Effect of upper voltage limit on the capacity of a $Li/LiNi_{0.8}Co_{0.2}O_2$ cell at the $C/5$ rate. End-of-discharge voltage: 2.5 V. Voltage limit against specific capacity of cathode.
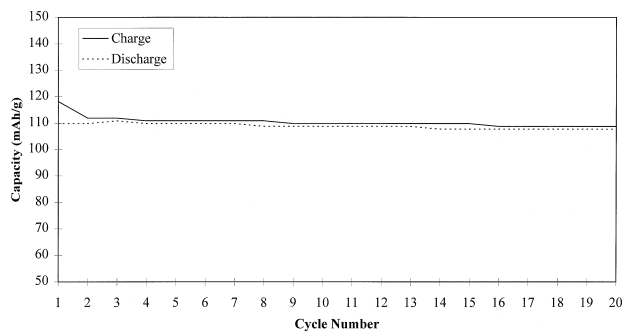

Fig. 6. Cycling performance of a $Li/LiMn_2O_4$ cell at the $C/4$ rate over the voltage range 3.5 to 4.3 V. Cycle number against specific capacity of cathode.
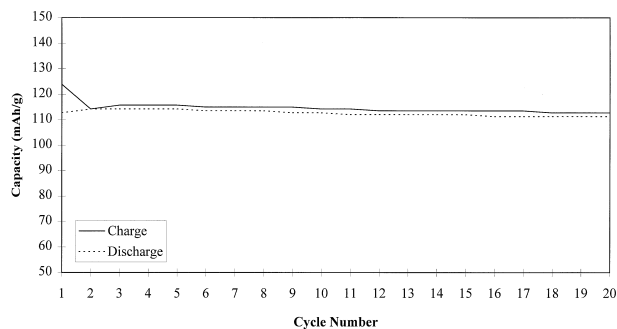

Fig. 7. Cycling performance of a $Li/Li_{1+x}Mn_2O_4$ cell at the $C/4$ rate over the voltage range 3.5 to 4.3 V. Cycle number against specific capacity of cathode.
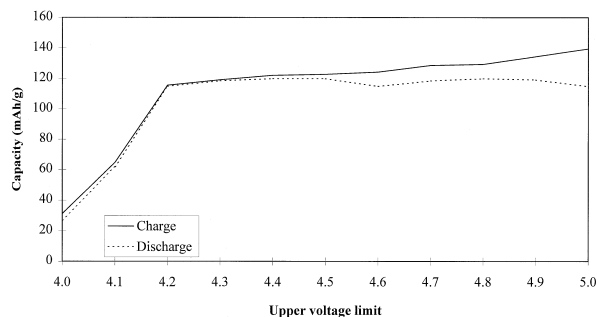

Fig. 8. Effect of upper voltage limit on capacity of a $Li/LiMn_2O_4$ cell at the $C/5$ rate. End-of-discharge voltage: 3.5 V. Voltage limit against specific capacity of cathode.
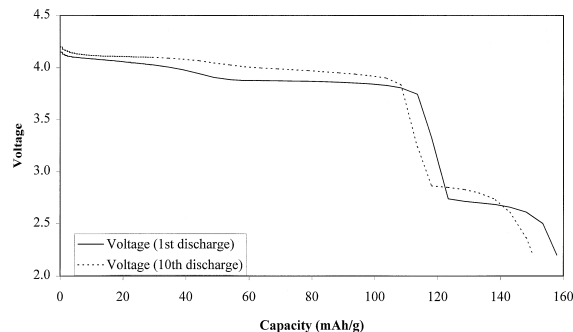

Fig. 9. Discharge performances of a $Li/LiMn_2O_4$ cell over two plateaux at the $C/5$ rate. End-of-discharge voltage: 2.2 V. Cell voltage against specific capacity of cathode.
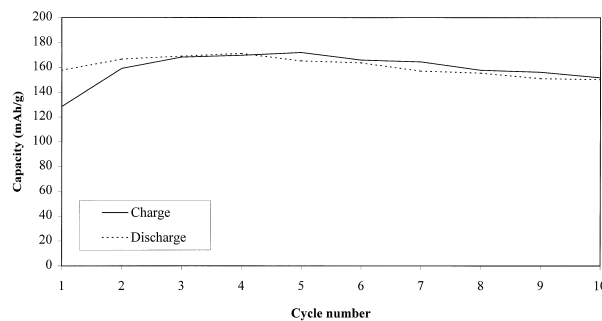

Fig. 10. Cycling performance of a $Li/LiMn_2O_4$ cell cycled over two plateaux at the $C/5$ rate over the voltage range 2.2 to 4.3 V. Cell voltage against specific capacity of cathode.

Table 2
A comparison of experimental specific energies for different cathode materials

Cathode	Apparent charging reaction	Reported capacity (mA h g^{-1}) [8]	% of theoretical capacity
$LiCoO_2$	$LiCoO_2 \rightarrow 0.58Li + Li_{0.42}CoO_2$	142	52
$LiNiO_2$	$LiNiO_2 \rightarrow 0.53 Li + Li_{0.47}NiO_2$	145	53
$LiNi_{0.8}Co_{0.2}O_2$	$LiNi_{0.8}Co_{0.2}O_2 \rightarrow 0.66Li + LiNi_{0.14}Co_{0.2}O_2$	180	66
$LiMn_2O_4$	$LiMn_2O_4 \rightarrow 0.74Li + Li_{0.26}Mn_2O_4$	120	81

actual capacity is lower than for cobalt or nickel oxides as the theoretical capacity is only one Li for two Mn—compared to one Li for one Co or Ni. The capacity obtained can depend strongly on the charging voltage. Fig. 8 shows that $LiMn_2O_4$ cells are not fully charged at 4.0 V (capacity around 30 mA h g^{-1}) but that around 110 mA h g^{-1} can be obtained if the charging voltage is raised to 4.2 V. Increasing the voltage to 5 V produced no increase in capacity but, above 4.5 V, excess charge was absorbed, presumably due to electrolyte decomposition. However an increase in capacity to near the theoretical of 148 mA h g^{-1} were obtained by Bates using a lithium ion-conducting solid electrolyte [7]. This indicates that the failure to achieve 148 mA h g^{-1} in cycling with organic electrolytes is not a function of the particular grade of lithium manganese oxide but is a function of the charging voltage and the ability of the electrolyte to withstand a high voltage. The full capacity can be achieved only at high voltage (5 V), which is not attainable with the liquid organic electrolytes that are presently available.

Lithium manganese oxide spinel can be cycled on either the upper (4 V) or lower (3 V) plateau. Attempts have been made to obtain the full capacity (1 Li:1 Mn) by cycling over both voltage levels. Results here show that $LiMn_2O_4$ will cycle well over the upper plateau (Figs. 6 and 7) and previous work [5] has shown that $LiMn_2O_4$ will also cycle well over the lower plateau. However when attempts are made to cycle over both voltage levels together, the capacity obtained is significantly less than would be expected from the sum of the capacity from each plateau (see Fig. 9). A possible reason for this is that the optimum $LiMn_2O_4$ composition in terms of stoichiometry is different for the second plateau. However the capacity obtained (around 160 mA h g^{-1}) is much greater than for only one plateau but this may not persist for long term cycling (see Fig. 10). However this can be used only in lithium metal cells, as there is only half the amount of lithium needed for a lithium-on cell. To obtain enough lithium, $Li_2Mn_2O_4$ would be needed but this does not cycle well. Hence the recent interest in $LiMnO_2$.

4. Comparison of experimental energy densities

A comparison of the experimental specific energies for different cathode materials when used in lithium-ion cells is given in Table 2.

These results show that the mixed lithium cobalt/nickel oxide gives a higher capacity than pure lithium cobalt oxide when charged to the normal limit (4.2 V) for organic electrolyte cells. However lithium cobalt oxide has the potential for higher capacity if a higher charging voltage could be used. However this will require an electrolyte which is more stable to higher voltages than current liquid organic electrolytes. Solid state electrolytes are stable to 5 V and with these electrolytes, cathode materials are stable for large numbers of cycles.

Lithium manganese oxide can achieve only about 75% of its theoretical capacity at maximum possible voltages using organic electrolytes, though the full capacity can be achieved at higher voltage using solid electrolytes. To use manganese, it is necessary to find variants of $LiMnO_2$ which would lead to high capacity and long cycle life. Addition of cobalt to $LiMnO_2$ to form $LiMn_{0.9}Co_{0.1}O_2$ has been reported to improve cycle life [9].

5. Conclusions

Commercially available lithium-ion cells normally use a lithium cobalt oxide cathode. This is too expensive for use in, say, electric vehicles. Other cathode materials such as lithium nickel, mixed cobalt/nickel, and manganese oxides are being investigated. The mixed cobalt/nickel oxide has higher capacity than the cobalt. The manganese oxides have possibilities as they are cheap and of low toxicity but their capacity are lower due to the different stoichiometry of $LiMn_2O_4$ in comparison with $LiCoO_2 \cdot LiMnO_2$. Perhaps with additional doping elements they may become candidates for cathodes in lithium-ion cells.

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