Fluoroethylene carbonate electrolyte and its use in lithium ion batteries with graphite anodes

Rod McMillan [*], Helen Slegr, Z.X. Shu, Weidong Wang

Institute for Chemical Process and Environmental Technology, National Research Council, Montreal Road, Ottawa, Ontario, Canada K1A 0R6

Abstract

The electrolyte decomposition during the first lithiation of graphite is reduced to 85 mA h/g in an electrolyte containing equal volumes of fluoroethylene carbonate (Fluoro-EC) and of a co-solvent propylene carbonate (PC). The volume fraction of Fluoro-EC can be further reduced to 0.05 in a tri-solvent system with a co-solvent containing equal volumes of ethylene carbonate (EC) and PC. A lithium ion cell containing Fluoro-EC PC and EC shows a long cycle life. The capacity decreases by 37% from the initial value in over 200 cycles. Cell current efficiency is 100%, thus solving the poor cell current efficiency when chloroethylene carbonate (Chloro-EC) is used in place of Fluoro-EC. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluoroethylene carbonate electrolyte; Lithium ion batteries; Graphite anodes

1. Introduction

In the past decade, there has been a growing interest in the search for suitable carbon materials as an intercalation host (anode) for lithium ion rechargeable batteries. Graphite has been considered as a favorable candidate because of its high capacity and low and flat voltage curve with respect to lithium metal. A major problem in using graphite, as the anode is the massive electrolyte decomposition during the first lithiation (intercalation) process, at least in a propylene carbonate (PC) based electrolyte [1–3]. This necessitates the presence of both excess lithium and electrolyte sources in the cell and reduces the apparent cell capacity.

Several approaches [4–7] have been explored in the past to reduce the extent of electrolyte decomposition at the graphite electrode. Two of the promising electrolytes among these are $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) or in ethylene carbonate/diethyl carbonate (EC/DEC) and indeed a form of these electrolytes has become an industry standard [8].

Recently, we reported results using chloroethylene carbonate (Chloro-EC) as an electrolyte solvent [9–11] in conjunction with PC and/or EC as co-solvents. For lithium graphite cells, our results showed that PC based electrolytes could be used with a highly graphitic electrode without an excessive amount of electrolyte decomposition. In a graphite/$LiCoO_2$ lithium ion cell, the same good attributes were found but so was a chemical shuttle which limited cell current efficiency to ca. 90%. This is illustrated in Fig. 1 where potential curves of the first two and a half cycles of a $LiCoO_2$/graphite lithium ion cell are shown. It can be seen that the cell current efficiency (discharge capacity divided by charge capacity of the preceding half cycle) is low, less than 50% for the first cycle. This is much less than can be accounted for by irreversible capacity associated with SEI [12] formation on the graphite or any electrolyte oxidation on the cathode. The chemical shuttle was postulated to be due to LiCl formed during the initial lithiation of graphite by reductive cleavage of Chloro-EC [13]. LiCl migrating to and oxidized to Cl_2 at the cell cathode in conjunction with Cl_2 diffusion back to the lithiated anode and reduction to Cl^- would result in an internal chemical shuttle. It was postulated that if the proposed mechanism was correct and if Chloro-EC was replaced by fluoroethylene carbonate (Fluoro-EC) the resultant cell current efficiency would be greater due to the lower solubility of LiF [14,15] as compared to LiCl. The reduced solubility would give a lower concentration of shuttle species and consequently a lower shuttle current. This would be expected to increase the cell efficiency.
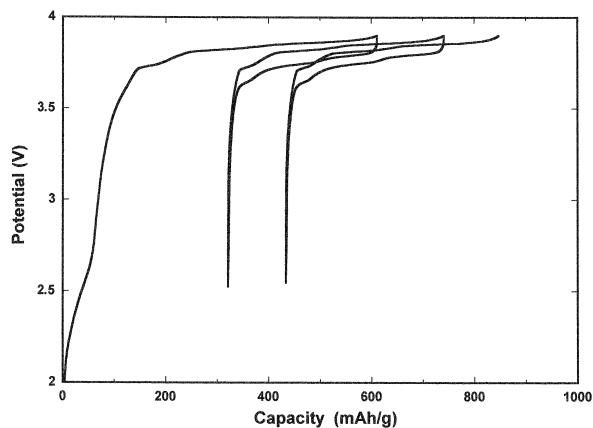
[*] Corresponding author

Fig. 1. Potential profiles of the first two and one half cycles of a representative $LiCoO_2$/KS15 graphite cell employing 1 M $LiClO_4$ Chloro-EC/PC (1/1) electrolyte. The cell is cycled at a 10 h rate for the cycles shown between 2.5 and 3.9 V. Capacity is per weight graphite.

Here, we present results for electrolytes where Chloro-EC is replaced by Fluoro-EC with excellent results. Lithium ion cell charge efficiency is greater than 99.5%.

2. Experimental

Monofluorinated EC (4-fluoro-1,3-dioxolan-2-one) was prepared from Chloro-EC (4-chloro-1,3-dioxolan-2-one, Fluka) by exchange with KF. Distillation yielded the pure product as confirmed by ^{19}F and proton NMR. For a bi-solvent system, the electrolyte was 1M $LiClO_4$ (Baker) or 1M $LiPF_6$ (Hashimoto) dissolved in a mixture of halogenated EC (Chloro-EC or Fluoro-EC) and a co-solvent PC. For a tri-solvent system, the electrolyte was 1 M $LiClO_4$ or 1M $LiPF_6$ dissolved in Chloro-EC or Fluoro-EC, EC and PC. $LiClO_4$ was dried under vacuum at 120°C overnight. $LiPF_6$ was used as received without further purification. All electrolyte solvents were dried over activated molecular sieves followed by distillation. In the case of Chloro-EC, Fluoro-EC, EC and PC, distillation was carried out under vacuum. The water content of the electrolyte was measured using Karl–Fisher titration and was less than 50 ppm. For some comparison experiments 1 M $LiPF_6$ EC/DMC and EC/DEC electrolyte (Mitsubishi Chemical) was used as received.

Cyclic voltammetry experiments were conducted in a three electrode cell in an inert atmosphere chamber under Argon at ambient temperature. A lithium wire was used as the reference electrode and a PT wire or Super S carbon as the working electrode. Pt mesh formed the counter electrode. A Par 273 potentiostat provided the controlling voltage. A sweep rate of 0.4 V/s was employed with a Pt electrode and 27 uV/s with a Super S electrode.

Constant current cycling experiments were carried out using a two electrode NRC designed and fabricated 2325 coin cell. The cell capacity was limited by that of the graphite electrode in both Li/graphite and graphite/$LiCoO_2$ cell configurations. The theoretical cell capacity was calculated assuming one mole of lithium intercalated per 6 mol of graphite (i.e., LiC_6).

Predominantly the carbon electrode was made of KS series Lonza artificial graphite, Ks15, (14 m^2/g by BET), but some experiments were conducted with commercial grade LGV 2188. The electrode contained 3–5% vinylidene fluoride resin (Elf Atochem). It was prepared using the method described previously [3,9]. Typically, the electrode density was 0.6 to 1.0 g/cm^3 and 0.004″ to 0.008″ thick.

In a lithium/graphite cell, the anode was lithium metal (Foote) and the cathode was graphite. In a lithium ion cell, the anode was graphite and the cathode was $LiCoO_2$ (Johnson Matthey). The cathode also contained 10% carbon black (Super S, S. Ensagri-Willebroek) and 5% vinylidene fluoride resin (Elf Atochem). In all cases, a polypropylene microporous membrane (Celgard 3501) was used as the separator.

The cycling equipment was as described in Ref. [3]. Unless otherwise stated, the electrochemical cells were cycled galvanostatically between potential limits of 10 mV and 2.0 V for lithium/graphite cells and between 2.5 and 3.9 V or 3.2 and 4.0 V for lithium ion cells.

The experimental conditions were not optimized for maximum capacity and cycle life.

Reported cell data represent multiple experiments yielding reproducible results. Values for reversible and irreversible capacities were reproducible to ±3 and 5%, respectively.

3. Results and discussions

3.1. Cyclic voltammetry

A necessary requirement for a lithium ion cell electrolyte with a graphite anode is that a SEI is formed on this electrode by reduction of electrolyte solvent so that minimal amount of electrolyte is consumed during electrochemical intercalation of lithium into the graphite. This aspect of the cathodic behaviour of Fluoro-EC was determined in part by cyclic voltammetry. In Fig. 2, the first cathodic potential vs. current curve of 1 M $LiPF_6$ PC and Fluoro-EC (FEC) electrolyte is shown where the cyclic sweep begins in the cathodic direction from ca. 3.0 V vs. the Li/Li$^+$ couple. Cathodic current begins with both electrolytes at similar potentials, ca. 2.9 V. Both electrolytes have similar waves at ca. 2–2.5 V but at lower potentials Fluoro-EC has less current until near 0 V where presumably Li deposition occurs. There is less cathodic capacity for the Fluoro-EC electrolyte at comparable potentials. While not shown, subsequent cathodic scans indicate that Fluoro-EC electrolyte passivates the working electrode. This is similar to that found for Chloro-EC
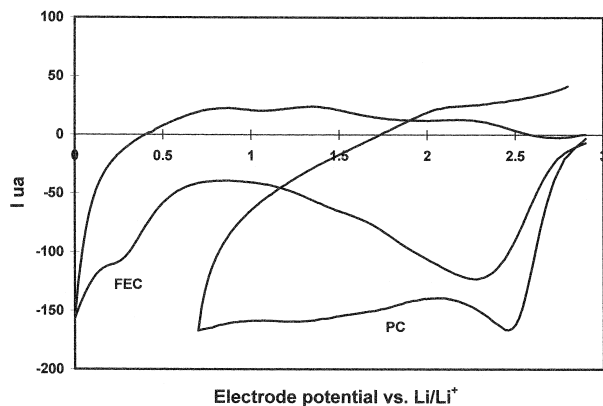
Fig. 2. Cyclic voltammetric plots of propylene carbonate (curve indicated by PC) and Fluoro-EC (curve indicated by FEC) electrolyte. The first cathodic going scan of each electrolyte is shown. The electrolyte is 1 M LiPF$_6$, the scan rate is 0.4 V/s And the working electrode is a PT wire.

electrolyte. These data indicate that Fluoro-EC is reduced and should thus be able to produce a SEI on graphite.

A necessary requirement for a lithium ion cell electrolyte is stability to oxidation at potentials up to 4.3 V vs. the Li/Li$^+$ couple. Cyclic voltammetry was conducted in the range of 3.0 to 5.0 V on Fluoro-EC electrolyte and for comparison EC/DMC and EC/DEC electrolyte. Both Pt and Super S working electrodes were used. To 4.3 V, anodic currents were similar for both electrolytes on both working electrodes and similar to that reported earlier [11] with no distinct oxidation waves observed. The anodic behaviour of these electrolytes above 4.3 V will be the subject of a later report. Fluoro-EC electrolyte is at least as stable as EC/DMC electrolyte to oxidation.

3.2. Li / Graphite cells

Coin cells with lithium metal anodes and graphite cathodes were fabricated with 1 M LiPF$_6$ Fluoro-EC electrolyte with various amounts of PC or PC/EC co-solvents. Fig. 3 shows a representative first discharge and charge

curve for such a cell where the galvanostatic current is such that the discharge capacity is delivered over 20 h, a C/20 rate. Here, the first discharge is electrochemical intercalation of lithium into the graphite cathode and the first charge is de-intercalation. The expected graphite staging is found between ca. 300 to 30 mV. At ca. 1.2 V, there is a potential plateau representing irreversible capacity, i.e., capacity which is not seen on the subsequent charge curve. The amount of irreversible capacity for the cycle is the difference between the discharge half-cycle and the charge half cycle capacities and for this case is 85 mA h/g of graphite and is associated with the SEI formation. The current efficiency is the charge capacity divided by the discharge capacity (de-intercalation/intercalation) expressed as percentage and here it is ca. 81%. Subsequent cycles of the cell show rapidly decreasing amounts of irreversible capacity as the SEI fully forms on the graphite surface. The cell current efficiency becomes 99.9% after three cycles.

The extent of the potential plateau at ca. 1.2 V, the amount of irreversible capacity and hence the current efficiency is a function of the volume ratio of Fluoro-EC to its co-solvents. Fig. 4 plots this dependence for electrolyte compositions where the volume ratio of Fluoro-EC is varied for 1 M LiPF$_6$ Fluoro-EC/PC electrolyte. For comparison, a similar dependence for Chloro-EC electrolytes is shown [11]. For volume ratios of Fluoro-EC greater than 0.2, the amount of irreversible capacity is independent of the volume ratio. This amount of Fluoro-EC is enough to fully form the SEI film.

For a lithium ion cell where all the lithium capacity needed to form the SEI on the graphite anode comes from the cathode, it is imperative to minimize the amount of irreversible capacity. Addition of EC to Fluoro-EC/PC electrolyte reduces the irreversible capacity. For the composition Fluoro-EC/PC/EC of 0.1:0.8:0.1, the irreversible capacity is 61 mA h/g. To find the optimum composition
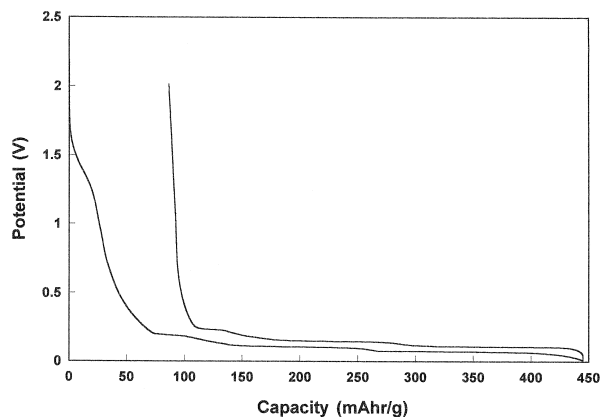

Fig. 3. Potential profiles of the first cycle of Li/KS15 graphite cell cycled at a 20 h rate. The electrolyte is Fluoro-EC/PC and EC in a volume ratio of 1:3.5:3.5.
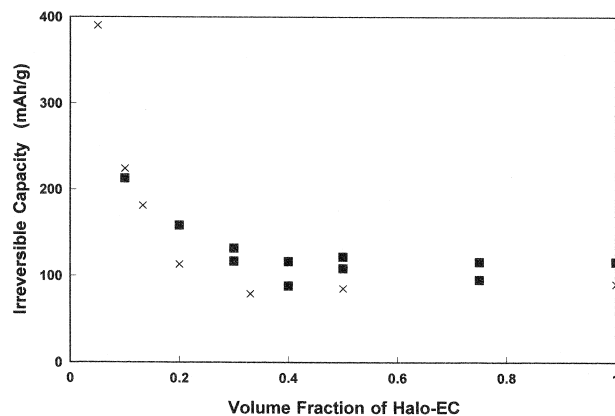

Fig. 4. Irreversible capacity of the first cycle of Li/KS15 graphite cells cycled at a 20 h rate as a function of the volume fraction of Chloro-EC (solid square markers) and Fluoro-EC (x markers). Electrolytes are 1 M LiClO$_4$ in Chloro-EC/PC electrolyte and 1 M LiPF$_6$ in Fluoro-EC/PC.
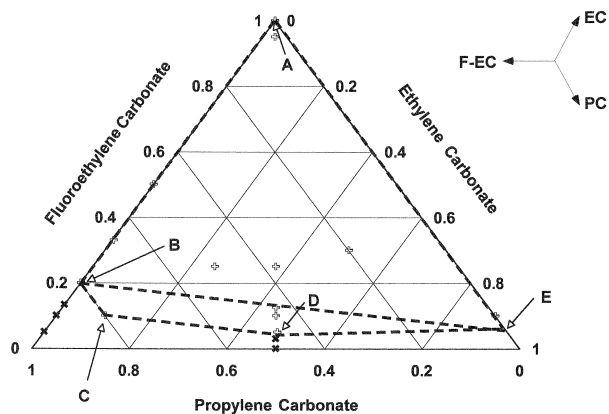
Fig. 5. Three-component composition diagram illustrating the variation in first cycle irreversible capacity for tri-solvent electrolyte systems with differing volume fractions of Fluoro-EC, PC and EC. Data collected from Li/KS 15 graphite cells cycled at a 20 h rate. Open crosses indicate less than 120 mA h/g irreversible capacity while solid xs indicate greater than 120 mA h/g irreversible capacity. Area bounded by B, C, D and E indicate compositions where the volume fraction of Fluoro-EC is less than 0.2.

of Fluoro-EC electrolyte, a large part of the three solvent compositional range was investigated employing lithium graphite cells. Fig. 5 summarizes the collected data. The data for the figure are indicated for first cycle irreversible capacities less than and greater than 120 mA h/g. This value was chosen as the maximum amount that could reasonably be tolerated in a lithium ion cell. For this criterion, the figure shows that for Fluoro-EC/PC electrolyte a volume fraction of 0.2 is required but by introducing EC as the third component the volume fraction of Fluoro-EC can be reduced. The composition, 0.1:0.8:0.1 is

point C on the Fig. 5. The volume fraction of Fluoro-EC can be further reduced to 0.05 indicated by point D with composition 0.05:0.475:0.475. Point E represents a lithium ion acceptable Fluoro-EC/EC electrolyte but has limited low temperature utility. Point A represents a pure Fluoro-EC electrolyte composition and has less than 120 mA h/g irreversible capacity. All the compositions within the region bounded by A, B, C, D and E have the required low irreversible capacity but the region bounded by B, C, D and E would be preferred for compositions where the amount of Fluoro-EC is minimized.

The cycle life of a representative lithium graphite cell is shown in Fig. 6. Here, the discharge (graphite intercalation) and charge (graphite de-intercalation) is shown vs. the cycle number for a cell with 1 M $LiPF_6$ Fluoro-EC/EC/PC electrolyte of volume composition 1:3.5:3.5. The cell was cycled at a 20 h rate for the first three cycles then at a 3 h discharge rate (D/3) followed by a 10 h charge rate (C/10). The first cycle current efficiency is ca. 81% and the cell shows rapid formation of the SEI with cycle number. The current efficiency is over 99.9% after three cycles. With higher discharge rate, the cell capacity initially drops by ca. 15% but with cycling the capacity increases. This effect has been observed previously and could be due to some delayed wetting effect of the porous PVDF bound graphite electrode initiated by local self-heating. At cycle 40, the cell was open circuited for a few days and on restarting had a slight capacity decrease for a few cycles. Over 200 cycles the capacity fade is small, less than 12%. This indicates that the graphite electrode can be cycled at high to moderate intercalation rates. The SEI must be well formed and stable.
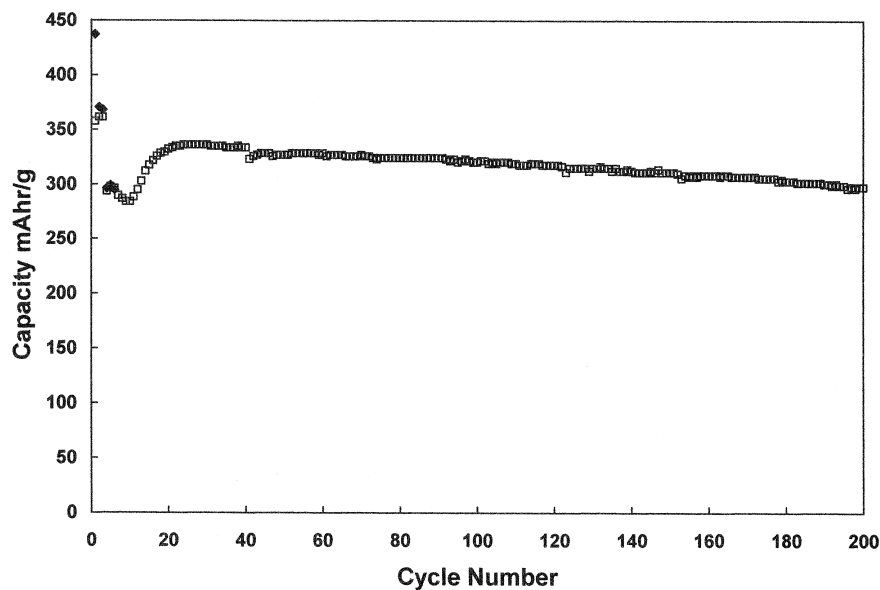

Fig. 6. A cycle life plot for a representative Li/KS15 graphite cell with 1 M $LiPF_6$ Fluoro-EC/PC/EC (1:3.5:3.5 v/v) electrolyte. A 20 h graphite intercalation and de-intercalation rate was used for the first three cycles. Subsequent cycles had intercalation and de-intercalation rates of D/3 and C/10 rate. Graphite intercalation capacity is shown with solid diamond markers while de-intercalation capacity is shown with open squares. Capacity is per weight graphite.
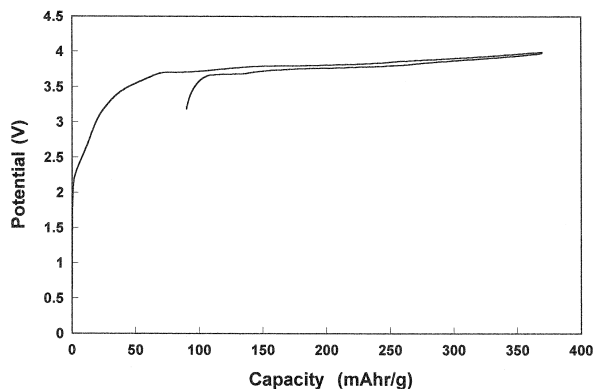
Fig. 7. Potential profile of the first cycle of a representative $LiCoO_2$/KS15 graphite cell employing 1 M $LiPF_6$ Fluoro-EC/PC/EC (1:3.5:3.5 v/v) electrolyte. The cell is cycled at a 20 h rate. Capacity is per weight graphite.

3.3. Lithium ion cells

The data presented above indicate that Fluoro-EC based electrolytes have the necessary requirements as electrolytes for electrochemically intercalated graphite electrodes. Namely, the irreversible capacity associated with this process can be minimized to levels found under comparable conditions for the commercial $LiPF_6$ EC/DMC electrolyte, ca. 80 mA h/g, along with similar reversible capacity, ca. 340 mA h/g, and rate capability, greater than 300 mA h/g capacity at D/3, as indicated by Fig. 6 and as reported earlier [9,11]. Does the same chemical shuttle exist in lithium ion cells as with Chloro-EC based elec-

trolyte? In order to answer this question, a series of lithium ion cells with graphite anodes and $LiCoO_2$ cathodes were tested. Fig. 7 presents the potential curve plotted as a function of the cell capacity per weight graphite for a cell of the above series. Here, the electrolyte was 1 M $LiPF_6$ in Fluoro-EC/PC/EC (1:3.5:3.5). The cell was cycled at a 20 h rate and limited to a upper trip voltage of 4.0 V. While the electrode balance for this cell was not optimized for maximum capacity and the upper trip voltage has not allowed full intercalation of the graphite, a fairly good reversible capacity is obtained. Some of the features of the graphite staging can be seen before the potential curve is dominated by the cathode potential curve. The irreversible capacity is similar to that found for the same electrolyte in a lithium/graphite cell. The curve of the figure can be compared to that of Fig. 1 for Chloro-EC electrolyte. For the case of Fluoro-EC, the irreversible capacity is much less and the reversible capacity larger.

Fig. 8 presents a plot of cell current efficiency vs. cycle number for the cell of Fig. 7. Here, the cell efficiency is the cell discharge capacity (graphite de-intercalation capacity) divided by the cell charge capacity (graphite intercalation capacity) for the proceeding half cycle expressed as a percentage. Here, we see that within four cycles the current efficiency has become greater than 99.5%. While this is not 100% which would be expected for a cell with no chemical shuttle, parasitic self discharge current or capacity fade, it does indicate that compared to Chloro-EC based electrolytes very little or no chemical shuttle is present with Fluoro-EC based electrolytes.
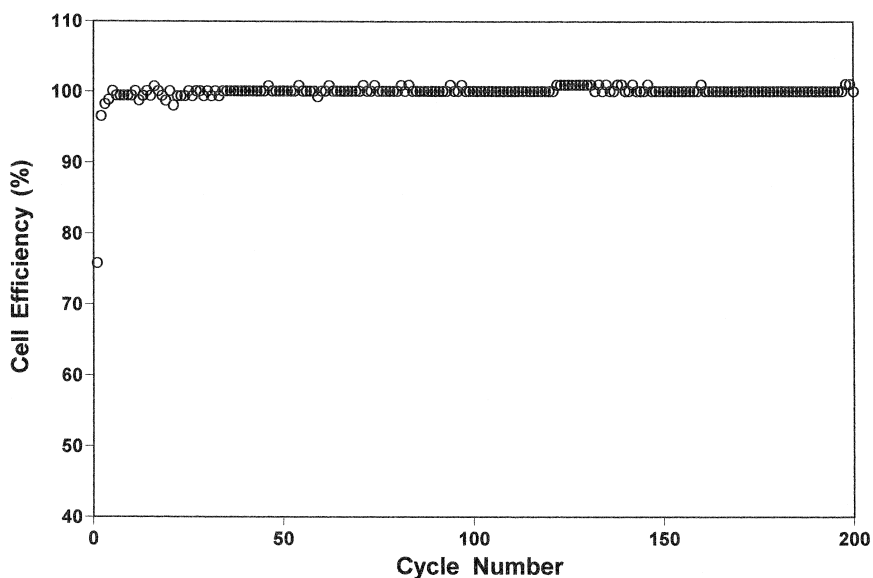

Fig. 8. A cell efficiency plot for the $LiCoO_2$/KS15 graphite cell of Fig. 7. The cell was charged and discharged at a 20 h rate for the first three cycles between 3.2 and 4.0 V. Subsequent cycles were at charge and discharge rates of C/10 and D/3. Cell efficiency is discharge capacity/ charge capacity of the preceding half cycle times 100%.
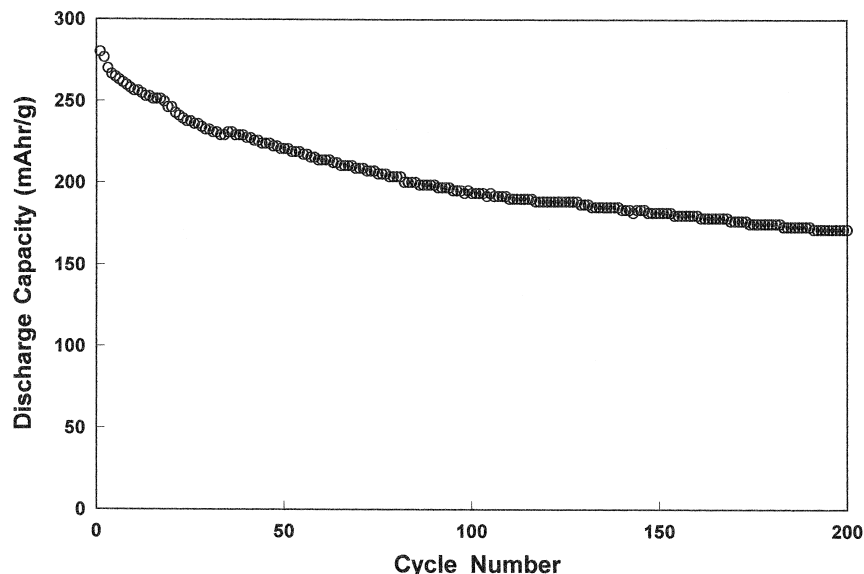
Fig. 9. A cycle life plot of discharge capacity vs. cycle number for the $LiCoO_2$/KS15 graphite cell of Figs. 7 and 8. Discharge capacity based on the weight of graphite is indicated.

Fig. 9 shows cycle life behaviour for the above cell. Capacity fade is quite large 37% fade over 200 cycles which may in part be due to incomplete intercalation of the graphite anode.

Work is continuing on Fluoro-EC electrolyte systems and includes safety studies in lithium ion cell systems by use of accelerating rate calorimetry, conductivity, rate and long term cycling studies of Fluoro-EC electrolytes in lithium ion cells and high voltage (> 4.3 V) electrode compatibility studies. Other fluoro substituted carbonate solvents are also being investigated.

4. Conclusions

A new electrolyte system containing Fluoro-EC and one or two co-solvents has been developed for a lithium ion rechargeable cell containing a graphitic anode. This electrolyte may in part contain PC as a co-solvent.

In a lithium/graphite cell, the electrolyte decomposition during the first lithiation of graphite is reduced to ca. 85 mA h/g with an electrolyte containing equal volumes of Fluoro-EC and PC and ca. 60 mA h/g with electrolyte with both PC and EC co-solvent. The volume fraction of Fluoro-EC can be reduced to 0.05 in a tri-solvent system with a co-solvent containing equal volumes of EC and PC. In our experiments, the rate capability of a Li/graphite cell with a Fluoro-EC electrolyte is similar to that of Chloro-EC electrolyte and EC/DMC electrolyte.

A lithium ion cell with an electrolyte containing Fluoro-EC and PC shows a long cycle life. A capacity decrease of 37% from the initial value is observed over 200 cycles. The cell efficiency is over 99.5% indicating that the chem-ical shuttle problem found with Chloro-EC electrolyte has been eliminated.

Acknowledgements

References

[1] M. Arakawa, J-I. Yamaki, J. Electroanal. Chem. 219 (1987) 273.
[2] A.N. Dey, B.P. Sullivan, J. Electrochem. Soc. 117 (1970) 222.
[3] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 140 (1993) 922.
[4] D.P. Wilkinson, J.R. Dahn, US Patent, No. 5, 130, 211, 1992.
[5] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 140 (1993) L101.
[6] R. Fong, H. Al-Janby, J.R. Dahn, US Patent, No. 5, 028, 500, 1991.
[7] J.M. Tarascon, D.C. Guyomard, Extended Abstract, The Electrochemical Society Spring Meeting, vol. 69, Honolulu, HI, May 16–21, 1993.
[8] H. Mao, P. Juric, U. von Sacken, Extended Abstract, The Electrochemical Society, Fall Meeting, vol. 38, New Orleans, Oct. 10–15, 1993.
[9] Z.X. Shu, R.S. McMillan, J.J. Murray, Rechargeable Lithium and Lithium-Ion Batteries, in: S. Megahed, B.M. Barnett, L. Xie (Eds.), The Electrochemical Society Proceedings Series, Pennington, NJ, 1994, PV 94–28, p. 431.
[10] Z.X. Shu, R.S. McMillan, J.J. Murray, I.J. Davidson, J. Electrochem. Soc. 142 (1995) L161.

[11] Z.X. Shu, R.S. McMillan, J.J. Murray, I.J. Davidson, J. Electrochem. Soc. 143 (1996) 2230.

[12] E. Peled, in: J-P. Garano (Ed.), Lithium Batteries, Academic Press, New York, 1983, p. 43.

[13] J-M. Seveant, in: D. Bethell (Ed.), Adv. Phys. Org. Chem., vol. 26, Academic Press, San Diego, 1990, p. 1.

[14] J. Butler, D. Cogley, J. Synott, J. Phys. Chem. 73 (1969) 4026.

[15] R. Jasinski, in: C.W. Tobias (Ed.), Advances in Electrochemistry and Electrochemical Engineering, vol. 8, Wiley-Interscience, New York, 1971, p. 253.