DEVELOPMENT OF AMBIENT TEMPERATURE LITHIUM-ION CELLS

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ABSTRACT

Four types of materials have been evaluated as anodes for Ii-ion cell fabrication. Among the materials evaluated, graphite and magnesium silicide (Mg_2Si) were identified to be suitable candidate anode materials. Experimental $C/LiCoO_2$ and $Mg_2Si/LiCoO_2$ cells, containing electrolyte solutions of 1.0M $LiPF_6$ in (EC + DEC) and 1.0M $LiPF_6$ in (EC + DMC), were fabricated and tested. Some difficulties were encountered during the fabrication of C/TiS_2 Li-ion cells. The difficulty is due to the complicated handling procedures involving initial preparation of active materials (lithiated TiS_2 or lithiated carbon) in one cell and then transfer of one of these to the final cell. 'I'he causes of the capacity fade with cycling observed in these cells were identified. This paper describes the results of the experimental work performed.

INTRODUCTION

JPL is involved in the NASA Code C sponsored program to develop Li-ion cells for future space applications. The major focus of the program is to develop the basic understanding of the cell chemistry, design and fabricate 5 Ah cells, demonstrate cycle life for LEO and GEO application, and determine safety under inadvertent abuse conditions. The work carried out so far has been in the areas of 1) anode materials, 2) electrode fabrication process, 3) Li intercalation technique, and 4) type of electrolyte and its composition[1-3]. Some of the important findings to this point are: 1) Graphitic carbons were found to exhibit higher reversible lithium capacity compared to coke materials, 2) Ethylene Propylene Diene Monomer (EPDM) is a suitable binder material for the fabrication of carbon electrodes, 3) The two step intercalation technique is effective in realizing the full reversible capacity of carbons compared to the standard one-step method, and 4) EC-based electrolytes are attractive for Li-ion cells. Work is in progress at JPL to evaluate candidate cathode materials for Li-ion cells and fabricate and test experimental cells for technology demonstration, This paper describes the results of the experimental work performed in these areas.

EXPERIMENTAL

Expanded nickel metal was used as a current collector and substrate for the anode (graphite and Mg_2Si) and TiS_2 cathode. Expanded aluminum "metal was used for the $LiCoO_2$ cathode. All electrodes were made by a pressing technique. Either ethylene propylene diene monomer (EPDM) or teflon were used as binders for anode fabrication, Typically, anodes were 10-15 mil thick. As for the oxide cathode components, it consists of $LiCoO_2$, Shawinigan black, and teflon binder, The TiS_2 cathode consists of TiS_2 material and EPDM binder. Electrochemical cells were constructed using these electrodes, lithium foil (Foote Mineral Corp.), porous polypropylene separators (Celgard no. 2400), and selected electrolytes.

Mixed (by volume ratio) solvent electrolytes containing ethers and carbonates were chosen for this study. Lithium hexafluoroarsenate ($LiAsF_6$) and lithium hexafluorophosphate ($LiPF_6$) were used as electrolyte salts. Specifically, the selected electrolytes were: (1) 1.0M $LiPF_6$ in (EC + DEC), (2) 1.0M $LiAsF_6$ in (EC + 2-MeTHF + DEC) with or without the addition of 2-Methyl furan [2-MeF], and (3) 1.0M $LiPF_6$ in (EC + DMC). The experimental cells were evaluated for charge/discharge characteristics and cycle life performance. Constant current was applied for charging and discharging the cells. Experiments were conducted in an oxygen and moisture-free dry box.

RESULTS AND DISCUSSION

(1) Anode Material Studies:

The suitability of four groups of materials has been evaluated as anodes for Li-ion cell fabrication. These materials arc: (1) Li alloys: such as binary Li-Pb, Li-Al alloys, and the addition of a third clement, such as Mn or Cr, into Li-Al, (the addition of these elements was attempted to improve the short cycle life of Li-Al binary alloy electrode due to its volumetric instabi lit y, however, the improvement was very limited.), (2) Mg_2Si compound: This material has been demonstrated to have a specific capacity of greater than 300 mAh/gm in half cell studies and is, basically, a good candidate alternate anode material for rechargeable lithium cells. Preliminary studies have demonstrated a cycle life of more than 70 cycles in full cells. However, the concern for using Mg_2Si as the anode material is its structural instability. It will gradually transform from a crystalline to an amorphous phase with the charge and discharge cycles, Therefore, ways to stabilize the host structure during cycling is an important issue for future studies. (3) Fullerene C_{60}: This ncw type of carbon material was also evaluated as an anode material, however, the dissolution of lithiated C_{60} into the electrolyte is a major problem, Therefore, there is a need to find a chemically compatible electrolyte. (4) carbon materials: Various types of carbon materials (such as pitch coke, petroleum coke, carbon fiber and graphite) were evaluated for their specific capacity as alternate anode materials. Among the carbon materials studied, graphite could yield the highest reversible lithium capacity (280 -320 mAh/gm).

(2) Effect of Electrolyte Composition:

The Li/Graphite half cells containing various electrolytes having different amount of

EC were evaluated for the reversible and irreversible lithium capacity. Some of the results have been reported[1] and the current results arc updated in Figure 1. Some of the important findings of the interaction between the electrolyte and the selected graphite material arc summarized in the following: (1) The general trend appears to be that the reversible Li capacity is about constant, and the irreversible Li capacity increases as the amount of EC increases. (2) Li/Graphite cells activated with 1 M $LiPF_6$/ 30% EC/ 70% DMC electrolyte delivered the highest reversible Li capacity (- 320 mAh/gm), and the lowest irreversible Li capacity (50 -70 mAh/gm). These results arc shown in the Figure 2. The same type of cells could deliver a capacity of more than 200 mAh/gm at the C/l.5 charge and discharge rate (Figure 3). (3) The irreversible Li capacity is more than the reversible Li capacity for the half cells containing 1 M $LiPF_6$/ 50% EC/ 50% DMC electrolyte. (4) The cells containing 1 M $LiPF_6$/ 70% EC/ 30% DMC electrolyte could not be cycled due to the high interracial resistivity. (5) The Li/Graphite half cells containing 1 M $LiPF_6$/ 10% EC/ 90% DEC electrolyte showed venting after storage for a few clays. This was identified to be duc to the reaction between lithium and the electrolyte. (6) The cycle performance of Li/Graphite cells containing 1 M $LiPF_6$/ EC/ DMC electrolyte having different amount of EC showed an interesting trend. The results showed that the cycle life increases as the amount of EC increases, however, the capacity delivered decreases (Figure 4). From these results and combined with previous results, the suggested optimum EC/DMC electrolyte composition is within the range of 30% EC and 50% EC, being c1osc to 30% EC.

(3) C/TiS_2 Ii-ion Cell Development:

TiS_2 was selected as a candidate cathode material for lithium ion cells initially for the following reasons: 1) TiS_2 was found to be intrinsically reversible compared to several chalcogenide and oxide cathode materials investigated so far for cells with lithium anodes, 2) the usable specific energy of TiS_2 is about 500 Wh/Kg and compares well with $LiCoO_2$ and $LiNiO_2$, 3) no conducting diluents are needed for TiS_2 cathodes, and 4) charge retention characteristics of lithiated TiS_2 are superior to those of lithiated metal oxides. The low operating voltage is the only known disadvantage of TiS_2 cathode material. However, the low operating voltage of the Li_xC/Li_xTiS_2 system (1.4 V -1.9 V) can be considered as an advantage as the cell can be used as a direct replacement for a 1.5 V cell. Hence, in tbc beginning of this work, it was felt that the advantages of TiS_2 material outweigh its disadvantages, and TiS_2 was selected for a detailed assessment as a cathode material for usc in Li-ion cell studies.

Three types of C-TiS_2 Li-ion cells (C/Li_xTiS_2, $LixC/TiS_2$ and Li_xC/Li_xTiS_2) activated with 1.0 M $LiAsF_6$ in (EC + 2-MeTHF + DEC) were constructed and tested. These cells showed capacity decline with cycling (Figure 5). Some of the results obtained suggest that the poor cycle performance is probably due to: (a) instability of lithiated TiS_2 and lithiated carbon materials in the dry room environment, (b) salt precipitation on the electrode surface during the drying process after the preparation of lithiated carbon and lithiated TiS_2 electrodes, and (c) difficulty in cell fabrication. The difficulty of C/TiS_2 Li-ion cell

fabrication is due to the complicated handling procedures involving initial preparation of active materials (lithiated TiS_2 or lithiated carbon) in onc cell and then transfer of this material to the final ccl]. For these reasons, the work on Li_xC/Li_xTiS_2 cell fabrication was postponed temporaril y.

(4) $C/LiCoO_2$ cell Development:

In contrast to the fabrication of C-TiS_2 Li-ion cells, the fabrication of $C/LiCoO_2$ cells is relatively easier. Several experimental $C/LiCoO_2$ Li-ion cells containing 1.0M $LiPF_6$ in (EC -t- DEC) electrolyte were fabricated to determine the effect of 1) composition of cathode material, 2) type and composition of electrolyte, 3) electrode capacity ratio, 4) charge cutoff volt age, and 5) cel 1 configurate ion on the rate capability, charge retention, and cycle life performance of the cells. These cells have a rated capacity of 350 mAh and are cathode limited in design. The experimental cells containing 1.0M $LiPF_6$ in (30% EC -t 70% DEC) have completed 137 cycles (Figure 6). The results obtained so far validate the suitability of the baseline design, The cells have an anode to cathode reversible capacity ratio of less than one. Ilowever, they arc actually of the cathode-limited design if the carbon material's lithium capacity is estimated using the theoretical capacity (372 mAh/gm). This apparent contradiction in limiting electrode is explained by the need to add excess lithiated cobalt oxide to supply the lithium lost initially by electrolyte decomposition. It is important to point out that the initial cathode loading is quite critical, in that excess amounts of cathode material may be detrimental to the ccl] cycling performance. In this case, the lithium will, without precise charge voltage control, most likely deposit on the surface of the carbon electrode which, in turn, may cause shorting of the Li-ion cells. This problem was resolved in the experimental cells by controlling charge with respect to a lithium reference. Charge was terminated when anode versus reference voltage reached 10 rnV. As for the experimental $C/LiCoO_2$ Ii-ion cells containing 1.OM $LiPF_6$ in (30% EC + 70% DMC) electrolyte, the cells have completed 48 cycles (Figure 7),

(S) $Mg_2Si/LiCoO_2$ Cell Development:

The effort of finding a better alternate lithium anode is still continuing at JPL. The compound Mg_2Si, having a CaF_2 structure, was selected for the evaluation as anode for ambient temperature rechargeable Ii-ion cell s. Mg_2Si has comparable voltage (vs. Li) to graphite and showed good reversible Li capacity in half cell studies. The designed 350 mAh cells containing Mg_2Si anodes and $LiCo0_2$ cathodes have completed 70 cycles at a C/5 charge rate and C/3 discharge rate, The cycling performance results are shown in Figure 8.

SUMMARY

Experimental $Li_xC/LiCoO_2$ cells, containing electrolyte solutions of 1.OM $LiPF_6$ in (EC + DEC) and 1.0M $LiPF_6$ in (EC + DMC), were fabricated and the cycle life testing of these cells is in progress. These cells have a rated capacity of 350 mAh and are cathode limited in design. These experimental cells have completed 137 and 48 cycles, respectively. The difficulty of graphite/titanium disulfide Li-ion cell fabrication is due to the

necessity of cell disassembly and re-assembly. Cell capacity fade with cycling was due to the high reactivity of lithiated TiS_2 and lithiated carbon, and salt precipitation on the surface of electrodes during drying period. The experimental $Mg_2Si/LiCoO_2$ Li-ion cells have completed 70 cycles to-date.

ACKNOWLEDGEMENTS

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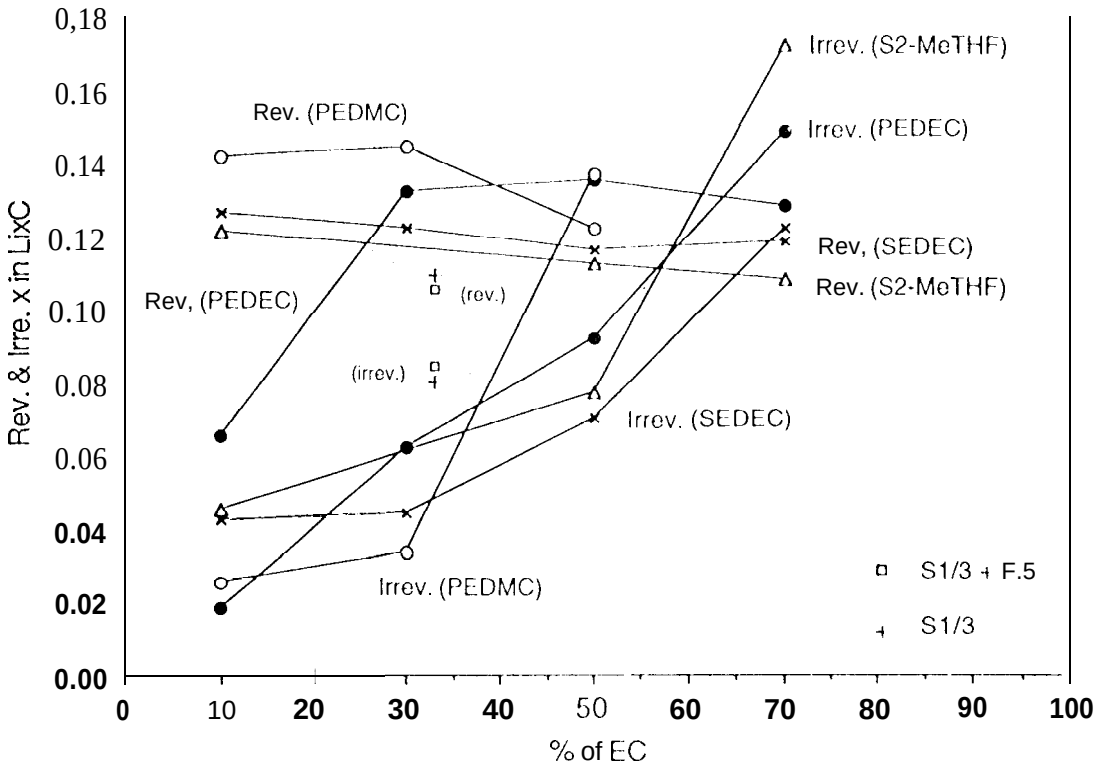

Figure 1. Comparison of the reversible and irreversible Li capacity of Li/LixC cells containing various electrolytes.

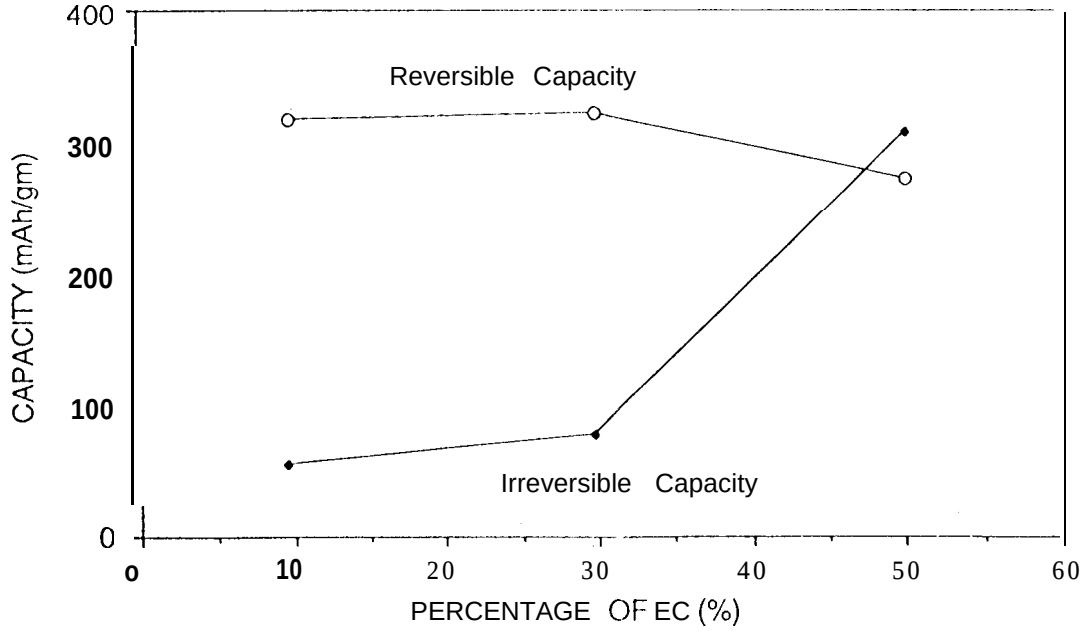

Figure 2. Lithium capacity of graphite material in cells activated with PEDMC electrolytes of various amount of EC.

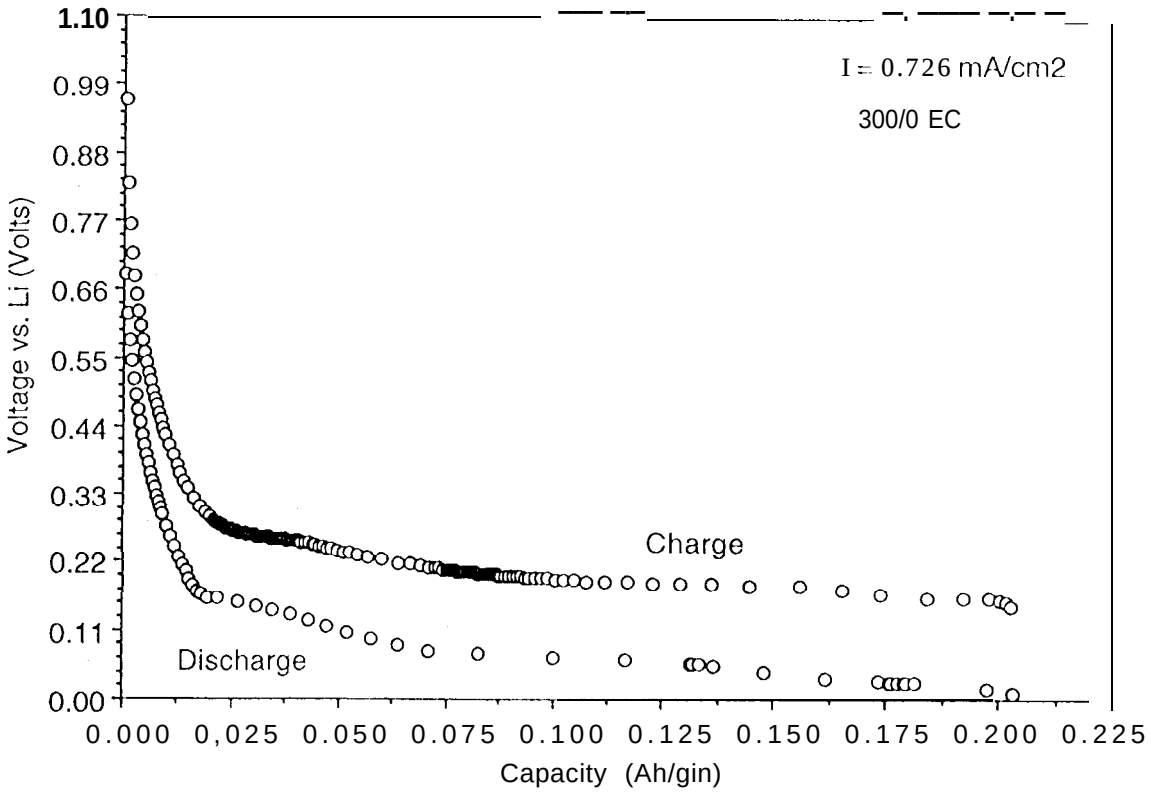

Figure 3. Cycling performance of cells containing PEDMC electrolytes having different amount of EC.

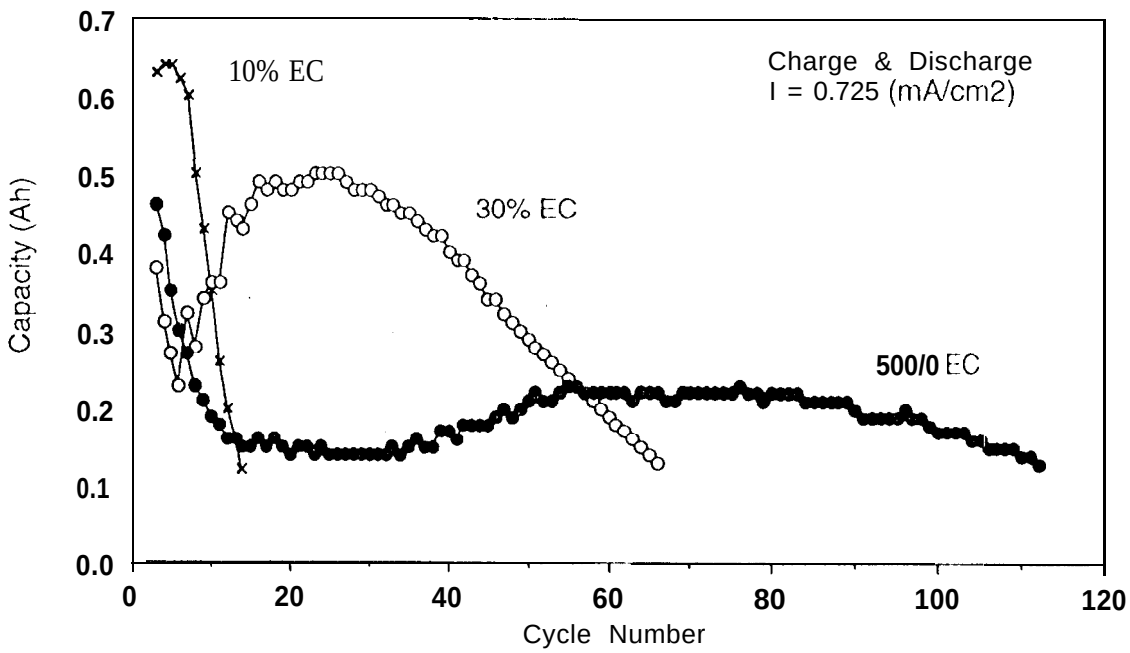

Figure 4. Comparison of cycle performance of Li/ECDMC/graphite cells activated with different amount of EC.

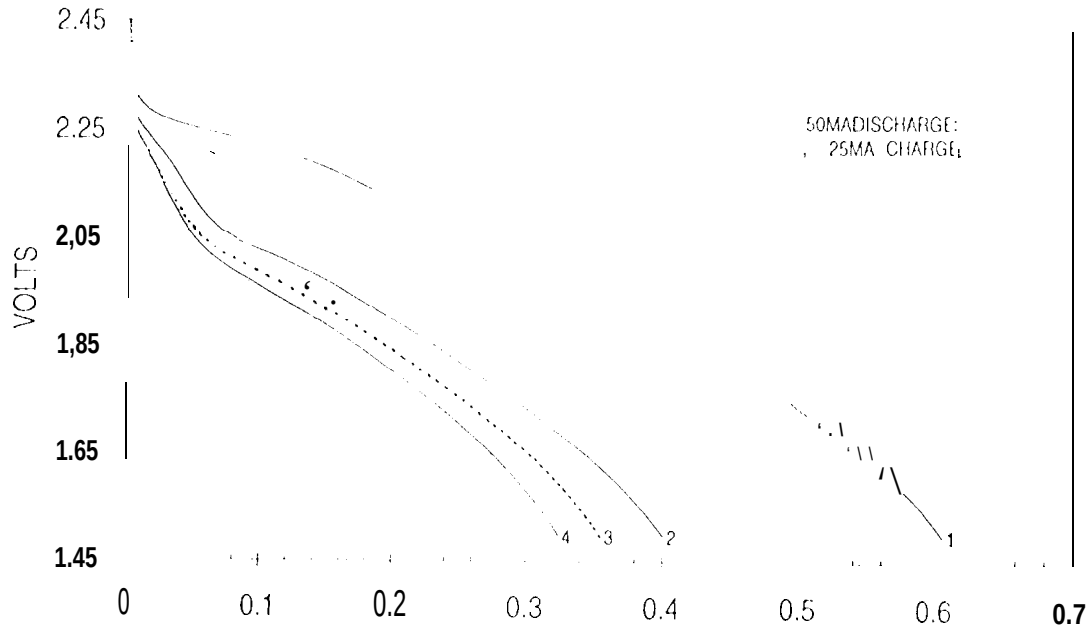

FIGURE 5CAPACITY DECLINE OF LixC/TiS2 CELL.

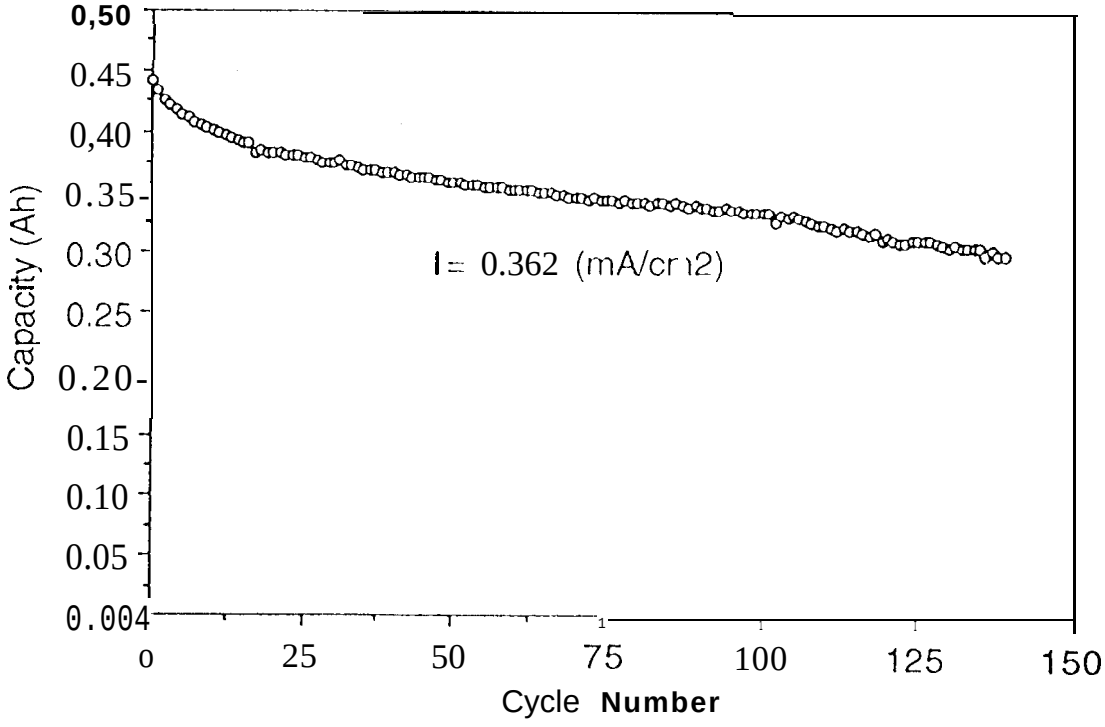

Figure 6. Cycling **performance** of C/ECDEC/LiCoO2 cell.

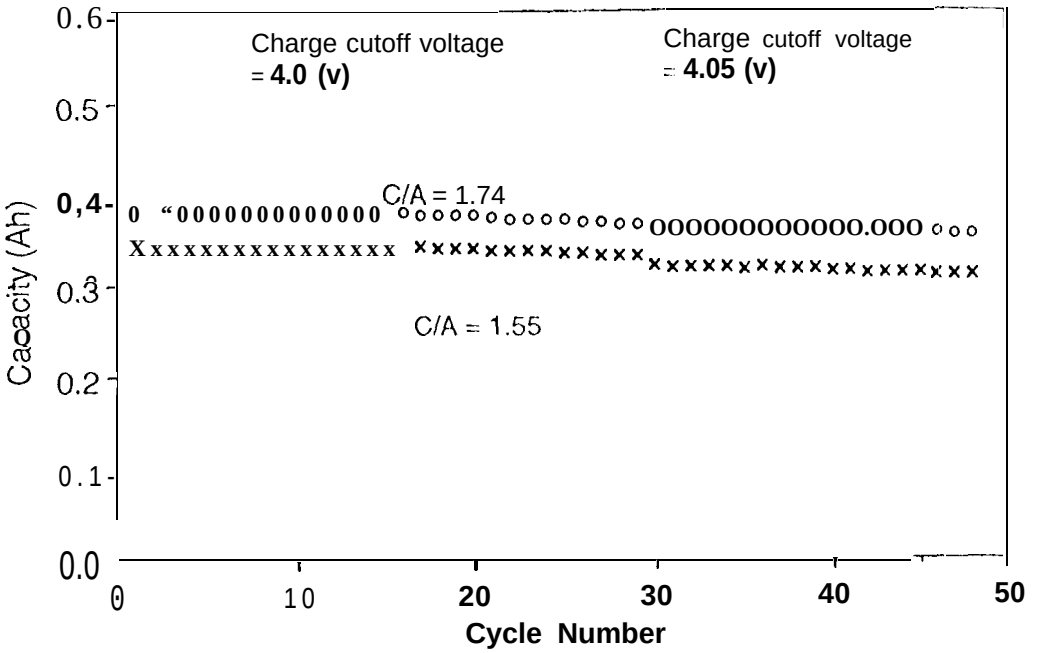

Figure 7. Cycle performance of Graphite/PEDMC/LiCoO2 cells having different cathode to anode weight ratio.

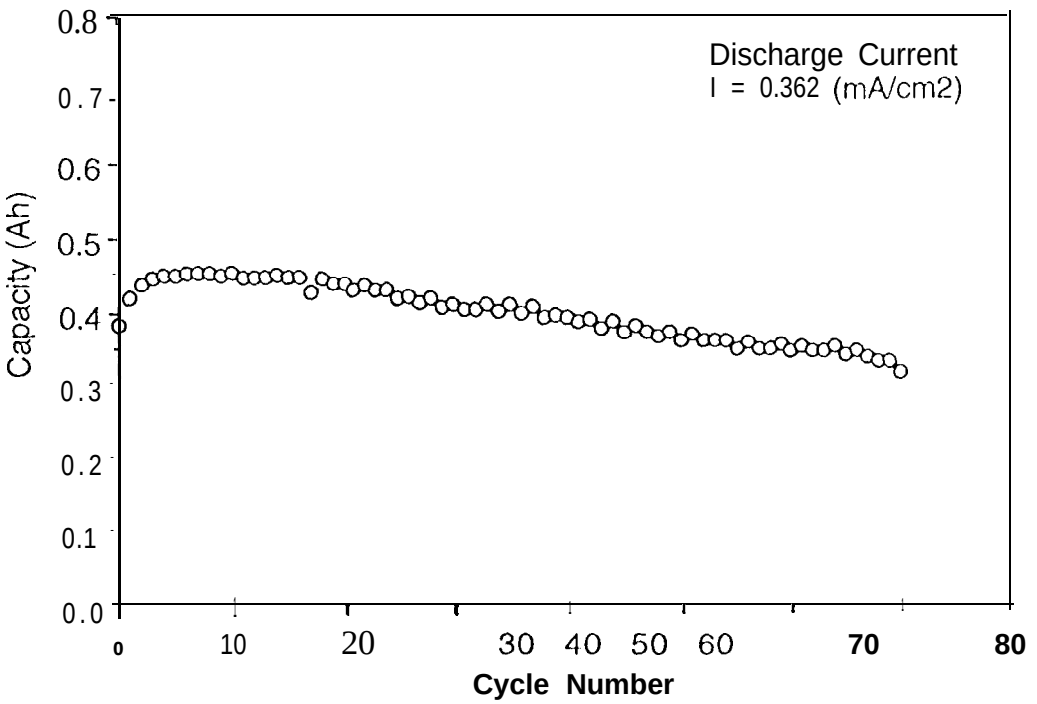

Figure 8. Cycle life performanceofMg2Si/LiCo02 cell.