DEVELOPMENT OF CARBON ANODE FOR RECHARGEABLE LITHIUM CELLS

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INTRODUCTION

Conventionally, rechargeable lithium cells employ a pure lithium anode. To overcome problems associated with the pure lithium electrode, it has been proposed to replace the conventional electrode with an alternate material having a greater stability with respect to the cell electrolytes. For this reason, several graphitic and coke based carbonaceous materials were evaluated as candidate anode materials. Graphitic carbons were found to exhibit higher reversible lithium capacity compared to the coke based materials[1]. At JPL, graphite material has been chosen as a candidate anode material for the Li-ion cell development. Ethylene Propylene Diene Monomer (EPDM) was selected as a suitable binder material for the fabrication of carbon electrodes[2]. The results of the electrode fabrication studies indicated that the amount of binder required for a carbon material is dependent on its surface area. Excessive amounts of binder were found to reduce the reversible lithium capacity and also the rate capability of the electrode. JPL has reported on a two step procedure for the formation of Li_xC electrode[3]. This process involves the intercalation of lithium into carbon in two different steps. Electrodes prepared by this method exhibited higher reversible Li capacity compared to those prepared by the single step process. Lithium capacity and reversibility of the carbon electrodes were also found to be significantly dependent on the nature of the electrolyte and its composition[4]. In this paper, we summarize the results of the studies on Li-ion cell development.

EXPERIMENTAL

The electrochemical performance of the graphite material was investigated using half cells employing Li as the negative electrode and carbon as the positive electrode. Both nickel and copper grid were used as current collector and substrate for the carbon electrode. Carbon electrode were made by pressing and lithiation was performed by electrochemical intercalation with Li. EPDM was used as a binder. All electrodes were prepared by mixing the carbon powder with a solution of EPDM binder in cyclohexane until a uniform slurry was obtained. The slurry was spread on both sides of the grid to form the electrodes. Then, the carbon/EPDM coating is dried by allowing the cyclohexane to evaporate. As a final step , both sides of the grid were pressed between a pair of stainless steel plates, to a pressure of about 450 lbs/in^2. Typically, electrodes were coated with 10-15 mg of carbon per cm^2, and were 10-15 mil thick. 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, six different groups of electrolytes were studied: (1) 1.5M $LiAsF_6$ in {x% Ethylene carbonate [EC] + (100-x)% 2-Methyl tetrahydrofuran [2-MeTHF]], where x = 10, 50 and 70 (These electrolytes will be abbreviated as SE2MeTHF(x%).), (2) 1.0M $LiAsF_6$ in {('70% EC + 30% Dimethoxy ethane (DME)}, this electrolyte will be abbreviated as SEDME(70%) & 1.OM LiPF6 in (70% EC+ 30% DME), and this electrolyte will be abbreviated as PEDME(70%), (3) 1.OM $LiAsF_6$ in (70% EC + 30% Dimethyl carbonate (DMC) }, this electrolyte will be abbreviated as SEDMC(70%) and 1.OM $LiPF_6$ in (70% EC + 30% DMC), this electrolyte will be abbreviated as PEDMC(70%), (4) 1.0M $LiAsF_6$ in (x% EC + (1 OO-X)% Diethyl carbonate [DEC] }, where x = 10,30, 50 and 70 (These electrolytes will be abbreviated as SEDER.), (5) 1.0M $LiPF_6$ in {x% EC + (1 OO-X)% DEC}, where x = 10,30,50 and 70 (These electrolytes will be abbreviated as PEDEC(x%).), and (6) 1.0M $LiAsF_6$ in (33.3% EC + 33.3% 2-MeTHF + 33.4% DEC) with or without the addition of 2.5% 2-Methyl furan [2-MeF] (These electrolytes will be abbreviated as S(1/3) and S(1/3+2MeF).). The experimental cells were evaluated for charge/discharge characteristics, faradaic utilization of the carbon active material, rate capability and cycle life. Constant current was used for charging and discharging the cells. Experiments were conducted in an oxygen and moisture free dry box.

RESULTS & DISCUSSIONS

(A) Electrochemical Intercalation Techniques: Once a suitable carbon electrode is formed, difficulties arise in incorporating lithium ions into the carbon anode, To incorporate lithium ion, a carbon electrode is typically immersed within an electrolyte bath with a lithium ion source which may be a lithium-containing electrode such as a piece of lithium metal, lithiated titanium disulfide TiS_2, or lithiated cobalt oxide, etc.. A current is then applied between the lithium source and carbon electrodes. Two electrochemical intercalation methods have been developed. The first of these is an intermittent discharge method. The initial application of current causes a portion of the lithium ions to react with carbon atoms on the surface of the carbon electrode, without any intercalation. Because the voltage (v. s. Li) of the carbon electrode drops to near O volts, it may appear that the electrode is no longer useful, The current is then deactivated and reapplied several times. Each subsequent re-application of current causes a greater reaction with lithium ions and ultimately results in reversible intercalation (Figure 1). The second method involves application of current in two stages wherein the second current level is substantially lower than the first current level. However, the second current is applied only once and results in substantial intercalation of lithium ions. In the first method, four or more steps are required to achieve substantially full intercalation.

In the two stage method, substantially full intercalation is achieved in two stages. Figure 2, illustrate a second method in which one current is used for an initial discharge stage and then a lower current is used for subsequent discharge stages. The processes for the step one discharge were studied by complex impedance measurements using three electrodes at different stages during the step one discharge. The results are given in Figure 3. At stage one, we found one semi-circle & a vertical (capacitor) line that reflects the initial film from the binder or other impurities. Ultimately, we found two semi-circles which reflects the formation of a new film (Figure 3). These results indicated that all the Li transferred during the step one discharge results in a stable film with no intercalation. Therefore, the step one

discharge' is irreversible. The chemistry of the film was examined by EDX at four conditions including (1) Fresh carbon electrode, (2) Fresh carbon electrode dipped in the electrolytes (1.5 M $LiAsF_6$ in 10% EC + 90% 2-MeTHF) and then washed by using pure solvent (2-MeTHF) to clean up the residual salts, (3) Cycled carbon electrodes, and (4) Cycled carbon electrode then washed by pure solvent, The most important finding is that a characteristic peak of oxygen appeared in the EDX result for cycled carbon electrode, this, in turn, implied that the film contains oxygen (Figure 4).

(B) Binder Effect: For ambient temperature fabrication of carbon electrode, a binder material must be provided to hold the carbon particles together. However, if too much binder is provided with the graphitic carbon, low specific energy, poor rate capability and inadequate lithium reaction occurs. Conversely, if an insufficient amount of binder is provided, the graphitic carbon particles tend to disperse or dissolve within the electrolyte bath. In Fig. 5, voltage is charted as a function of the value of' x in Li_xC for O. S%, 1% and 3% EPDM compositions to illustrate the effect of the amount of EPDM binder on the reaction of lithium-ions with graphitic carbon. The discharge curves were obtained using the first stage of a two stage technique. A relatively low current level of 0.188 mA/cm^2 was used for the discharge of the 3% EPDM carbon electrode. These results illustrate that even at the relatively low current, very little lithium ion reaction was achieved for a 3% EPDM composition. Nevertheless, even with 2% EPDM, very little intercalation was found to occur. Fig. 6 illustrates electrochemical intercalation and deintercalation curves for lithium into and out of a graphitic carbon having a 0.5% EPDM composition.

Although 1% EPDM can be used to achieve a reversible cell, 1% is not an optimal EPDM binder percentage. The use of a 0.5%, by weight, EPDM binder allows for adequate cohesion of the graphitic carbon particles while also allowing for an effective subsequent intercalation of lithium ions into the carbon. Although a composition of 0.5% EPDM is optimal, a composition of up to 1% EPDM may also be effective for binding the carbon. In general, the most effective percentage of EPDM depends on the total surface area of the graphitic carbon. Table I provides rate capability information for a lithium cell incorporating a 0.5% EPDM/carbon-based electrode. In a 1 ampere-hour cell, a C/20 discharge rate and a C/3 charge rate is achieved while maintaining a capacity greater than 200mAh/gm. These results verify that a graphitic carbon electrode having a 99.5% carbon and 0.5% EPDM binder composition is an effective composition for use as a carbon/lithium-ion electrode in a lithium cell. The EPDM percentage of 0.5% is effective for use with most commercial grades of graphitic carbon. Other percentages within the rage of 0.5% - 1.0% may also be effective. However, as noted above, the optimal EPDM percentage depends upon the surface area of the graphit ic carbon.

(C) Evaluation of carbon materials: The carbon materials that had been evaluated include: pitch coke material, the same type of petroleum coke materials with different particle size, PAN carbon fiber, and graphite materials. The coke materials that we have evaluated showed a typical powder x-ray diffraction pattern of broad peaks compared to the sharp and narrow peaks for graphite materials. Two step Li reaction of pitch coke material with initially high current, followed by a low current Li intercalation, showed about 50 % of Li capacity to be reversible. For petroleum coke materials, we examined the Li reversible capacity (by 1 V cut offj of the same petroleum coke materials but with different particle size. Experimental results showed that the reversible Li capacity is about the same (0.06 Li per carbon) for both petroleum coke materials having different particle size. The major difference is that the irreversible Li capacity is much larger for the small particle size coke materials. These indicate that the surface of carbon material plays an important role in the electrochemical intercalation process. Also, the reversible Li capacit y in the PAN-based carbon fiber material was evaluated. The results indicated that about 0.1

Li per carbon can be reversibly cycled at a slow charge and discharge rate. For the case of graphite material, 0.124 Li per carbon can be reversibly cycled after a two step Li reaction. To make a comparison, reversible Li capacity of different types of carbon materials is summarized in Table 11.

(D) Type of electrolyte and its composition: Seventeen different mixed solvent electrolytes containing ethers and carbonates were evaluated as candidate electrolytes for Li-ion cells. The results obtained to date indicate that the electrochemical performance of the carbon material identified is dependent significantly on the nature of the electrolyte employed. The experimental results of Li/C cells containing various electrolytes are summarized below:

(1) 'l'he reversible Li capacity for the cells containing SE2MeTHF electrolyte having various amount of EC was approximately 0.12 Li/C. However, the irreversible Li capacity increases sharply with increase in the amount of EC. These results indicate increased electrolyte decomposition in electrolytes containing higher levels EC.

(2) The interracial resistivity was very high for cells containing PEDME, SEDME, PEDMC and SEDMC electrolytes. Due to the high resistivity, these cells were not able to be cycled. Detailed analysis of these cells revealed that the separator used (Celgard 2400) was not wet. The dry condition may have been caused by the high percentage (70%) of EC used, which, in turn, increased the electrolyte viscosity.

(3) The discharge curves (Figure 7) of Li/Li XC cells containing SEDEC electrolytes reveal a high peak voltage (1,2 V vs. Li) which may be an effect of the LiAsF6 salt. This peak voltage decreases slightly with increase in the EC content in the electrolyte. The cells activated with electrolytes containing more EC exhibited higher voltage discharge profiles under the same discharge current density. The higher voltages may be explained by increase in the practical surface area of the carbon electrodes which, in turn, is probably due to the EC solvent co-intercalation into the carbon particles. The increased Li capacity of the first step discharge is mostly used for the formation of a protective film on the carbon to cover the increased surface area. The Li capacity used for film formation is actually a waste of Li and electrolyte. For all the four combination of EC in the SEDEC group, the reversible Li capacity is in the range of 0,12 Li/C. However, the irreversible Li consumption increases sharply as the EC amount in the electrolyte increases to above 30% (Figure 9).

(4) Figure 8 exhibits the first step discharge of half cells containing PEDEC with various amount of EC. 'J'he discharge Li capacity in the Li/C Cells containing PEDEC electrolytes had a similar trend as cells containing SEDEC electrolytes. However, the peak voltage of these cells was lower (0.6 -0.7 Volts vs. Li). For cells containing PEDEC electrolytes, the reversible Li capacity was in the range of 0.131 i/C, Figure 9 shows that the irreversible Li consumption increases sharply as the EC amount increases, and eventually reaches a state of having more irreversible capacity than reversible capacity for PEDEC(70%). Therefore, the optimum EC amount in PEDEC electrolyte used in rechargeable Li cells with a Li XC anode is between 30 and 50%.

(5) Li/C cells containing S(1/3) and S(1/3+2-MeF) electrolytes delivered about the same amount of total discharge capacity (O. 19 Li/C). However, the cells having 2-MeF in the electrolyte showed slightly less charge capacity (0.075 Li/C) than those not containing 2-MeF (0.08 Li/C).

Experimental results obtained so far indicate that increase of ethylene carbonate (EC) was found to improve the rate capability of the cells. However, the increase in EC content was

also found to increase the amount of electrolyte decomposition. The electrolytes containing EC and diethyl carbonate (DEC) with lithium hexafluorophosph hate ($LiPF_6$) salt were found to be promising for Li ion cells.

(E) Lithium-ion Cell Development:

(a) Li_xC/Li_xTiS_2 system: Although the Li_xC/Li_xTiS_2 cell has lower voltage than the $Li_xC/LiCoO_2$ cell. It have comparable specific energy because Li_xTiS_2 has higher specific capacity than $LiCoO_2$. Earlier work at JPL showed that the Li metal-TiS_2 cell was attractive in terms of specific energy and reversibility. However, some difficulties were encountered during the fabrication of Li_xC/Li_xTiS_2 cells. This comes from the intrinsic problems in the areas of: (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 electrode, and (c) difficulty in cell fabrication. The difficulty of Li_xC/Li_xTiS_2 ccl] fabrication 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. For these reasons, the work on Li_xC/Li_xTiS_2 cell fabrication was temporaril y postponed.

(b) $Li_xC/LiCoO_2$ system: Experimental $Li_xC/LiCoO_2$ cells were fabricated and the cycle testing of these cells is in progress (Figure 10). PEDEC electrolyte was selected as the candidate electrolyte for these in-house Li-ion cells. Aluminum and nickel grids were used as the current collectors for the $LiCoO_2$ cathode and graphitic carbon anode respectively. The cells so far have completed 19 cycles and have no noticeable loss in discharge capacity.

SUMMARY

This study includes fabrication steps for forming a carbon electrode composed of graphitic carbon particles adhered by an EPDM binder. An effective binder composition is determined for achieving a carbon electrode capable of subsequent intercalation by lithium ions. Two differing multi-stage intercalation processes are proposed, In the first, a fixed current is repetitively applied. in the second, a high current is initially applied, followed by a single subsequent lower current stage. Resulting carbon/lithium-ion electrodes arc well suited for use as an anode in a reversible, ambient temperature, lithium cell. In addition, the electrochemical intercalation of lithium into carbon was also investigated in several mixed solvent electrolytes containing ethers and carbonate, The results obtained to date indicate that electrolyte decomposition occurs at the carbon electrode surface during the initial stages of the discharge process. The extent of decomposition was found to be significantly dependent on the electrolyte composition. Electrolytes containing higher percentages of EC showed improved rate capability, but also, more electrolyte decomposition. Electrochemical performance of the carbon electrodes is closely related with the type of electrolytes used. Some carbon and electrolyte combinations may yield reversible Li capacity of more than 300 mAh/gm. However, these electrodes can not be practically used as anode material for rechargeable Li cells if the irreversible Li capacity is too large. In this studies, experimental $Li_xC/LiCoO_2$ cells, containing electrolyte of 1.0M LiPF6 in EC + DEC, were fabricated and the cycle life testing of these cells is in progress.

ACKNOWLEDGEMENTS

REFERENCES

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(2) "Alternate Anode Materials for Ambient Temperature Secondary Lithium Cells", C.-K. Huang, S. Surampudi, A. Attia and G. Halpert, Presented at the 180th Meeting of Electrochem. Sot., Phoenix, Arizona, Oct. (1991).

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(4) "Effect of Electrol yte Composition on Carbon Electrode Performance", C.-K. Huang, S. Surampudi, D. H. Shen and G. Halpert, Proceedings of the 184th Meeting of Electrochem. Sot., New Orleans, Louisiana, Oct. (1993).

TABLE 1. Rate Capability of Li out (C) and Li in (D) in Li_xC Anode

CURRENT (mA)	CAPACITY (mAh)
D 26	783
c 50	789
D 26	791
c 100	763
D 50	728
c 50	741
D 50	734
c 100	716
D 50	714
c 200	697
D 50	710
c 300	670

* CAPACITY: > 200 mAh/gm at $1mA/cm2$.

TABLE II. The Comparisen of Reversible Li Capacity of Carbon Materials Evaluated

(1) PITCH COKE: 0.070 Li PER CARBON

(2) PETROLEUM COKE: 0.057-0.077 Li PER CARBON

(3) PAN FIBER: 0.097 Li PER CARBON

(4) GRAPHITE: 0.124 Li PER CARBON
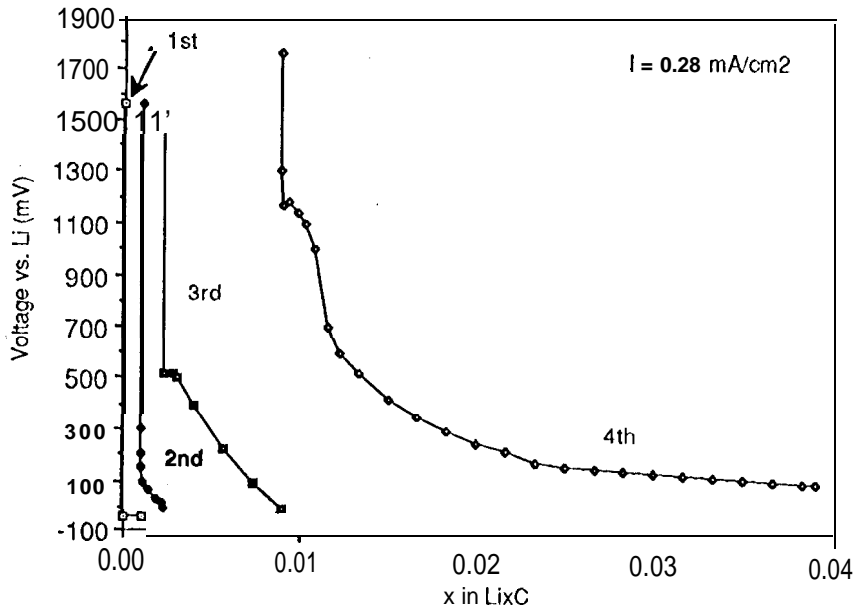

* PAN FIBER HAS VERY LOW RATE CAPABILITY.

Figure 1, The improved discharge performance of Li intercalating into carbon using intermittent discharge technique.
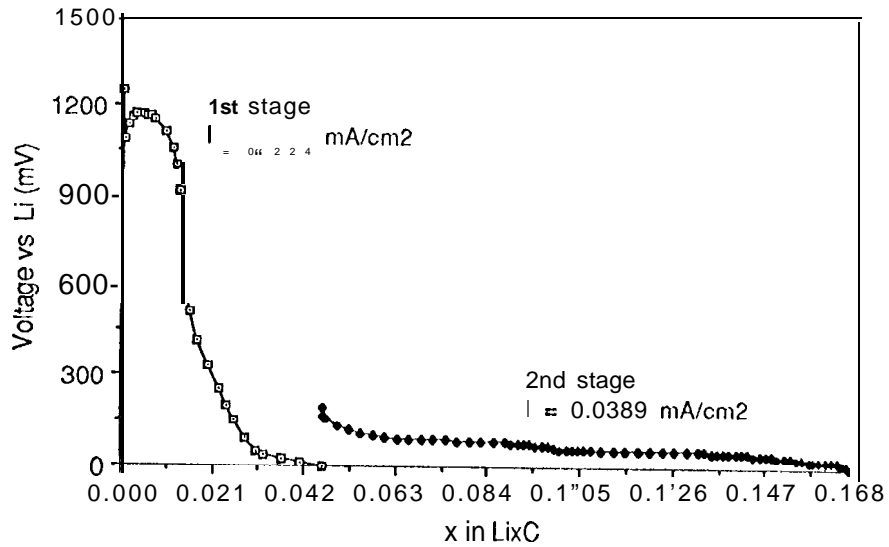

Figure 2. Electrochemical intercalation of Li into graphite by two-stage method.
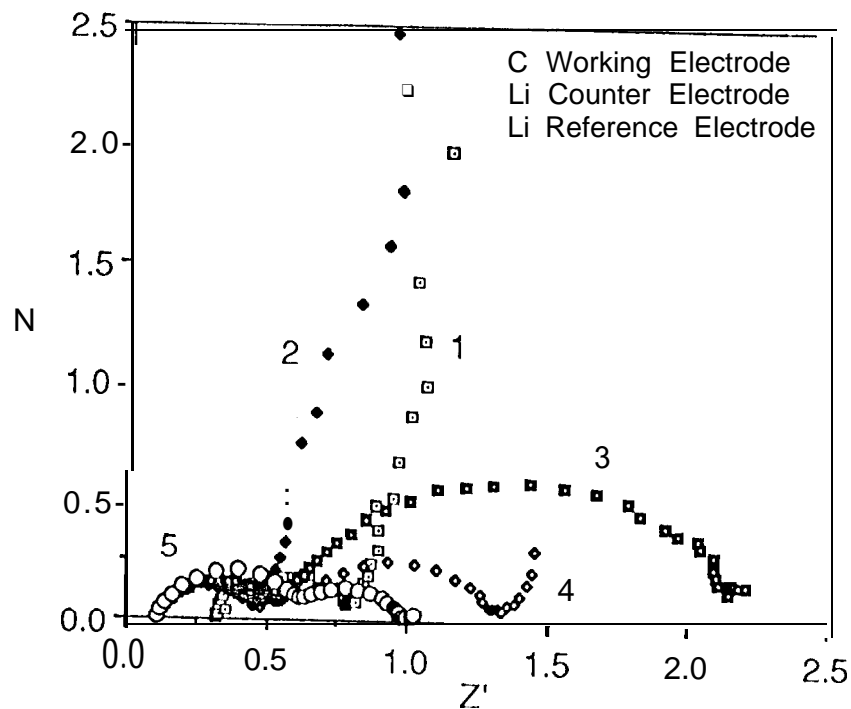
Figure 3. AC measurement of Li/C cell at different stages during first discharge of the two-step intercalation technique.
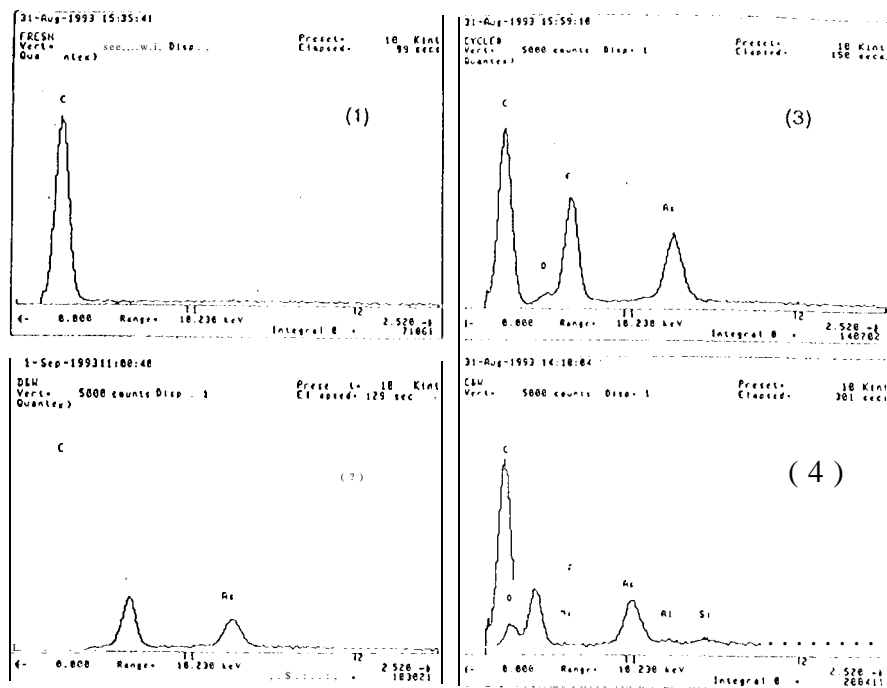
Figure 4. The chemistry of carbon surface film was examined by EDX at four condition: (1) Fresh carbon electrode (2) Fresh carbon electrode dipped in the electrolytes and then washed by using pure solvent to clean up the residual salts (3) Cycled carbon electrodes (4) Cycled carbon electrode then washed by pure solvent.
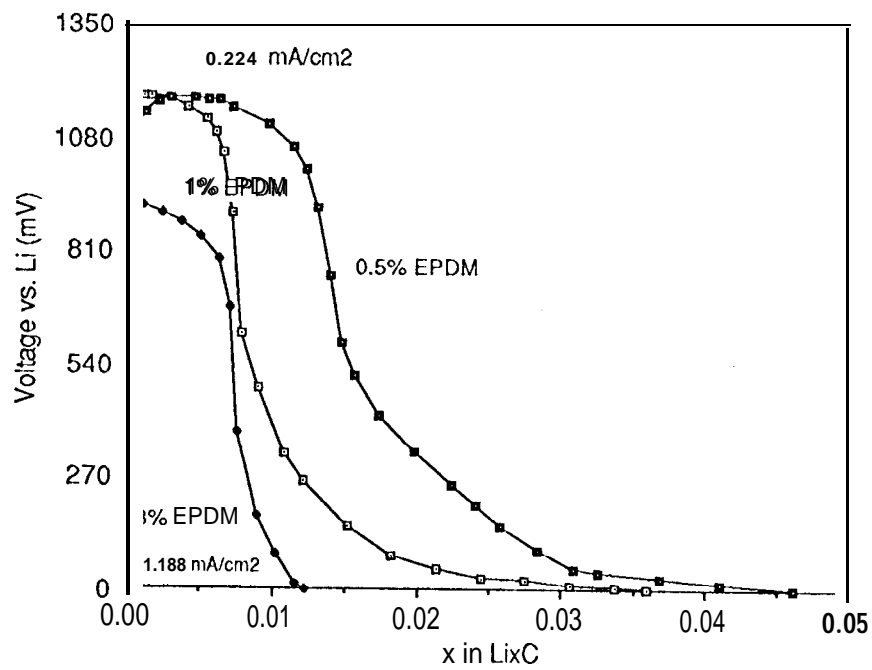
Figure 5. The effect of the percent amount of EPDM binder on the reaction of lithium with graphitic carbon.
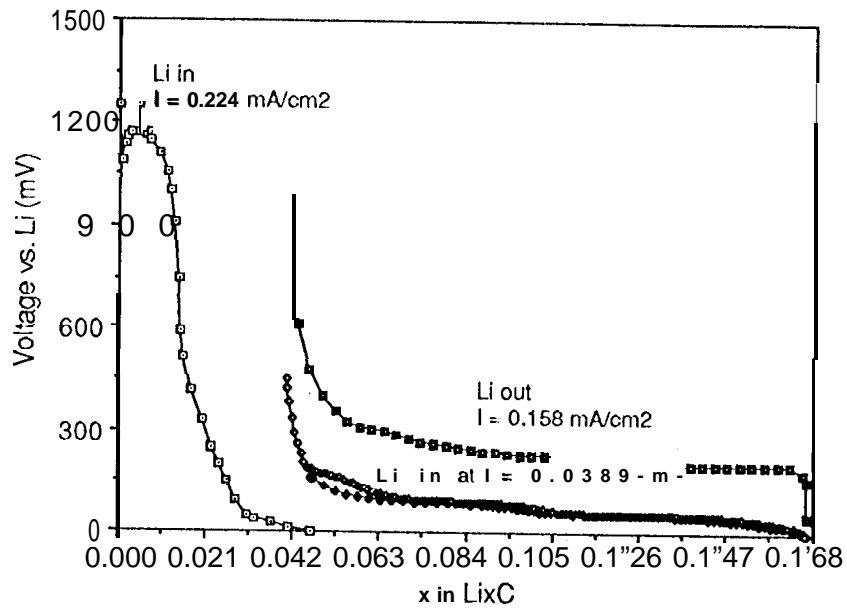
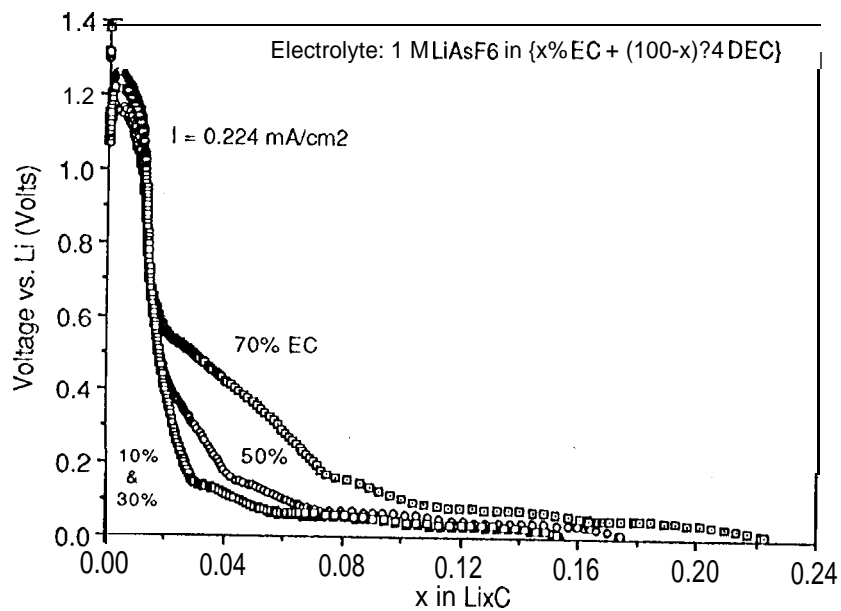Figure 6. Electrochemical Li intercalation and de-intercalation in graphite.

Figure 7. Comparison of the first step discharge of Li/LixC cells
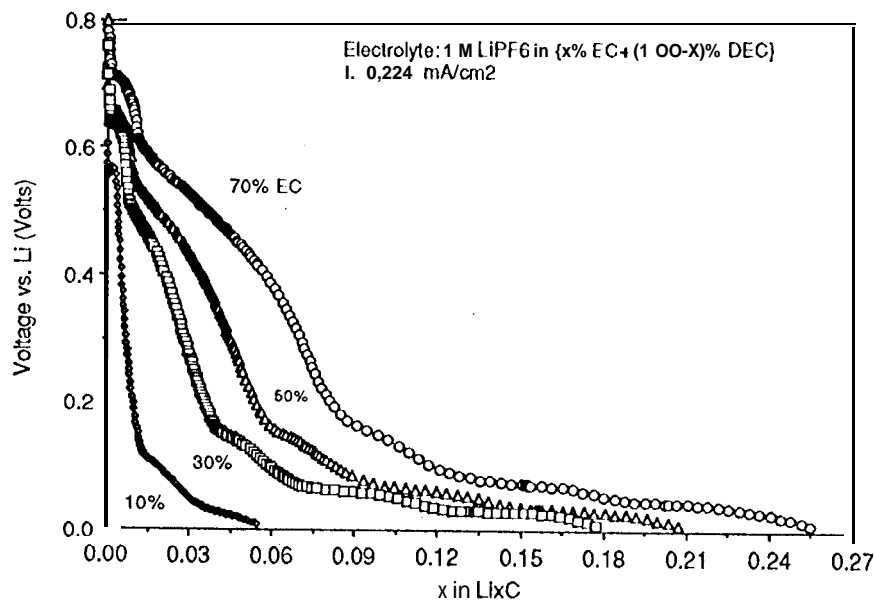containing electrolyte having different amount of EC.

Electrolyte: 1 M LiPF6 in {x% EC + (1 OO-X)% DEC}
I. 0,224 mA/cm2

Figure 8. Comparison of the first step discharge of Li/LixC cells
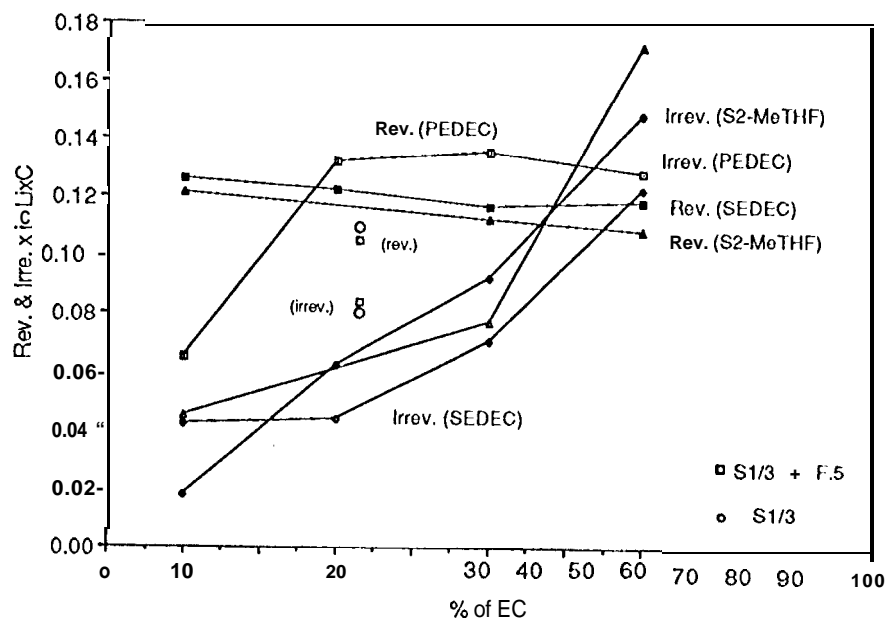containing electrolyte having different amount of EC.

Figure 9. Comparison of the reversible and irreversible Li capacity of Li/LixC cells
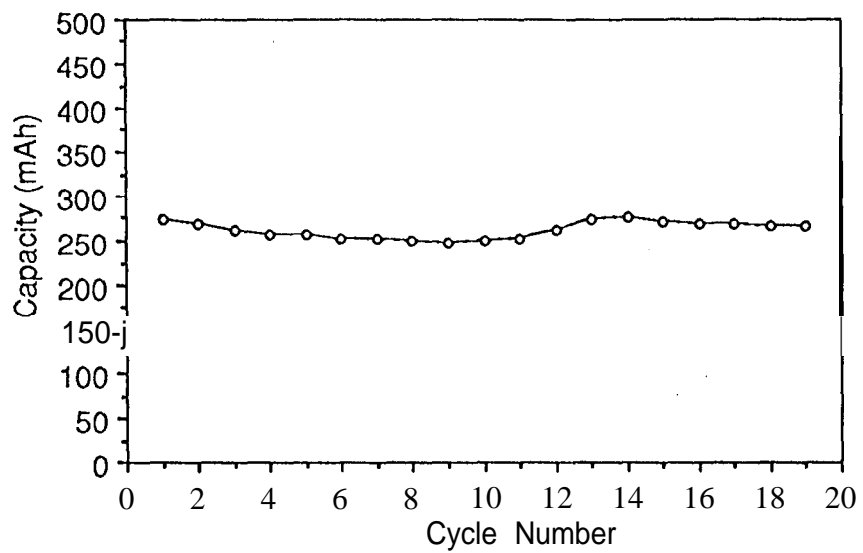containing various electrolytes.

Figure 10. Cycling performance of a C/LiCoO2 250 mAh cell.