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EFFECT OF SOLUTION ADDITIVES ON THE PERFORMANCE OF PMAN CARBON ANODES IN 1M $LiPF_6$/EC-DMC SOLUTIONS

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1. ABSTRACT

A study was undertaken to examine the use of a number of solution additives in 1M $LiPF_6$/ethylene carbonate (EC)-dimethyl carbonate (DMC) solutions to improve the performance of carbon anodes derived from polymethylacrylonitrile (PMAN)-divinylbenzene (DVB) copolymers. The study goals were to improve the cycle life and reduce the formation of the passivation layer during the first reduction, thereby minimizing the irreversible-capacity losses. Additives studied were 12-crown-4 (12-Cr-4) ether, decalin, and dilithium phthalocyanine (Li_2Pc). The carbon performance was characterized by galvanostatic cycling, cyclic voltammetry, and complex-impedance spectroscopy. Limited success was obtained with 12-Cr-4 ether at 0.25M and decalin at 1 v/o. Poor results were noted with Li_2Pc at 0.025M and 0.5M.

2. INTRODUCTION

The composition of the solvents and supporting electrolytes used in ambient-temperature Li-metal and Li-ion cells can have substantial effects upon the electrochemical performance [1-3]. Some of these effects are related to solution conductivity, Li^+ coordination, and passive-film formation on the anode. Similar issues arise when various salts and gaseous solution additives are considered. The additives can have a major impact on the formation of the film that forms chemically with Li-metal anodes and electrochemically with Li-ion carbon anodes in aprotic electrolyte solutions. This film is crucial for proper functioning of both types of Li cells.

Macrocyclic polyethers are one category of material that has received considerable interest. Danil de Namor *et al.* showed through thermodynamic, structural, and conductance studies that coranand materials should be suitable performance-enhancing additives for Li-battery technology–for both Li metal as well as Li-ion systems [4]. One of these cyclic polyethers, 12-Cr-4 ether, has been shown to improve the performance of graphite anode materials in Li-ion cells [5-7]. Cells that use propylene carbonate (PC)-based electrolytes showed reduced co-intercalation of PC into the graphite as well as improved solution conductivity and cell cycling at 0.5M to 1M 12-Cr-4 ether. Shu *et al.* reported that 0.1M to 1.0M 12-Cr-4 ether reduced the reactivity of lithiated graphite towards PC and EC [8-9]. Similar performance enhancements were also noted for coke anode materials [7].

Some work has been done using transition-metal phthalocyanines as cathodes in Li cells with PC-based electrolytes [10]. Generation of propylene gas was observed during the discharge of such cells, with only a small amount of gas generation in the case of Li_2Pc [11]. More recently, Machill and Rahner reported the use of Li_2Pc as an additive to 1M $LiClO_4$ in PC improved the cycleability of metallic Li and Li-Al anodes

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[12]. They found a reduced increase with time of the charge-transfer semicircle in the complex-impedance spectra for the Li anode in the presence of 0.001M Li_2Pc. They interpreted this as a reduction in the thickness of the passivation layer. The cycleability of the Li was also improved under these conditions.

The use of 1 to 5 v/o decalin (hexahydronaphthalene) as an electrolyte additive was reported to increase the cycleability of Li metal anodes in several aprotic electrolytes [13,14]. A reduction in self-discharge was also noted for coke and graphite intercalation anodes when cycled in electrolytes containing decalin [15].

The promising results reported by others when these additives were employed in Li-metal cells and, in some cases, Li-ion cells, prompted us to evaluate them for our carbon materials and electrolyte system. Consequently, we undertook the evaluation of decalin, 12-Cr-4 ether, and Li_2Pc in 1M $LiPF_6$/EC-DMC using carbon anodes derived from PMAN-DVB copolymers. Electrochemical characterization involved galvanostatic cycling, cyclic voltammetry, and complex-impedance spectroscopy.

3. EXPERIMENTAL PROCEDURES

3.1 Materials

The carbon precursor was prepared by an inverse-emulsion technique from a copolymer of PMAN and DVB as a crosslinking agent in a mole ratio of 3:1, respectively [16, 17]. The samples were cured under argon at 65°C for 16 hours with ammonium persulfate as a free-radical initiator. The materials were then ground, washed, and stabilized in air at 240°C for 12 hours before pyrolysis. The resulting polymer precursor powder was pyrolyzed under Ar/5% H_2 at a heating rate of 2°C per minute to 700°C and was held there for 5 hours to establish an equilibrium microstructure.

The electrolyte solution for the characterization tests was 1M $LiPF_6$ in EC/DMC (1:1 v/v), made in house [18] or purchased from Merck. The water content of the solution, as measured by Karl-Fischer titration, was <50 ppm. Li foil (Foote Mineral) was used for the counter and reference electrodes. The Li_2Pc and 12-Cr-4 ether (Aldrich) were used as received. After drying over 4A molecular sieves, the water content of the decalin (Aldrich) was 38 ppm.

3.2 Cells

The three-electrode system used to test the carbons has been previously described [18]. The anode was made with carbon powder, 15 w/o polyvinylidene fluoride (PVDF, Kynar 461) as a binder, and 5 w/o Super 'S' carbon as a conductive additive. The slurry made using dimethylformide was then pasted onto a Cu substrate using the "doctor blade" technique. After pasting, the anodes were vacuum dried for an hour at 140°-160°C. The anode discs were 1.27 cm in diameter (1.27 cm^2 area) and 0.007 to 0.021 cm thick. The anode was separated from the 0.025-cm-thick Li counter electrode by two Celgard 2500 separators. A Li flag was used as a reference electrode. The mass of active carbon ranged from 2 mg to 6 mg. Cell assembly was conducted in a dry room maintained at a dew point of less than -60°C. The cells were evacuated and backfilled with electrolyte solution in a glove box where the moisture and oxygen content were <10 ppm each. After filling, the cells were allowed to stand at open circuit overnight before testing.

The cell used for cyclic voltammetry consisted of Li counter and reference electrodes and a rod of glassy carbon sheathed with polytetrafluoroethylene, leaving only the polished end exposed to the solution. The area of the glassy carbon electrode was 0.07 cm^2.

3.3 Apparatus

Galvanostatic testing of the cells was performed using an Arbin Corp. Battery Test System. The test profile consisted of cycling at 0.50 $mA.cm^{-2}$ between 2 V and 0.01 V for 20 cycles. (This corresponded to an average rate of 0.62 C to 0.29 C.) An open-circuit wait of 600 s was imposed between charge and discharge. The cells were then subjected to an additional 12 cycles at rates of 0.25 $mA.cm^{-2}$ to 4 $mA.cm^{-2}$, to obtain rate-capability information. The nominal open-circuit voltage (OCV) of a fresh cell was ~3.25 V.

Cyclic voltammograms were generated using a Princeton Applied Research Model 263 potentiostat. The cell was scanned between voltage limits of 3 V and 0.01 V at a sweep rate of 1 $mV.s^{-1}$.

Complex-impedance measurements were performed using a Solartron Model 1250 Frequency Response Analyzer coupled to a Solartron Model 1286 Electrochemical Interface. The impedance spectra were normally taken over a frequency range of 65 kHz to 100 mHz. Complex-impedance spectra of the carbon samples during galvanostatic cycling were taken at open circuit before intercalation and at 2 V, 0.5 V, and 0.01 V during the first intercalation. Similar measurements were taken at 2 V, at the end of one complete intercalation/ deintercalation cycle and periodically during subsequent cycles. The current was allowed to decay to <50 μA at each of the measurement potentials before the cell was removed for impedance testing.

4. RESULTS AND DISCUSSION

4.2 Decalin

4.2.1 Galvanostatic Cycling

The results of the galvanostatic cycling at 0.5 $mA.cm^{-2}$ are summarized in Table I for the first and 20th cycles. The load capacity refers to intercalation of Li^+, while unloading refers to deintercalation of Li^+. Q_{irr} is the irreversible capacity loss during the first cycle. Fade is defined as the loss of capacity per cycle between the 11th and 20th cycles. Most tests were replicated twice.

At a level of 1% (by volume), decalin improved the total and reversible (unload) capacities and increased the coulombic efficiency relative to the control. Unfortunately, it also increased the irreversible capacity. At a level of 8% or 20% decalin, a drastic reduction in the irreversible capacity was observed. However, there was also a corresponding reduction in the reversible capacity, to almost nothing during the first cycle, with coulombic efficiencies of <10%. The efficiencies improved by the 20th cycle, but were still much lower than the average control efficiency of 97.2%. The efficiency data for the decalin solutions for the first 20 cycles are summarized in Figure 1 for 1% and 8% decalin. (The efficiency and fade data are not meaningful under the low-capacity conditions associated with 20% decalin.)

The reversible capacity as a function of rate is shown in Figure 2 for solutions with decalin. (Data for 0.5 $mA.cm^{-2}$ are for the 20th cycle.) The performance was severely compromised at decalin levels of 8% and 20%. At 1% decalin, however, the rate capability was improved over the control.

An entirely different behavior was observed when the cells were tested under potentiostatic-hold conditions during the complex-impedance measurements. The total and reversible capacities dramatically increased as were the coulombic efficiencies relative to the galvanostatic-cycling tests, but they were still much less than those for the control (additive-free) solution. The performance deteriorated at the higher levels of decalin.

4.2.2 Cyclic Voltammetry

The cyclic voltammograms (CVs) for glassy carbon in 1M $LiPF_6$/EC-DMC solution for the first two cycles are shown in Figure 3. The corresponding CVs for the same solution with 1% decalin are shown in Figure 4. (The use of glassy carbon avoids the complications of intercalation reactions that would occur with a PMAN electrode and allows study of passive-film formation during the first reduction step.)

The shapes of the CV curves were similar. There were broad reduction peaks at ~1.7V and 1.17 V and a sharp reduction peak near 0.45 V for the control solution for the first cycle. However, the 1.7 V peak was absent and a second reduction peak at 0.65 V was observed, along with the major reduction peak at 0.45 V, for the first cycle for the decalin sample (Fig. 4). (Instrument noise is evident during the first cycle between 1.3 V and 1.9 V.) The peaks became smaller on subsequent cycles and eventually disappeared. These peaks are related to the formation of a passivation layer on the glassy carbon because of irreversible solvent-reduction processes. The decalin sample, however, also showed a small, corresponding oxidation peak during the first cycle at 0.55 V; it was still present during the second cycle at about the same level. This reversible oxidation peak was not observed for the control solution

4.2.3 Complex Impedance

The complex-impedance spectra for PMAN carbon during the first reduction are shown in Figures 5a–5c at open-circuit voltage (OCV) and at 0.01 V as a function of decalin concentration. High levels of decalin resulted in a dramatic increase in the radius of the semicircle associated with the charge-transfer processes during reduction to form the passivation layer. This behavior was observed at 2 V and 0.5 V, as well. This is consistent with the poor behavior observed during galvanostatic testing. After complete formation of the passivation layer (typically, after four to five cycles), a second semicircle associated with intercalation is observed.

At 0.01 V, an inductive loop was observed for the control solution (Fig. 5c). This is related to the generation of unknown intermediate species during passive-film formation. Similar behavior has been reported for the Ca electrode in $Ca/SOCl_2$ cells [19]. The inductive loop disappears after four to five cycles, as the passive film becomes more coherent and complete [18].

4.3 12-Crown-4 Ether

4.3.1 Galvanostatic Cycling

The addition of 12-crown-ether at a concentration of 0.25M resulted in a substantial increase (>25%) in the total capacity of PMAN carbon during the first intercalation (Table I). However, it also resulted in a 50% increase in the irreversible capacity. Although the reversible capacity for the 20th cycle in the presence of 0.25M 12-Cr-4 ether was about 25% higher than that of the control, the cell fade more than tripled and the coulombic efficiency dropped slightly.

When the concentration of 12-Cr-4 ether was doubled to 0.5M, the total capacity of PMAN carbon for the first cycle was comparable to that for the control solution but the irreversible capacity increased, resulting in a lower coulombic efficiency (37.3% vs. 47.9%, respectively). By the 20th cycle, the reversible capacity had dropped to about half of that for solution with 0.25M 12-Cr-4 ether, the fade had increased by half, and the coulombic efficiency suffered further decline.

The effect of rate on reversible capacity for solutions with 12-Cr-4 ether is shown in Figure 6. (The data for 0.5 $mA.cm^{-2}$ are for the 20th cycle.) Up to ~2 $mA.cm^{-2}$, the reversible capacities of PMAN was greater in the presence of 0.25M 12-Cr-4 ether. At 0.5M, however, the capacities dropped well below those of the control for all rates.

4.3.2 Cyclic Voltammetry

The CVs for the first two cycles for glassy carbon in 1M $LiPF_6$/EC-DMC with 12-Cr-4 ether are shown in Figure 7. They were similar to those for the control solution (Fig. 3), except for the absence of the broad reduction peak at 1.17 V. This would suggest similar, but not identical, processes involving the passivation layer for these solutions on glassy carbon. The data for PMAN carbon (Table I), however, indicate large effects upon performance when 12-Cr-4 ether is present.

4.3.3 Complex Impedance

The complex-impedance spectra for PMAN carbon during the first reduction are shown in Figures 8a and 8b at OCV and at 0.01 V, respectively, as a function of 12-Cr-4 ether concentration. At both concentrations of 12-Cr-4 ether, there was a large increase at all potentials in the radius of the semicircle associated with the charge-transfer processes during reduction. The radius was slightly smaller at the higher concentration of 12-Cr-4 ether. The inductive loop typically observed for PMAN carbon at 0.01 V still remained in the presence of 12-Cr-4 ether.

4.4 Dilithium Phthalocyanine

4.4.1 Galvanostatic Cycling

At a level 0.025M Li_2Pc, the irreversible capacity for PMAN carbon during the first cycle (Table I) was comparable to that of the control solution. Unfortunately, the total as well as the reversible capacities were dramatically less. In addition, the coulombic efficiency dropped from 47.9% to 33.8%. By the 20th cycle, the reversible capacity had dropped to a fourth of that for the control solution and the fade had increased by a factor of almost five. The coulombic efficiency remained well below that of the control as well.

When the concentration of Li_2Pc was doubled to 0.05M, the total capacity increased to greater than that of the control but the irreversible capacity also increased significantly. The performance was improved over that observed with 0.025M Li_2Pc, but overall, the reversible capacity and the coulombic efficiency were lower with 0.05M Li_2Pc relative to the control solution. By the 20th cycle, these differences were accentuated, although not as great as for 0.025M Li_2Pc. The reversible capacity and coulombic efficiency increased and the fade decreased relative to 0.025M Li_2Pc.

The effect of rate on the reversible capacity for solutions with Li_2Pc is shown in Figure 9. The performance was adversely affected at both concentrations of Li_2Pc.

These data may relect the presence of electroactive impurities in the Li_2Pc as well as the effects of Li_2Pc itself. As received, the Li_2Pc was only 70% pure and contained 2-ethoxyethanol as a solvent adduct. The effect of this impurity on the performance is unknow at this time. This identical material was used by Machill and Rahner in their work [12]. However, the concentrations used in this work were significantly greater than the concentration of 0.001M used by Machill and Rahner. It may be possibe to realize improved performance with PMAN carbon anodes at much lower levels of Li_2Pc.

4.4.2 Cyclic Voltammetry

The CVs for the first two cycles for glassy carbon in 1M $LiPF_6$/EC-DMC with Li_2Pc are shown in Figure 10. These CVs are dramatically different from those for the control solution (Fig. 3), in that only a broad reduction peak near 1.2 V was evident on the first cycle. The sharp reduction peak normally observed at 0.45 V was absent. The lack of a major reduction peak and that the second-cycle CV looked very much like the first-cycle CV indicates very little passive-film formation occurred in the presence of Li_2Pc relative to the other solutions evaluated. These data show some reversible process was occurring during cycling.

This may be related to the presence of electroactive impurities in the Li_2Pc. The reduction currents were an order of magnitude greater than those of the other solutions tested in this work.

4.4.3 Complex Impedance

The complex-impedance spectra for PMAN carbon during the first reduction are shown in Figures 11a and 11b at OCV and at 0.01 V, respectively, as a function of Li_2Pc concentration. (See Fig. 5c for the spectrum at 0.01 V for the control.) The spectra for solutions with Li_2Pc showed the classical porous-electrode (capacitive) response that was absent for the control solution. At 0.01 V, the semicircle associated with charge-transfer processes was similar for the control solution and the solution with 0.025M Li_2Pc. The diameter more than doubled at a Li_2Pc concentration of 0.05M. The spectra for the Li_2Pc solutions were distinct in that the inductive loop typically observed for the control solution (Fig. 5c) had disappeared. This indicates that the presence of Li_2Pc had a substantial influence on the processes involving passive-film formation.

5. CONCLUSIONS

The use of decalin as an additive for 1M $LiPF_6$/EC-DMC solution results in enhanced improvement in the performance of PMAN carbon anodes at a level of 1%. The coulombic efficiency and reversible capacity are increased but at the expense of higher irreversible capacity during the first reduction and slightly higher fade. The use of higher levels of 8% and 20% causes drastic deterioration in the reversible capacities by interfering with the intercalation process. The CV of glassy carbon in the solution containing 1% decalin is very similar to that of the control solution, except for an additional broad reduction peak at 0.65 V near the main reduction peak at 0.45 V. Both CVs show large irreversibilities caused by solvent-reduction processes during passive-film formation.

The use of 12-Cr-4 ether as an additive at a concentration of 0.25M results in an initial improvement in the reversible capacity at rates up to 2 $mA.cm^{-2}$, but with a concomitant increase in the irreversible capacity during the first reduction. In addition, the coulombic efficiency is reduced and there is greater fade relative to the control solution without additives. Consequently, the performance is not be maintained during prolonged cycling. At a concentration of 0.5M, 12-Cr-4 ether causes significant deterioration in performance relative to the 0.25M solution–lower reversible capacity, lower coulombic efficiency, and greater fade. The CV of glassy carbon in the solution with 0.25M 12-Cr-4 ether is similar to that of the control, except for the lack of the broad reduction peak at 1.17 V. The overall long-term effects of additions of 12-Cr-4 ether at levels of 0.25M and 0.5M are not sufficiently beneficial to merit its use. However, longer-lasting improvements may be realized at concentrations <0.25M. More work is planned in this area.

The use of Li_2Pc at levels of 0.025M and 0.05M had detrimental effects upon the performance of PMAN carbon electrodes in 1M $LiPF_6$/EC-DMC solutions. The coulombic efficiency and reversible capacity are dramatically reduced, the fade is drastically increased, and there is no improvement in the irreversible capacity relative to the solution with no additives. The CV of glassy carbon in the solution with 0.025M Li_2Pc lacks the major reduction peak at 0.45 V observed for the other solutions which indicates little passive-film formation. The presence of the 2-ethoxyethanol impurity in the Li_2Pc may be partially responsible for the observed electrochemical behavior, or the concentration used in this work may have been excessive. More work is necessary to resolve this issue.

Even if these solution additives are effective in improving the efficiency and performance of carbon anodes in Li-ion cells, the issue of stability at high positive potentials (i.e., >4 V) still needs to be addressed. This

situation would exist when the additives are used in a complete cell with high-potential cathodes (e.g., lithiated oxides of Mn, Co, and Ni).

6. Acknowledgments

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TABLE I. EFFECT OF SOLUTION ADDITIVES ON THE PERFORMANCE OF 700°C PMAN CARBON

	First Cycle				20th Cycle				
Additive	Load ($mAh.g^{-1}$)	Unload, ($mAh.g^{-1}$)	Effic. (%)	Q_{irr} ($mAh.g^{-1}$)	Load ($mAh.g^{-1}$)	Unload ($mAh.g^{-1}$)	Effic. (%)	Fade ($mAh.g^{-1}cyc^{-1}$)	Comments
None (baseline)	484.0	231.8	47.9	252.2	130.3	126.6	97.2	-0.69	Std. 32 cycles
1 v/o Decalin[1]	651.5	334.2	51.3	334.2	235.3	230.0	97.7	-1.39	Std. 32 cycles
8 v/o Decalin	28.4	0	0.1	28.4	2.51	1.13	45.2	0.03	Std. 32 cycles
8 v/o Decalin	355.8	170	47.8	185.8	21.2	21.1	99.5	-0.14	Impedance test[2]
20 v/o Decalin	2.43	0.31	12.6	2.1	0.1	0.1	86.2	0	Std. 32 cycles
20 v/o Decalin	221.2	81.3	36.8	139.9	10.7	10.2	95.7	-0.027	Impedance test[2]
0.25M 12-Cr-4	662.4	285.6	43.1	376.9	170.1	163.7	96.2	-2.11	Std. 32 cycles
0.50M 12-Cr-4	472.6	176.4	37.3	296.2	81.4	76.3	93.7	-3.02	Std. 32 cycles
0.025M Li_2Pc[3]	374.5	126.4	33.8	248.1	37.0	34.0	91.9	-3.36	Std. 32 cycles
0.050M Li_2Pc[3]	508.9	212.8	41.8	296.1	86.4	83.2	96.3	-2.30	Std. 32 cycles

[1] Decalin dried overnight over 4A molecular sieves.

[2] Impedance testing done under potential hold at 2V, 0.5V, and 0.1V for first cycle, until current decayed to <50μA; standard 32-cycle test used open-circuit, 10-minute wait between charge and discharge.

[3] Li phthalocyanine was only 70% pure; contained 2-ethoxyethanol as solvent adduct. Appeared to come out of solution during testing.

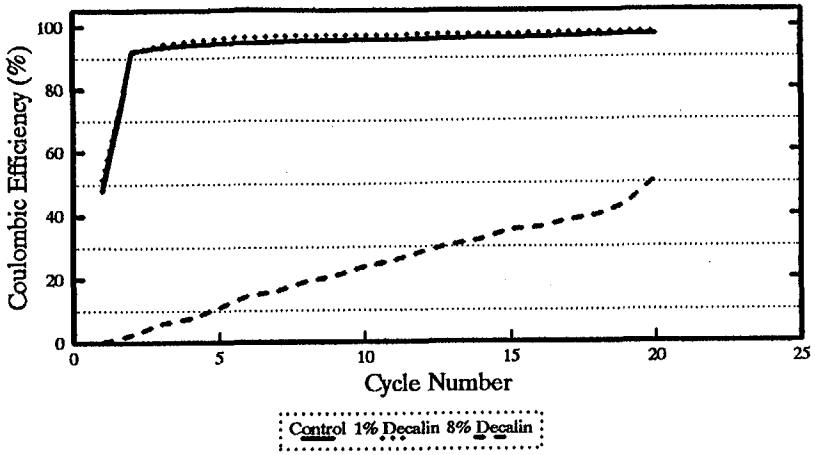

Fig. 1 EFFICIENCY VS. CYCLE NUMBER FOR PMAN CARBON IN DECALIN SOLUTIONS

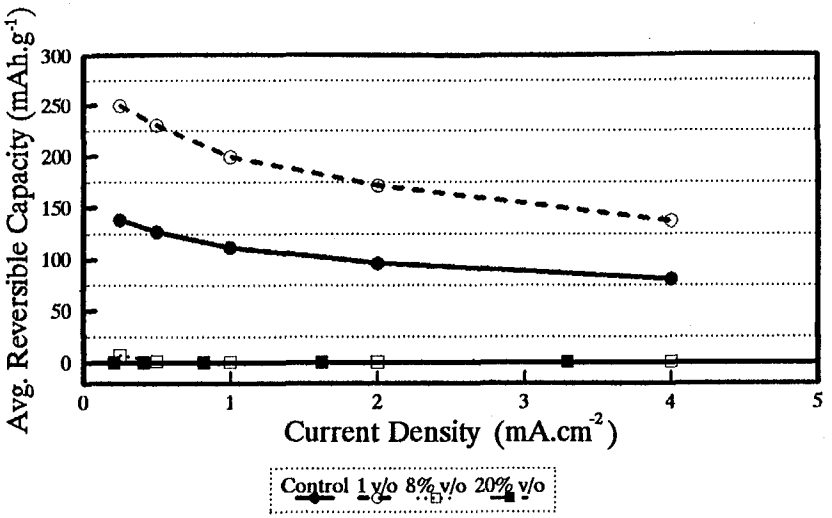

Fig. 2 PERFORMANCE OF PMAN CARBON AS A FUNCTION OF RATE IN DECALIN SOLUTIONS.

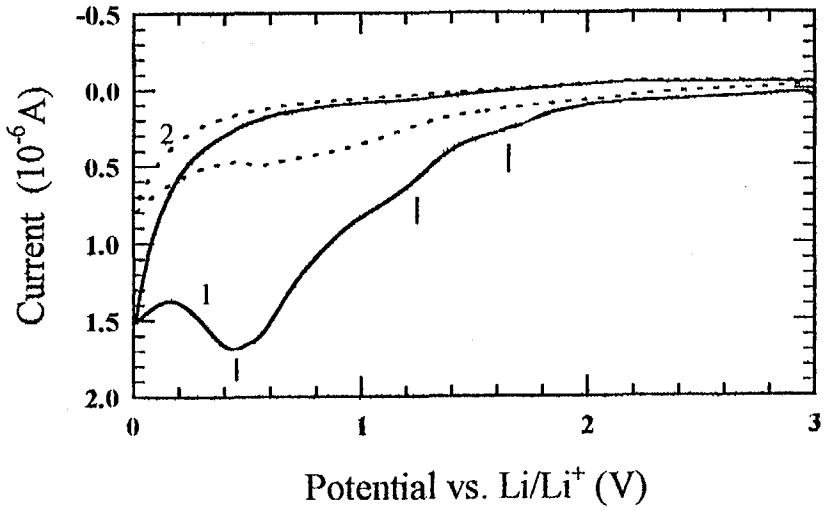

Fig. 3 CYCLIC VOLTAMMOGRAMS OF GLASSY CARBON IN 1M/$LiPF_6$/EC-DMC SOLUTION (CONTROL). SCAN RATE = 1mV.S^{-1}.

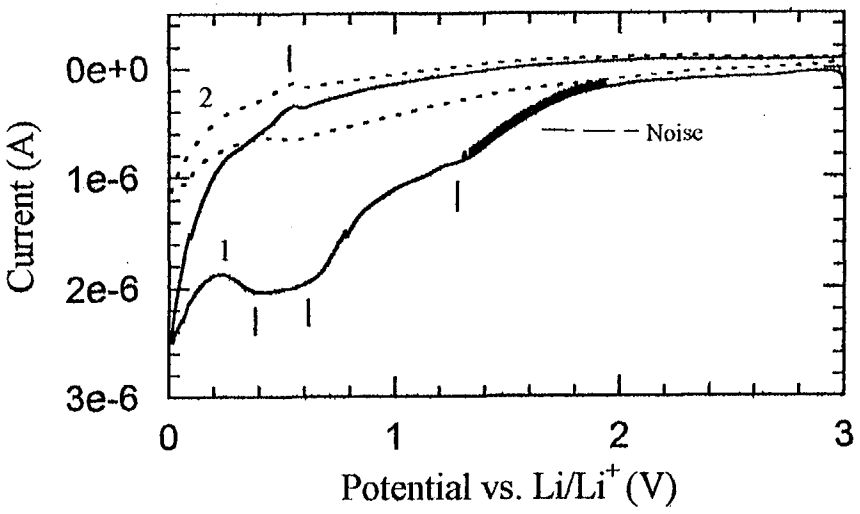

Fig. 4. CYCLIC VOLTAMMOGRAMS OF GLASSY CARBON IN 1M/$LiPF_6$/EC-DMC WITH 1% DECALIN. SCAN RATE = 1mV/s.

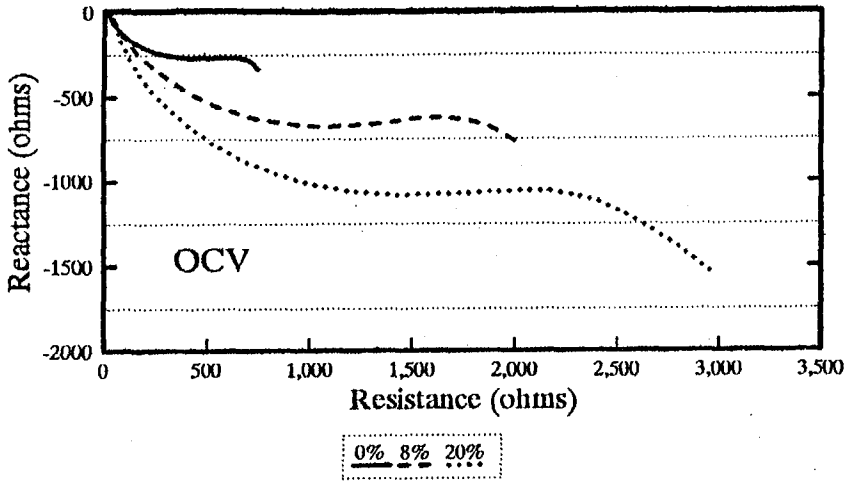

Fig. 5a. COMPLEX IMPEDANCE SPECTRA AT OCV OF PMAN CARBON IN 1M/$LiPF_6$/EC-DMC WITH DECALIN.

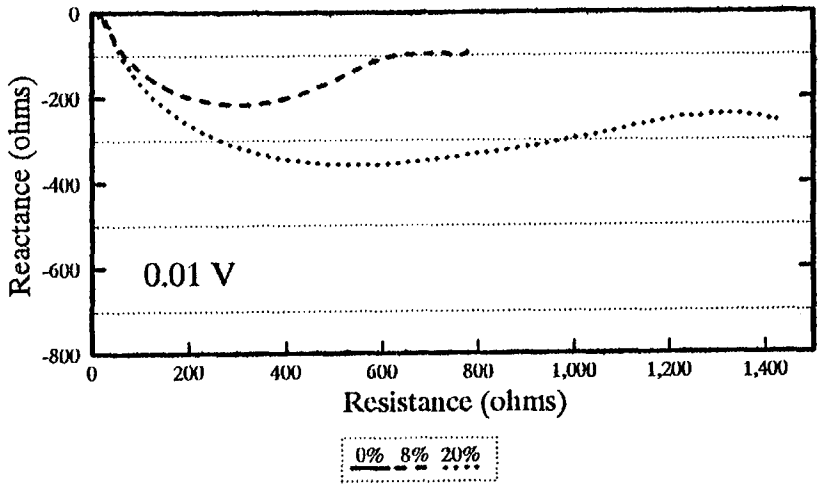

Fig. 5b. COMPLEX IMPEDANCE SPECTRA AT 0.01 V OF PMAN CARBON IN 1M $LiPF_6$/EC-DMC WITH DECALIN.

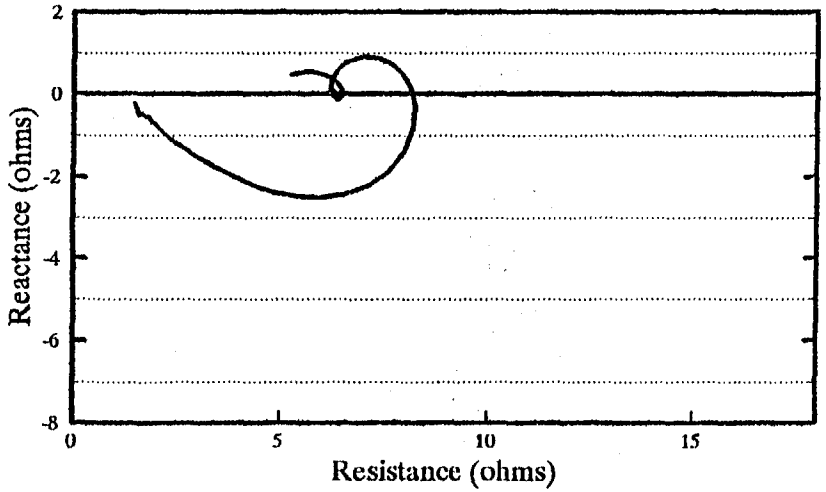

Fig. 5c. COMPLEX IMPEDANCE SPECTRA AT 0.01 V OF PMAN CARBON IN 1M $LiPF_6$/EC-DMC (CONTROL).

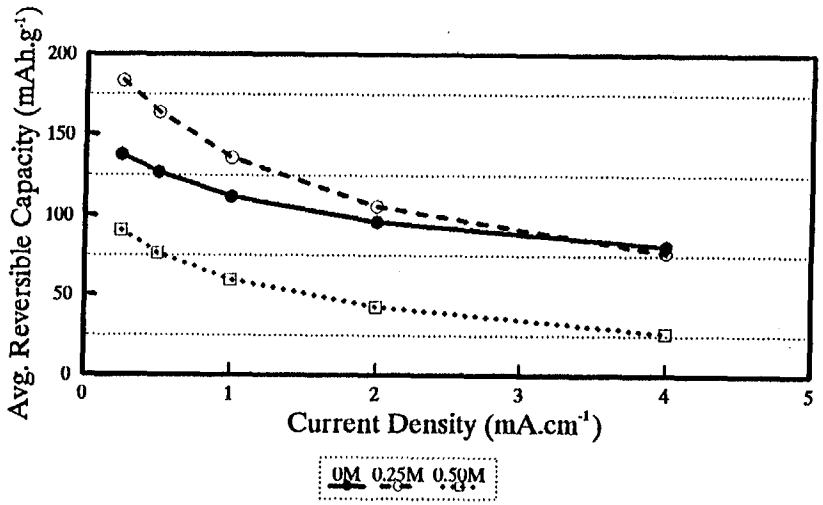

Fig. 6. REVERSIBLE CAPACITY AS A FUNCTION OF RATE OF PMAN CARBON IN 1M/$LiPF_6$/EC-DMC WITH 12-Cr-4 ETHER.

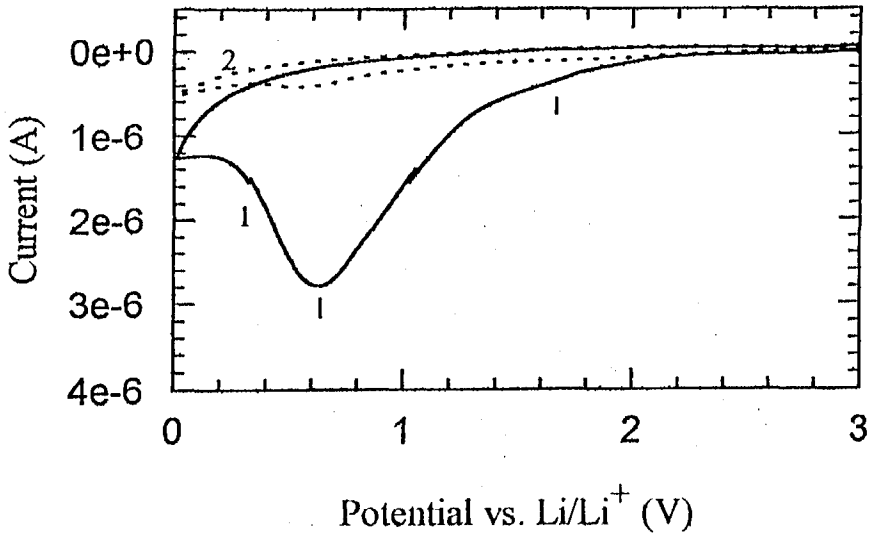

Fig. 7. CYCLIC VOLTAMMOGRAM OF GLASSY CARBON IN 1M/$LiPF_6$/EC-DMC WITH 0.25M 12-Cr-4 ETHER. SCAN RATE = $1mV.S^{-1}$.

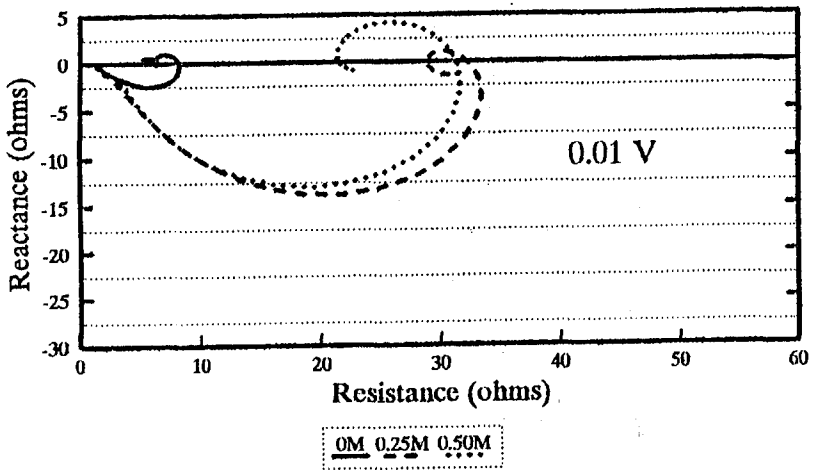

Fig. 8b. 1 COMPLEX IMPEDANCE SPECTRA AT 0.01 V OF PMAN CARBON IN 1M/$LiPF_6$/WITH 12-Cr-4 ETHER.

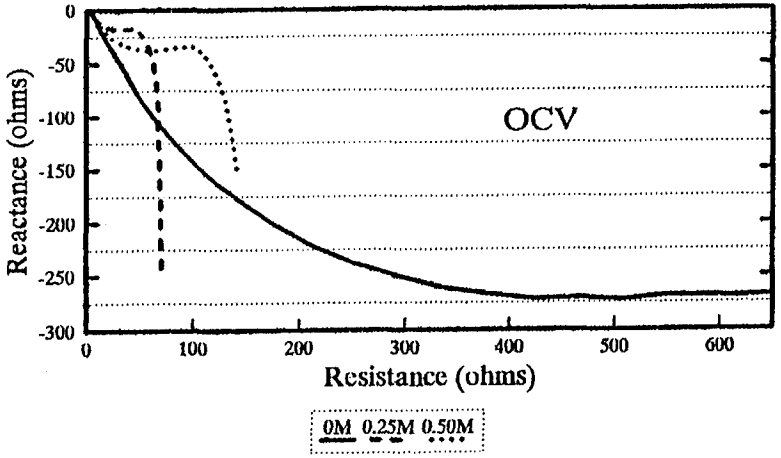

Fig. 8a. 1 COMPLEX IMPEDANCE SPECTRA AT OCV OF PMAN CARBON IN 1M/$LiPF_6$/EC- EC-DMC WITH 12-Cr-4 ETHER.

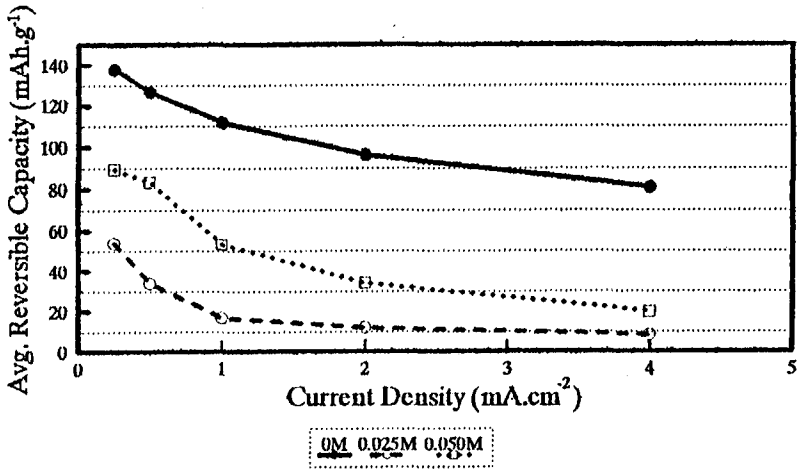

Fig. 9. REVERSIBLE CAPACITY AS A FUNCTION OF RATE OF PMAN CARBON IN 1M/$LiPF_6$/EC-DMC WITH Li_2Pc.

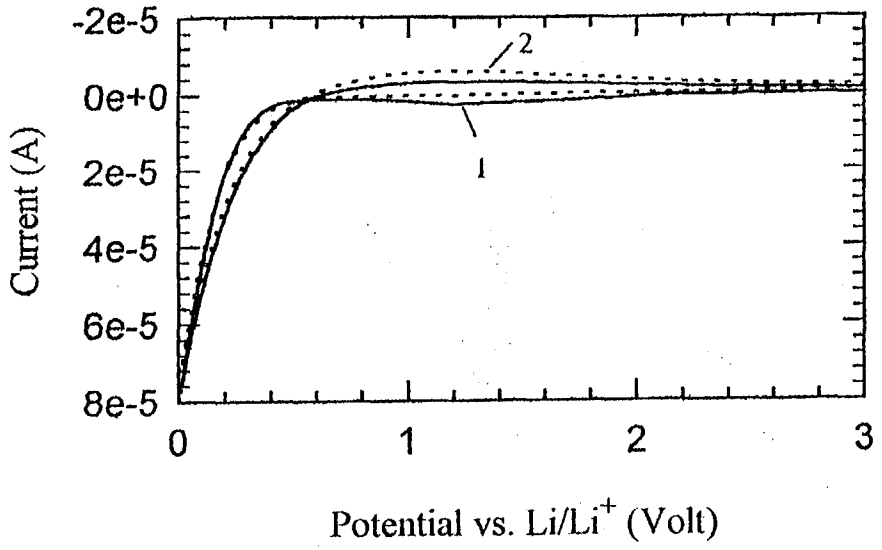

Fig. 10. CYCLIC VOLTAMMOGRAM OF GLASSY CARBON IN 1M/$LiPF_6$/EC-DMC WITH 0.025M Li_2Pc.

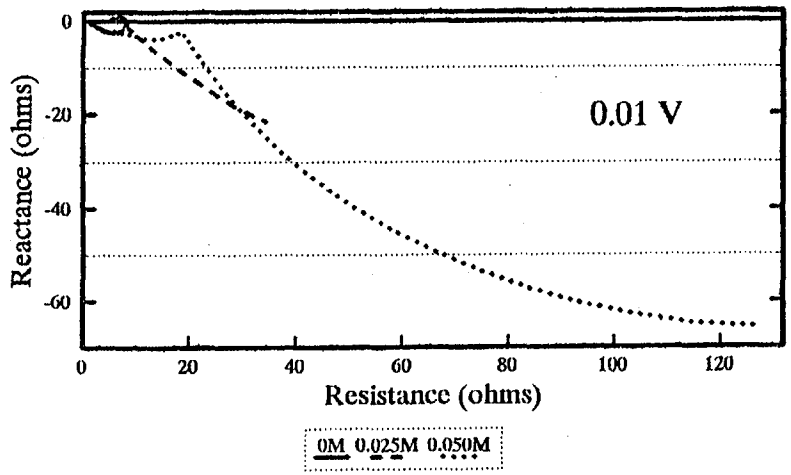

Fig. 11b. COMPLEX IMPEDANCE SPECTRA AT 0.01 V OF PMAN CARBON IN 1M $LiPF_6$/EC-DMC WITH Li_2Pc.

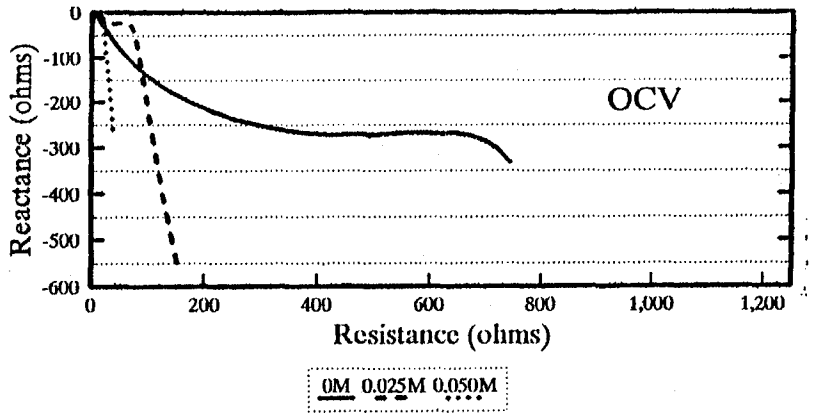

Fig. 11a. COMPLEX IMPEDANCE SPECTRA AT OCV OF PMAN CARBON IN 1M/$LiPF_6$/EC-DMC WITH Li_2Pc.