

STORAGE CHARACTERISTICS OF LITHIUM ION CELLS

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ABSTARCT

Prototype aerospace lithium ion cells have shown impressive performance in several categories, such as specific energy, energy density and low-temperature performance. However, their tolerance to extended storage periods, which is a critical requirement for near and outer planetary missions, is yet to be established. Storage tests have therefore been carried out under different conditions of storage, i.e., storage temperature, state of charge, storage time and storage mode, on various lithium ion chemistries under real-time as well as accelerated mode. These studies are further corroborated by three-electrode cell studies during high temperature storage, to segregate and understand the capacity loss sustained by the carbonaceous anodes and metal oxide cathodes.

INTRODUCTION

The constraints on the battery and volume in aerospace applications in general, and in NASA's planetary missions in particular, dictate the use of lithium ion rechargeable batteries in place of the conventional nickel systems, at least in applications requiring moderate cycle life. Prototype lithium ion cells, fabricated in U.S. under contact with the NASA/DoD consortium and being tested at JPL, have shown impressive performance characteristics. The specific energy and energy densities are impressive exceeding 110 Wh/kg and 200 Wh/l, respectively. The cycle life is excellent, with more than 80% of capacity retained after 500 deep discharge cycles. Further, one critical performance characteristic for the Mars missions is low temperature performance. The batteries need to perform well at -20°C at moderate discharge rates ($C/5$). Several modifications have been made to the lithium ion chemistry, mainly with respect to the electrolyte, both at JPL¹ and elsewhere²⁻⁵ in the last couple of years to achieve the desired low temperature performance commensurate with the needs of the upcoming Mars missions, i.e., Mars 2001 Lander and Mars 2003 Lander and Rover missions.

In addition to the specific energy and low temperature performance, another performance criterion, yet to be demonstrated with lithium ion batteries, is the tolerance to extended storage as in the pre-cruise and cruise periods (or calendar life). For the Mars programs, the cruise period is relatively short, about 12 months; a calendar life of two years is thus required for these missions. There are, however, more challenging

missions being planned by NASA to the Outer Planets, such as the Europa Orbiter, the Solar Probe and the Pluto Fly-by. The required calendar lives for these missions range from six to twelve years. Likewise, the Low Earth Orbit (LEO) and Geosynchronous Earth Orbit (GEO) satellites need a calendar life in excess of 5 years.

In order to assess the storageability of lithium ion cells, we have carried out both real-time and accelerated storage tests, under different storage conditions, i.e., storage temperature, state of charge and storage duration. In addition, we examined the storage behavior under three different modes of storage, i.e., under open circuit, at low rates of cycling and at a clamped voltage. The latter condition is relevant to the Mars 2001 Lander mission, whereas the former mode is relevant to the Mars 2003 Rover mission. To further corroborate the findings from these studies, we have also carried out high-temperature storage tests on three-electrode cells built in-house with different electrolytes.

EXPERIMENTAL

The prototype aerospace cells were fabricated in U.S. by three different manufacturers under contract with the NASA/DoD. The latter was recently initiated with the main intent of developing domestic capability to manufacture lithium-ion cells and batteries with smart chargers for the common needs of both NASA and Airforce.⁶ Under this program, various lithium ion cells, in both prismatic and cylindrical configuration, and with capacities ranging from 4 to 40 Ah, are being evaluated at JPL under generic performance conditions as well as those relevant to Mars 2001 Lander and 2003 Rover missions. The prototype ion cells contain proprietary components (mainly electrolytes and electrode materials) and designs to achieve the desired low temperature performance and/or cycle life. It was deemed essential to keep the manufacturers anonymous here to promote parallel development at each of the respective organizations.

The effects of electrolyte on the storage characteristics were studied in three-electrode, O-ring sealed, glass cells. These contained electrodes supplied by one of the manufacturers and lithium reference electrodes with two layers of porous polypropylene (Celgard 2500) separator. The electrolytes used for the three-electrode cell studies include: 1) ternary equi-proportion mixture of EC:DEC:DMC, a JPL formulation, 2) EC:EMC:DMC, a formulation which has emerged from the Army Research Laboratories and 3) a vendor-proprietary mixture with a relatively high EC content. The electrolytes were prepared from stock solutions containing LiPF_6 salt of desired concentration in carbonate-based solvents, purchased from Mitsubishi Chemicals (battery grade), with less than 50 ppm of water.

Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer and an M388 software were used with this

potentiostat for impedance measurements. Charge - discharge measurements and cycling were performed with an Arbin battery cycler. The cycling tests were done on at c.d.'s of $\sim 0.25 \text{ mA/cm}^2$ (C/10) and $\sim 0.5 \text{ mA/cm}^2$ (C/5) to the cut-off voltages of 4.1 V and 3.0 V for charge and discharge, respectively, with 15 min of interval between the charge/discharge steps. The charging process also included a tapered current or constant voltage phase for three hours.

RESULTS AND DISCUSSION

Storage characteristics of prototype sealed cells

Lithium ion cells sustain temporary capacity loss, commonly termed as self-discharge upon storage.⁷ In addition, the cells experience an irreversible or permanent capacity loss, which is of greater concern to aerospace applications. The temporary capacity loss for lithium ion cells is generally lower compared to that of the nickel systems. The permanent capacity loss, on the other hand, may be higher with certain electrolytes.

Eight week and 40 week real-time storage tests

Real-time storage tests lasting over eight weeks were carried out on three different chemistries at two different states of charge (50% and 100%) and two different temperatures (0 and 40°C). Fig.1 shows the effects of temperature and state of charge on the temporary capacity loss. As may be seen from the figure, the capacity retention is over 90 % (i.e., self-discharge is less than 5 %) in many of the cases. Further, the capacity retention is expectedly lower at higher storage temperature. The self-discharge rate, on the other hand, seems to be relatively independent of the state of charge. Comparing the three different sources, cells from vendor 3 have the best capacity retention, followed by vendor 1. Cells A and B from vendor 1 represent different cell sizes and the self-discharge rates are consistent between them. Cells from Vendor 2, however, show unusually poor capacity retention.

The permanent capacity loss, which is of greater concern to the Mars missions, under the above storage conditions is illustrated in Fig. 2. Once again the cells stored at high temperature have experienced higher permanent capacity loss. The capacity loss during storage at 0°C is relatively small, averaging around less than 2%, whereas at 40°C, its ranges from 2-16 %. These values may be significantly higher compared to commercial cells, which is presumably due to the increased reactivity of the low temperature electrolytes used in these prototype cells. The reactivity of the electrodes with the electrolytes has earlier been attributed to the capacity loss in the Li ion cells with LiMn_2O_4 cells.^{8,9} The state of charge seems to have some effect; lower state of charge marginally decreases the permanent capacity loss. Comparing the three different sources, the permanent capacity loss is the lowest for vendor 2, whereas vendor 1 and vendor 3

cells behaved similar. The permanent capacity fade may be attributed to an increased in the interfacial impedance during storage, as supported from the three-electrode cell studies described below. Similar real-time storage tests for an extended storage period of 40 weeks are currently underway.

Accelerated storage tests

The increase in the cell impedance or the decay in the cell capacity may be affected by various storage parameters, i.e., storage temperature, storage duration, state of charge and storage mode (open circuit, on buss or cycling at low rates). The latter is an important parameter for the missions; Mars 2001 Lander requires the batteries to be on the buss during cruise, whereas the Mars 2003 Rover requires the batteries to be off the buss, in the open circuit condition. In order to obtain a quantitative understanding of the effects of these parameters, we have carried out design experimentation studies with four parameters, i.e., temperature, storage period, state of charge, and storage mode, each of these parameters at three chosen levels (Table 1). Reducing this to a L^9 matrix, nine tests were thus run to quantitatively understand their effect on the capacity degradation during storage. Cells from two different sources were used for these studies. The storage periods chosen for these studies are rather short and the temperatures are correspondingly high, due to need to provide timely support to the Mars 2001 Lander project.

The temporary capacity loss (or the self-discharge) from these studies is illustrated in Figs 3A-C, as a function of different storage parameters. Expectedly, temperature has the strongest effect followed by storage time. The temporary capacity loss increases exponentially with the temperature and almost linearly with the storage time. There is, however, no clear trend with the state of charge.

The effect of the storage temperature on permanent capacity loss for two different systems is shown in Fig. 4A. As may be seen from the figure, the permanent capacity loss increases exponentially with the storage temperature in the cells from Vendor 1. The cells from Vendor 2, however, do not show such a clear trend. Also, the capacity loss is lower compared to the cells from Vendor 1. Fig. 4B shows the effect of storage time on the permanent capacity loss. The latter increases almost linearly initially and tends to level off in the later stages in the case of Vendor 1 cells. Once again, the capacity lost is significantly lower for the Vendor 4 cells. Fig. 4C shows the effect of state of charge, which is relatively small compared to temperature and storage time. Also, there is no clear trend between the state of charge and the capacity loss. With the mode of storage (Fig. 4D), on the other hand, there are some useful trends. The capacity loss is higher when the cell is in the open circuit condition, compared to the case where the cell is cycled at low rates (C/50) or connected to the buss. The latter is difficult to understand, since storage on buss results higher cell voltages compared to storage under open-circuit conditions, which, in turn, are expected to permit increased reactions between electrolyte and thus an increased capacity loss. These results are also consistent with the low temperature performance subsequent to storage. Cells stored at low temperatures, for

shorter period and in the voltage-clamp mode performed better in the post-storage low-temperature discharges.

Further analysis has been carried out on the above data to estimate the capacity loss over a 10-month period, which is the cruise period for the Mars missions. The capacity loss as a function of temperature has an exponential dependence as pointed out above, and may be represented by the equation : $y = 0.5524e^{0.0614x}$. Based on this, an Arrhenius-type plot was constructed (Fig.3E), from which the capacity loss at other temperatures was calculated. Likewise, the capacity loss versus storage time was fit to a first order kinetic equation, $y = 13.78 \log(t) + 0.569$, which was extrapolated to different storage times. The capacity loss thus calculated for a storage at 40°C over eight weeks is in agreement with the data from real-time storage tests. Similar extrapolations made for a 10-month storage at 10°C, which would be the storage temperature show a capacity loss of ~ 2%, which is in the acceptable range for the Mars missions.

Storage characteristics of three-electrode laboratory cells

In order to obtain a quantitative understating of the permanent capacity loss in terms of changes in the individual electrode capacities and their interfacial stabilities, cylindrical laboratory glass cells were built with three different electrolytes, i.e., 1) EC:DMC:DEC (1:1:1), 2) EC:DMC:EMC (1:1:1) and a manufacturer-proprietary formulation with a higher EC content. These cells were of ~350 mAh. The cells were subjected to two different high-temperature storage tests, at 60°C for one week and 55°C for ten days and the results from the former test are briefly presented here. The changes in the interfacial resistance were followed with electrochemical impedance (EIS) measurements.

Storage tests at 60°C

During storage in the open-circuit mode, the state of charge as well as the potentials of both the electrodes change as a result of self-discharge. Figs. 5A and 5B show the variation of cathode potential and cell voltage, and anode potential, respectively. As may be seen from the figures, the cathode potentials are high and flat in the high EC content electrolyte compared to the other two, suggesting a relatively low self-discharge. In the EC:DEC:DMC and EC:DMC:EMC ternary mixtures, on the other hand, the anode potentials are low, implying a less resistive surface film (SEI) on the graphite anode in these electrolytes, compared to the EC-rich formulation. The discharge curves before and after the storage in these solutions confirm that the overall self-discharge is the lowest in the high EC-based solutions (11%) compared to the EC:DMC:EMC (26%) and EC:DMC:DEC (29%) solutions (Fig. 6).

EIS Studies

Electrochemical impedance spectroscopy (EIS) measurements were made on the three-electrode cells in the above solutions before and after storage. A comparison of the impedance behavior of the anode and cathode with that of the cell (Fig. 7) indicates that the cell impedance is largely dictated by the cathode. The contribution from the anode appears only at high frequency, where the impedance at moderate to low frequencies is due to the cathode. A generalization, however, can't be made on this aspect, since it is specific to the materials and loading at each of the electrodes, and to the electrolyte.

Fig. 8 shows the increase in the cell impedance after one week storage at 60°C. The EIS measurements in Fig. 8 were recorded at identical states of charge, i.e., the cells were charged to their original (100%) state of charge subsequent to the self-discharge. For the sake of clarity, data for only two electrolytes are shown here and the data from the third electrolyte follow similar trend. As may be seen from the figure, the cell impedance grows during the high temperature storage. In addition to the overall cell impedance, individual electrode impedances were also recorded before and after storage. Figs. 9A and 9B illustrate the changes in the anode and cathode impedances before and after the high temperature storage. Also, similar measurements (not shown here) were made after the high temperature storage and before recharging the cell to verify the existence of the anode surface film (SEI) during high temperature exposure. The ac impedance data were analyzed using conventional equivalent circuit, consisting of a electrolyte resistance in series with a parallel combination of capacitance and resistance representing the surface film and another parallel combination of capacitance (double-layer) and resistance (charge transfer) to represent the faradaic process. In other words, the first relaxation loop is attributed to the charging of the surface layer and second (low frequency) loop to the charge transfer process.¹⁰

Analyses of the above data indicate some interesting observations. Firstly, the cathode spectra show two relaxation loops, suggesting the presence of a surface film on cathode, much like the SEI on the anode. The surface film on the cathode may be formed differently, compared to the carbon SEI, which forms mainly upon a reductive decomposition of the solvent species. The cathode surface film might be due to a chemical reaction between solution species and the interfacial intercalated lithium on the cathode. The latter is partly metallic and hence has a more reduction potential compared to ionic lithium in solution. Secondly, the SEI on the graphite is still intact and also grows further during high temperature storage, contrary to some reports in the literature that it would dissolve at high temperatures.¹¹ Further tests to confirm this are in progress. The changes in the resistance of the SEI on the MCMB anode and $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ cathode during the above high temperature storage are illustrated in Figs. 10 A and B, respectively. As may be seen from these figures, the SEI builds on both the anode and cathode. In other words, the interfacial impedance increases at both the anode and cathode, thus contributing to a build-up of cell impedance during storage, which in turn results in a permanent capacity loss upon storage.

ACKNOWLEDGMENTS

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Table 1: L^9 matrix for understanding the effects of temperature, time, state of charge and mode of storage on the storage characteristics.

Experiment #	Duration, weeks	Storage Temp	SOC	Storage Cond
1	2	25	50	Open Circuit
2	2	40	70	On Buss
3	2	55	100	Cycling
4	4	25	70	Cycling
5	4	40	100	Open Circuit
6	4	55	50	On Buss
7	6	25	100	On Buss
8	6	40	50	Cycling
9	6	55	70	Open Circuit

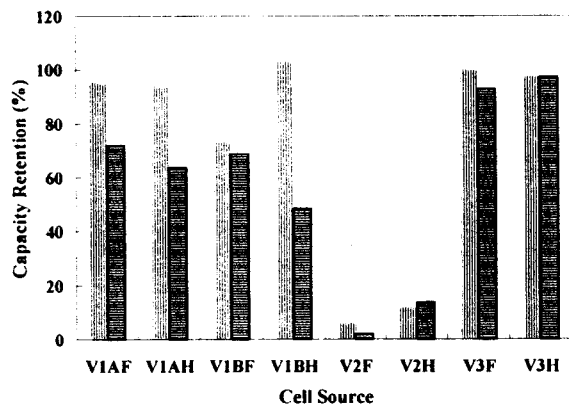


Fig. 1: Capacity retention of Li ion cells after storage at 0°C (vertical pattern) and 40° C (horizontal) at F) 100% and H) 50% SOC for eight weeks.

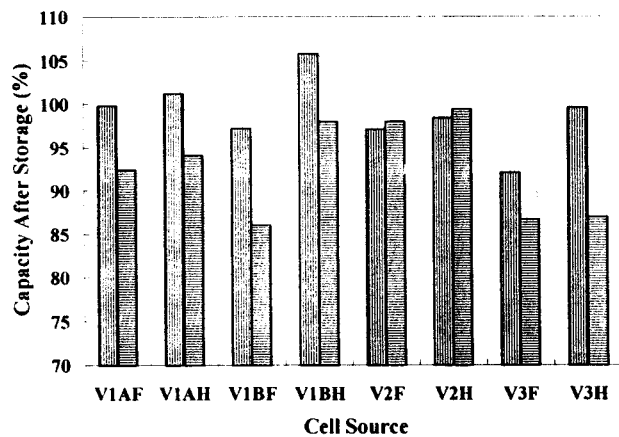


Fig. 2: Capacity after storage of Li ion cells subjected to storage at 0 (vertical pattern) and 40° C (horizontal) at F) 100% and H) 50% SOC for eight weeks.

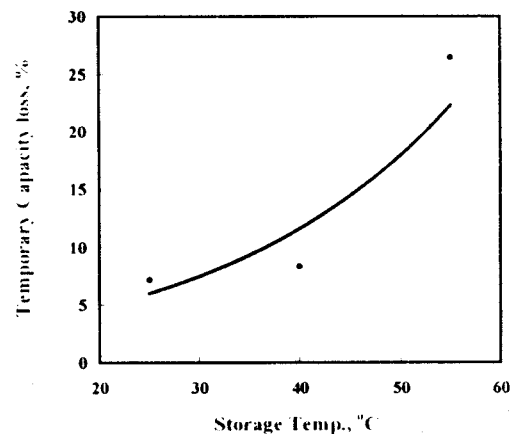


Fig. 3A: Variation of temporary capacity loss with temperature.

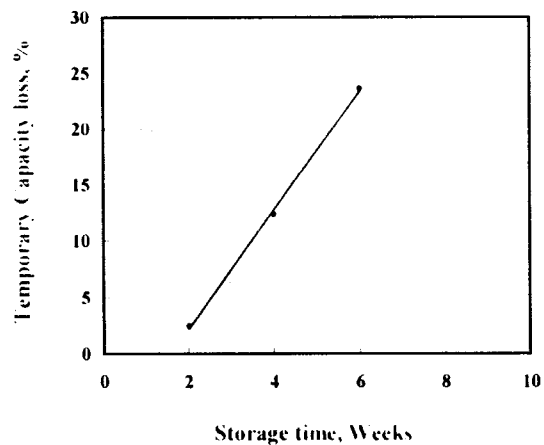


Fig. 3B: Variation of temporary capacity loss with storage time.

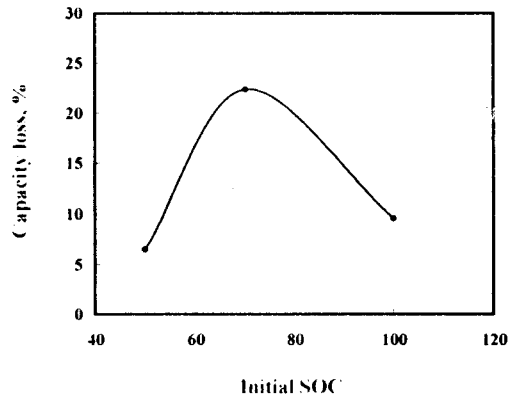


Fig. 3C: Variation of temporary capacity loss with the state of charge.

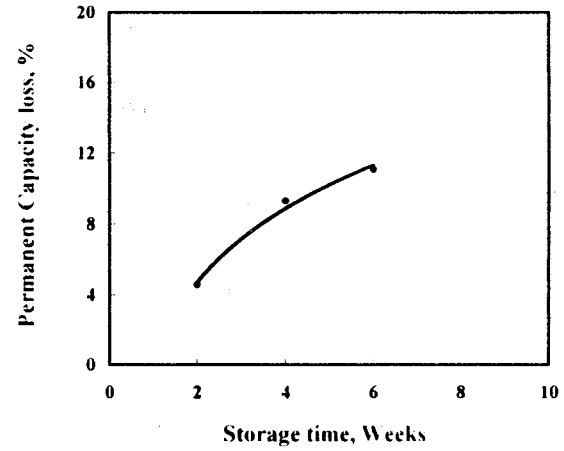


Fig. 4B: Variation of permanent capacity loss with time.

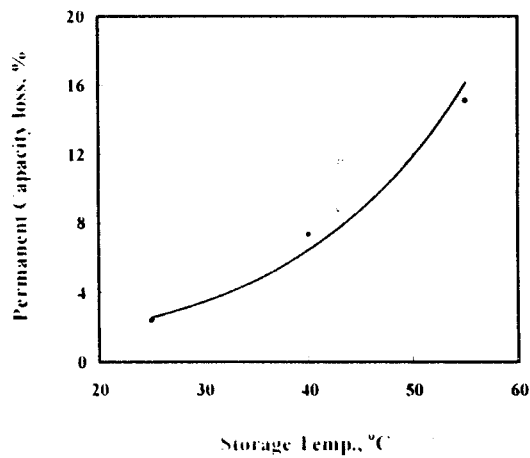


Fig. 4A: Variation of permanent capacity loss with storage temperature.

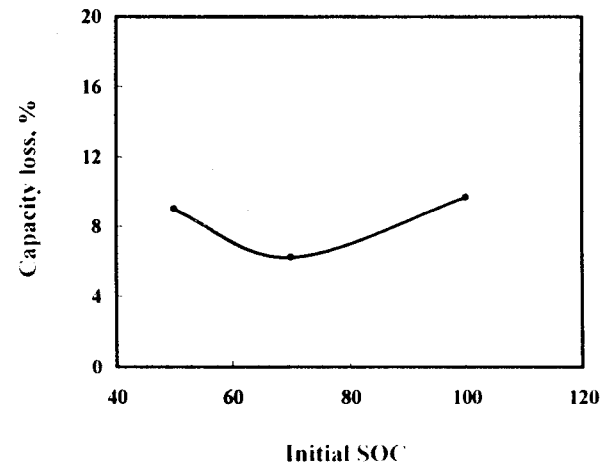


Fig. 4C: Variation of permanent capacity loss with SOC.

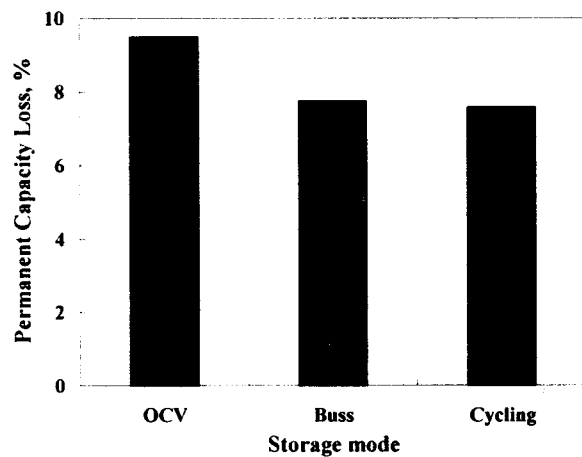


Fig. 4D : Variation of permanent capacity loss with mode of storage.

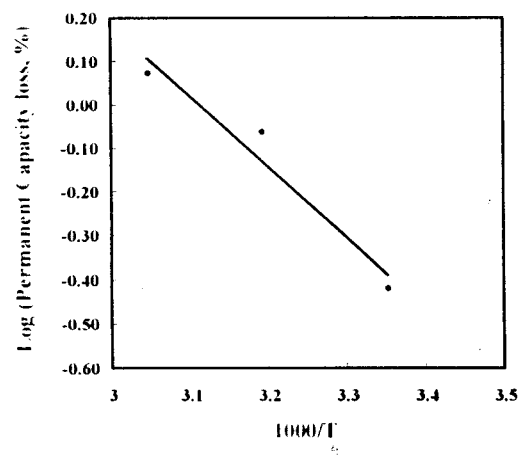


Fig. 4E: Arrhenius plot of permanent capacity loss.

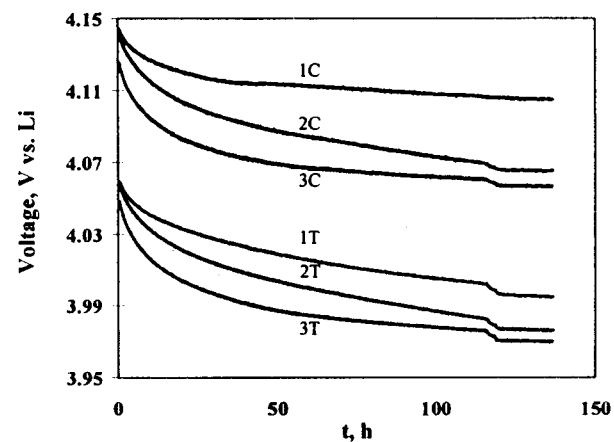


Fig. 5A: Variation of cell voltage (T) and cathode potential (C) in cells with electrolytes containing 1) High EC, 2) EC:DMC: EMC and 3) EC:DEC:DMC.

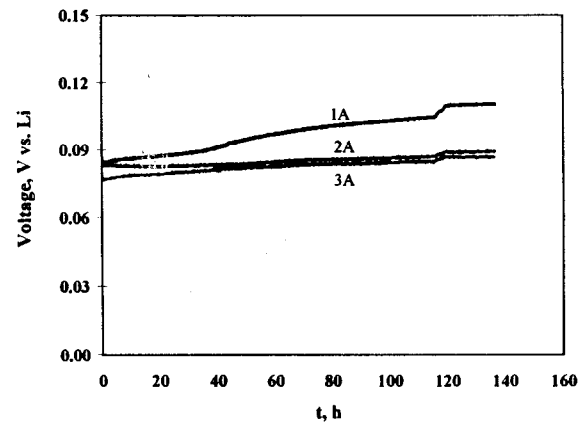


Fig. 5A : Variation of anode potential in cells with 1) High EC, 2) EC:DMC: EMC and 3) EC:DEC:DMC solvents.

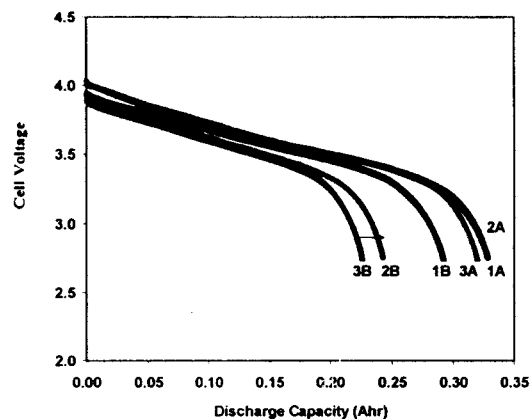


Fig. 6: Discharge curves of cells with 1) High EC, 2) EC:DMC: EMC and 3) EC:DEC:DMC solvents A) before and B) after storage.

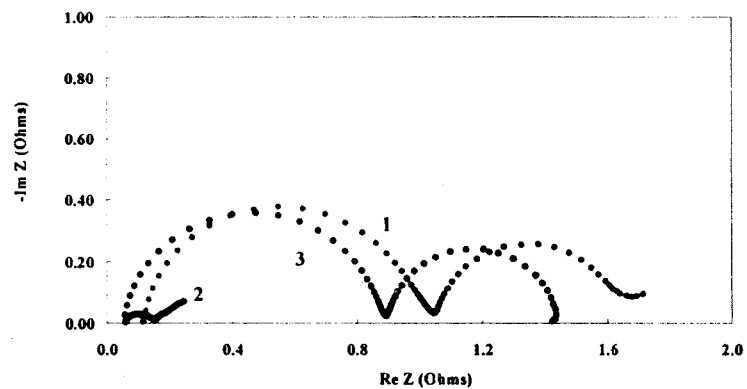


Fig. 7: Typical AC impedance of $LiNi_{1-x}Co_xO_2$ cathode, 2) graphite anode and 3) the complete cell.

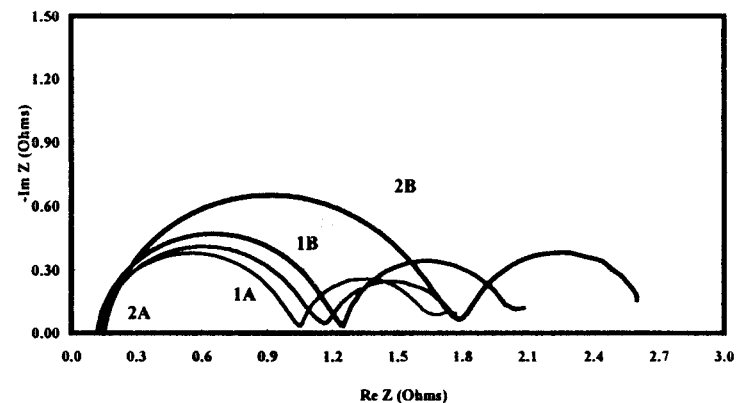


Fig. 8: EIS plots of Li-C/ $LiNi_{1-x}Co_xO_2$ cells in 1) high EC content and 2) EC:EMC:DMC solutions A) before and B) after storage at $60^\circ C$ for one week.

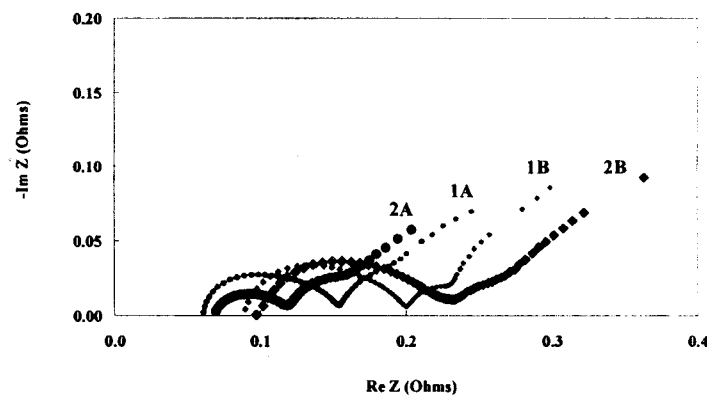


Fig. 9A: EIS plots of graphite anode in 1) high EC content and 2) EC:EMC:DMC solutions A) before and B) after storage at $60^\circ C$ for one week.

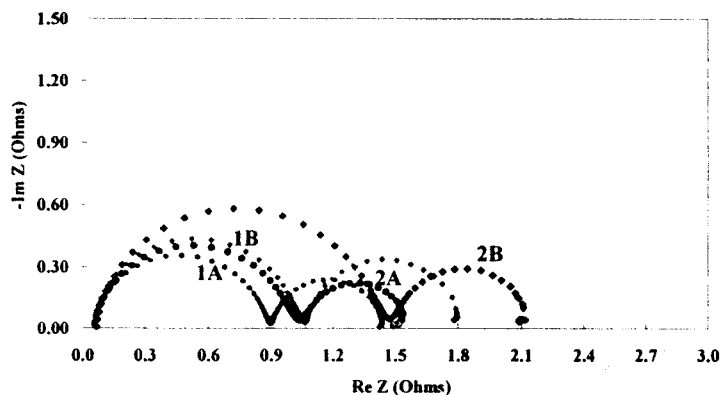


Fig. 9B : EIS plots of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ in 1) high EC content and 2) EC:EMC:DMC solutions A) before and B) after storage at 60°C for one week.

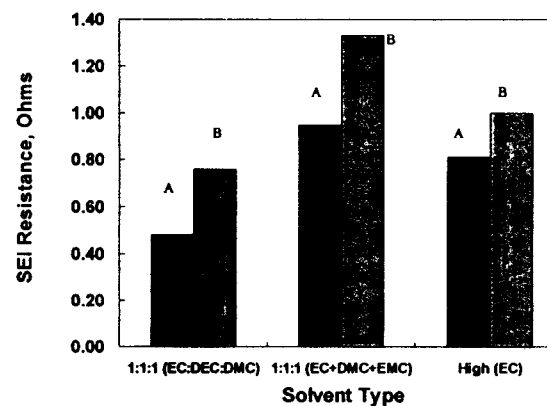


Fig. 10B: Variation of the SEI impedance on $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode in different electrolytes A) before and B) after storage at 60°C for one week.

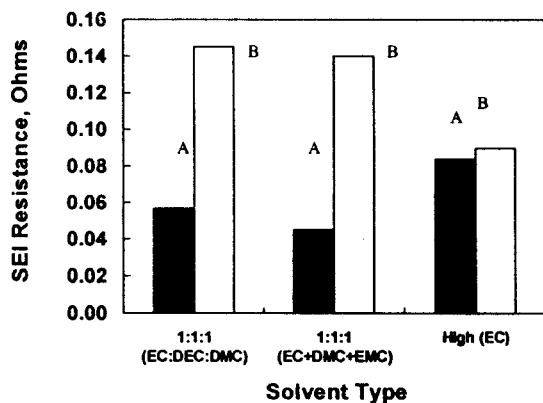


Fig.10A: Variation of the SEI impedance of graphite anode in different electrolytes A) before and B) after storage at 60°C for one week.