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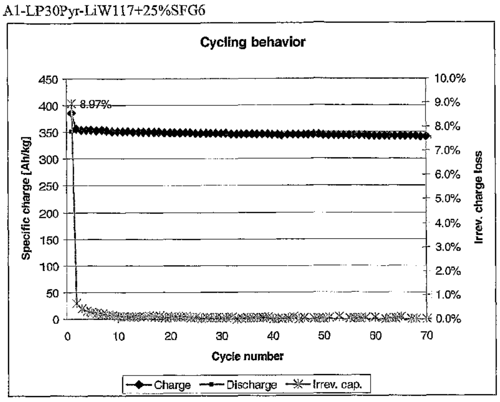
[Continued on next page]

(54) **Title:** A NON-AQUEOUS ELECTROLYTE FOR A RECHARGEABLE ELECTROCHEMICAL CELL AND NON-AQUEOUS ELECTROLYTE RECHARGEABLE ELECTROCHEMICAL CELL

A1-LP30Pyr-LiW117+25%SFG6



(57) **Abstract:** It is the aim of the present invention to retain the benefits of a lithium ion cell capable of operating at temperatures down to as low as about -40°C while minimizing the permanent cycle capacity loss under the circumstance of establishing the first cycle irreversible capacity loss at a tolerable level. This aim is achieved by a non-aqueous electrolyte for a rechargeable electrochemical cell, comprising a) a film forming organic component; b) an alkali metal salt; and c) as an additive a nitrogen-containing hetero-aromate and/or its derivatives and/or mixtures thereof; and/or d) as an additive a compound selected from a group containing aniline, pyrrole, 2-methyl-1-pyrroline, 1-methylpyrroline and 1-vinyle-2-pyrrolidine. Surprisingly, these additives have the properties of supporting the immediate generation of superior solid electrolyte interphases on the carbon/graphite anode in order to suppress its exfoliation when propylene carbonate is used as film forming organic compound. Depending on the choice for the anode material which significantly has an impact on the irreversible first cycle capacity loss, an electrochemical cell equipped with this electrolyte maintains its capacity over a comparably high number of charging/decharging cycles with capacity losses far below 0.5% per cycle.

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Description

A non-aqueous electrolyte for a rechargeable electrochemical cell and non-aqueous electrolyte rechargeable electrochemical cell

The invention relates to a non-aqueous electrolyte for a rechargeable electrochemical cell. Further, the invention relates to a non-aqueous electrolyte rechargeable electrochemical cell.

Alkali metal rechargeable cells such as the cell disclosed in the European patent application EP 1 215 746 typically comprise a carbonaceous anode electrode and a lithiated cathode electrode. Due to the high potential of the cathode material (up to 4.3 V vs. Li/Li for $Li_{1-x}CoO_2$) and the low potential of the carbonaceous anode material (0.01 V vs. Li/Li for graphite) in a fully charged lithium ion cell, the choice of the electrolyte solvent system is limited. Since carbonate solvents have high oxidative stability toward typically used lithiated cathode materials and good kinetic stability toward carbonaceous anode materials, they are generally used in lithium ion cell electrolytes. To achieve optimum cell performance (high rate capability and long cycle life), solvent systems containing a mixture of a cyclic carbonate (high dielectric constant solvent) and a linear carbonate (low viscosity solvent) are typically used in commercial secondary cells. Cells with carbonate based electrolytes are known to deliver more than 1,000 charge/discharge cycles at room temperature.

A typical electrolyte involves the provision of ethylene carbonate (EC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and diethyl carbonate (DEC) as the solvent system for the activating electrolyte. However, lithium ion cell design generally involves a trade off in one area for a necessary improvement in another, depending on the targeted cell application. The achievement of a lithium-ion cell capable of low temperature cycleability by use of the above quaternary solvent electrolyte, in place of a typically used binary solvent electrolyte (such as 1.0 M $LiPF_6$/EC:DMC = 30:70, v/v which freezes at -11°C), is obtained at the expense of increased first cycle irreversible capacity during the initial charging (approximately 65 mAh/g graphite for 1.0 M $LiPF_6$/EC:DMC:EMC:DEC = 45:22:24.8:8.2 vs. 35 mAh/g graphite for 1.0 M $LiPF_6$/EC:DMC = 30:70).

Due to the existence of this first cycle irreversible capacity, lithium ion cells are generally cathode limited. Since all of the lithium ions, which shuttle between the anode and the cathode during charging and discharging originally come from the lithiated cathode, the larger the first cycle irreversible capacity, the lower the cell capacity in subsequent cycles and the lower the cell efficiency. Thus, it is desirable to minimize or even eliminate the first cycle irreversible capacity in lithium ion cells while at the same time maintaining the low temperature cycling capability of such cells.

According to the disclosure in the above mentioned patent application , these objectives are achieved by providing an organic carbonate in the quaternary solvent electrolyte. Lithium ion cells activated with these electrolytes exhibit lower first cycle irreversible capacities relative to cells activated with the same quaternary solvent electrolyte devoid of the carbonate additive. As a result, cells including the carbonate additive presented higher subsequent cycling capacity than the control cells. The cycleability of the present invention cells at room temperature, as well as at low temperatures, i.e., down to about -40°C, is as good as cells activated with the quaternary electrolyte devoid of a carbonate additive.

Therefore, it is commonly known that when an electrical potential is initially applied to lithium ion cells constructed with a carbon anode in a discharged condition to charge the cell, some permanent capacity loss occurs due to the anode surface passivation film formation. This permanent capacity loss is called first cycle irreversible capacity. The film formation process, however, is highly dependent on the reactivity of the electrolyte components at the cell charging potentials. The electrochemical properties of the passivation film are also dependent on the chemical composition of the surface film.

The formation of a surface film is unavoidable for alkali metal systems, and in particular, lithium metal anodes, and lithium intercalated carbon anodes due to the relatively low potential and high reactivity of lithium toward organic electrolytes. The ideal surface film, known as the solid-electrolyte interphase (SEI), should be electrically insulating and ionically conducting. While most alkali metal, and in particular, lithium electrochemical systems meet the first requirement, the second requirement is difficult to achieve. The resistance of these films is not negligible, and as a result, impedance builds up inside the cell due to this surface layer formation which induces unacceptable polarization during the charge and discharge of the lithium ion cell. On the other hand, if the SEI film is electrically conductive, the electrolyte decomposition reaction on the anode surface does not stop due to the low potential of the lithiated carbon electrode.

Hence, the composition of the electrolyte has a significant influence on the discharge efficiency of alkali metal systems, and particularly both the first irreversible capacity loss and subsequent permanent capacity loss in secondary cells. For example, when 1.0 M $LiPF_6$/EC:DMC = 30:70 is used to activate a secondary cell, the first cycle irreversible capacity is approximately 35 mAh/g of graphite. However, under the same cycling conditions, the first cycle irreversible capacity is found to be approximately 65 mAh/g of graphite when 1.0 M $LiPF_6$/EC:DMC:EMC:DEC = 45:22:24.8:8.2 is used as the electrolyte. In contrast, lithium ion cells activated with the binary solvent electrolyte of ethylene carbonate and dimethyl carbonate cannot be cycled at temperatures less than about -11°C. The quaternary solvent electrolyte of EC, DMC, EMC and DEC, which enables lithium ion cells to cycle at much lower temperatures, is a compromise in terms of providing a wider temperature application with acceptable cycling efficiencies.

These objectives are achieved by adding a carbonate additive in the above described quaternary solvent electrolytes. In addition, this invention may be generalized to other nonaqueous organic electrolyte systems, such as binary solvent and ternary solvent systems, as well as the electrolyte systems containing solvents other than mixtures of linear or cyclic carbonates. For example, linear or cyclic ethers or esters may also be included as electrolyte components. Although the exact reason for the observed improvement is not clear, it is hypothesized that the carbonate additive competes with the existing electrolyte components to react on the carbon anode surface during initial lithiation to form a beneficial SEI film. The thusly formed SEI film is electrically more insulating than the film formed without the carbonate additive and, as a consequence, the lithiated carbon electrode is better protected from reactions with other electrolyte components. Therefore, lower first cycle irreversible capacity is obtained.

Unfortunately, even the cell comprising this type of improved electrolyte show a non-negligible permanent capacity loss which is distressing since these losses occur significantly in the subsequent cycles following the first irreversible cycle loss event.

Therefore, it is the aim of the present invention to retain the benefits of a lithium ion cell capable of operating at temperatures down to as low as about -40°C while minimizing the permanent cycle capacity loss under the circumstance to establish the first cycle irreversible capacity loss at a tolerable level.

This aim is achieved according to the present invention by a non-aqueous electrolyte for a rechargeable electrochemical cell, comprising

a) a film forming organic component;
b) an alkali metal salt; and
c) as additive a nitrogen-containing hetero-aromate and/or its derivatives and/or mixtures thereof.

Alternatively or additionally, this aim is achieved according to the present invention by a non-aqueous electrolyte for a rechargeable electrochemical cell, comprising

a) a film forming organic component;
b) an alkali metal salt; and
c) as additive a compound selected from a group containing aniline, pyrrole, 2-methyl-1-pyrroline, 1-methylpyrroline and 1-vinyle-2-pyrrolidine.

Surprisingly, these additives have the properties of supporting the immediate generation of superior solid electrolyte interphases on the carbon/graphite anode in order to suppress its exfoliation when propylene carbonate is used as film forming organic compound. Depending on the choice for the anode material which significantly has an impact on the irreversible first cycle capacity loss, an electrochemical cell equipped with this electrolyte maintains its capacity over a comparably high number of charging/decharging cycles with capacity losses far below 0.5% per cycle.

With respect to an advanced covering of the anode with the SEI, the film forming organic component may be selected from a group containing 1,2 dimethoxyethane, 2-methyl tetrahydrofuran, ethylene carbonate and propylene carbonate, methyl propionate and methyl lactate.

In order to design the desired broad range of operating temperatures what in detail implies to design a proper viscosity for enhanced conductivity, beside the film forming organic component an organic co-solvent is comprised selected from a group containing acyclic organic carbonates, such as dimethyl carbonate, ethyl-methyl carbonate, diethyl carbonate, or mixtures thereof.

Suitable alkali metal salts are selected from a group containing $LiPF_6$, $LiClO_4$, $LiAsF_6$, $LiBF_4$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiSbF_6$, $LiAlCl_4$, $LiGaCl_4$, $LiNO_3$, LiSCN, $LiO_3SCF_2CF_3$, $LiC_6F_5SO_3$, LiO_2CCF_3, $LiFSO_3$, $LiB(C_6H_5)_4$ and $LiCF_3SO_3$ or mixtures thereof. Suitable salt concentrations typically range between about 0.5 to 1.5 molar.

Suitable additives from the nitrogen-containing aromate type and/or its derivatives can be selected from a group containing pyridine, 2-picoline, 3-picoline, 4-picoline, 2-vinylpyridine, 4-vinylpyridine, and dimethyl-pyridine-amine (DMPA) and boran-pyridine-complex and, of course, mixtures thereof. Thereby, the amount of the additive may range between about 0.1 to 5 vol%.

Superior electrolyte composition may comprise ethylene carbonate and dimethyl carbonate in equi-molar or -volumic amounts, lithium-hexafluorophoshate in the range of 0.5 to 2 mol/l and 0.2 to 2.5 vol% 2-picoline, preferably 1 vol% 2-picoline.

Another superior electrolyte composition may comprise propylene carbonate, lithium-hexafluorophosphate in the range of 0.5 to 2 mol/l and 0.5 to 5 vol% pyridine, preferably 2 vol%. This electrolyte overcomes a preconception known in the art insofar as the prior art teaches that the use of propylene carbonate without an additional content of an acyclic organic carbonate inevitably leads to the exfolation of the graphite anode. This exclusion is completely diametrally opposed against the existing request that the use of propylene carbonate would be highly appreciated due to its superior temperature behaviour and to the desired use of un-expensive high-crystalline graphites, which are by a factor 6 to 10 cheaper than synthetic carbons.

Subsequently, an inventive non-aqueous electrolyte rechargeable electrochemical cell, such as an alkali metal ion accumulator, will comprise an anode, a cathode and an electrolyte,

a) said anode comprises a carbonaceous electrode;
b) said cathode comprises a metal oxide electrode containing alkali metal ions; and
c) said electrolyte having a composition according to any of the preceding claims 1 to 9.

Example of the invention are described in detail according to the drawings which show in a combined manner the cycling behaviour of distinct electrlyte composition comprising the additives according to the present invention. For a person skilled in the art it is apparent that various variations and modification are within the scope of the present invention.

Fig. 1 to 15 show the cycling behaviour for fifthteen different composition of the electrolyte and eventually different anode and cathode materials.

The table below gives an overview over the specific cell parameters of the 15 cell considered hereafter:

Cell name	**Anode**	**Cathode**	**Eletrolyte**	**Additive**
A1-LP30Pyr-LiW117+25%SFG6				
A2-LP30Pyr05-LiW117+5%KS6				
A6-LP30Pyr1-LiW1178%KS6				
C4-LP30Anilin1-LiW1178%KS6				
B3-LP302pic1-LiW1178%KS6				
A2-LP302pic1-LiW117+25SFG6				
A2-LP303pic1-LiW1178%KS6				
B2-LP304vp1-LiW1178%KS6				
B1-LP302vp1-LiW1178%KS6				
A2-LP302vp(2-Vinylpyridin)02-LiW1178%KS6				
C1-LP30pyrr02-LiW1178%KS6				
A4-LP302m1pyrr1-LiW1178%KS6				
A6-LP302m1pyrr3-LiW1178%KS6				
B3-LP301v2pyrrolidinon-LiW1178%				
A4-LP30DMPA(4-Dimethylaminopyridin)1-LiW1178%KS6				

The figure 1 to 15 show with respect to the abszissa the number of dicharge/charging cycles. The left ordinate gives the specific charge of the cell in Ah/kg and the graph for charge and dicharge cycles are the line having rhombus symbols and square symbols resp. The right ordinate gives the irreversible charge loss and the graph for this is the line having asteric symbols.

Without going to much into detail, all graphs show for the specific charge a relativ constant course in the region of about 350 Ah/kg what is extraordinary in comparison to the theroretical normative value of 372 Ah/kg for carbon. Additionally, all the curves for the irreversible loss show a course generally far below 1%. Some of the extraordinary results like shown in figures 1, 2, 7 and 8 indicates losses which are hardly to observe due to convergence of the graph with the 0%-line.

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Patent Claims

1. A non-aqueous electrolyte for a rechargeable electrochemical cell, comprising
   a) a film forming organic component;
   b) an alkali metal salt; and
   c) as additive a nitrogen-containing hetero-aromate and/or its derivatives and/or mixtures thereof.

2. A non-aqueous electrolyte for a rechargeable electrochemical cell, comprising
   a) a film forming organic component;
   b) an alkali metal salt; and
   c) an additive selected from a group containing aniline, pyrrole, 2-methyl-1-pyrroline, 1-methylpyrroline and 1-vinyle-2-pyrrolidinone.

3. The electrolyte according to claim 1 or 2, characterized in that the film forming organic component is one or more compound selected from a group containing 1,2 dimethoxyethane, 2-methyl tetrahydrofuran, ethylene carbonate and propylene carbonate, methyl propionate and methyl lactate.

4. The electrolyte according to any of the preceding claims, characterized in that beside the film forming organic component an organic co-solvent is comprised selected from a group containing acyclic

organic carbonates, such as dimethyl carbonate, ethyl-methyl carbonate, diethyl carbonate, or mixtures thereof.

5. The electrolyte according to any of the preceding claims, characterized in that the alkali metal salt is selected from a group containing lithium-hexafluorophosphate ($LiPF_6$), lithium-chlorate ($LiClO_4$), lithium-hexafluoroarsenate ($LiAsF_6$), lithium-tetrafluoroborate ($LiBF_4$), lithium-trifluorocarbonsulfide ($LiCF_3SO_3$) and lithium-trifluorosulfitecyanate ($LiN(CF_3SO_2)_2$) or mixtures thereof.

6. The electrolyte according to any of the preceding claims, characterized in that the nitrogen-containing aromate and/or its derivatives are selected from a group containing pyridine, 2-picoline, 3-picoline, 4-picoline, 2-vinylpyridine, 4-vinylpyridine, and dimethyl-pyridine-amine (DMPA) and boran-pyridine-complex or mixtures thereof.

7. The electrolyte according to any of the preceding claims, characterized in that the amount of the additive range from 0.1 to 5 vol%.

8. The electrolyte according to any of the preceding claims, characterized in that comprised are: ethylene carbonate and dimethyl carbonate in substantially equi-molar or substantially equi-voluminous amounts, lithium-hexafluorophoshate in the range of 0.5 to 2 mol/l and 0.2 to 2.5 vol% 2-picoline, preferably 1 vol% 2-picoline.

9. The electrolyte according to any of the preceding claims 1 to 7, characterized in that

comprised are: propylene carbonate, lithium-hexafluorophosphate in the range of 0.5 to 2 mol/l and 0.5 to 5 vol% pyridine, preferably 2 vol%.

10. A non-aqueous electrolyte rechargeable electrochemical cell, such as an alkali metal ion accumulator, comprising an anode, a cathode and an electrolyte,

a) said anode comprises a carbonaceous electrode;
b) said cathode comprises a metal oxide electrode containing alkali metal ions;
c) said electrolyte having a composition according to any of the preceding claims 1 to 9.

A1-LP30Pyr-LiW117+25%SFG6

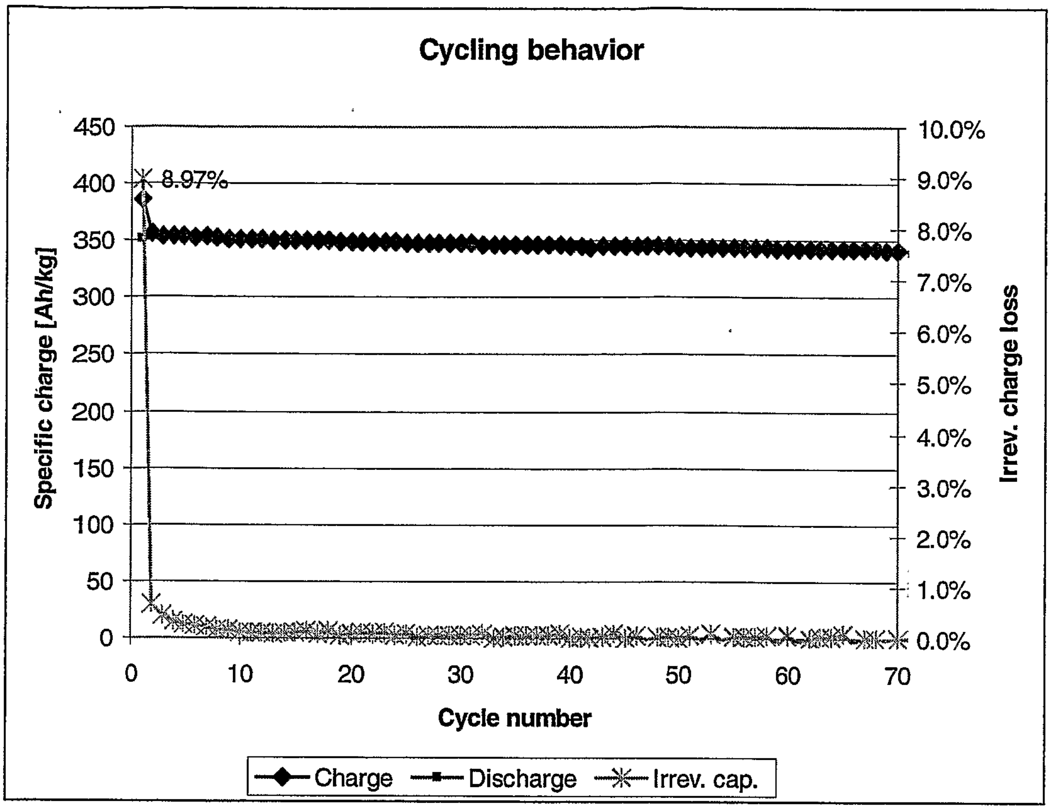

Fig. 1

A2-LP30Pyr05-LiW117+5%KS6

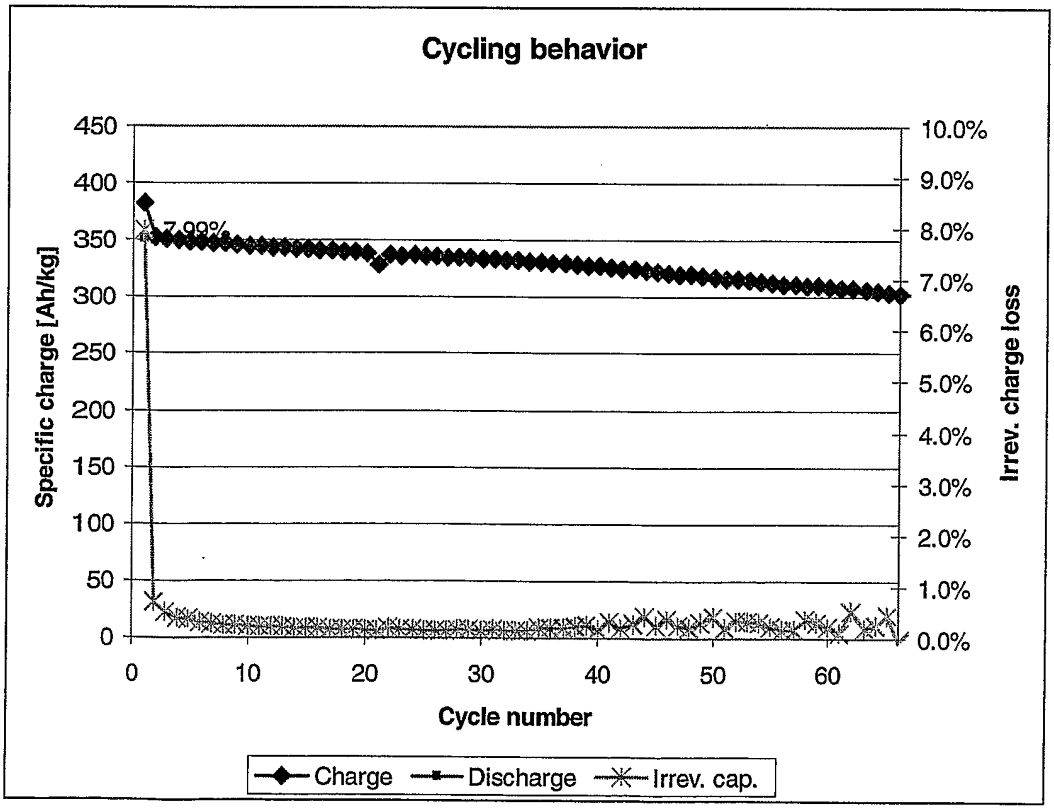

Fig. 2

A6-LP30Pyr1-LiW11 78%KS6

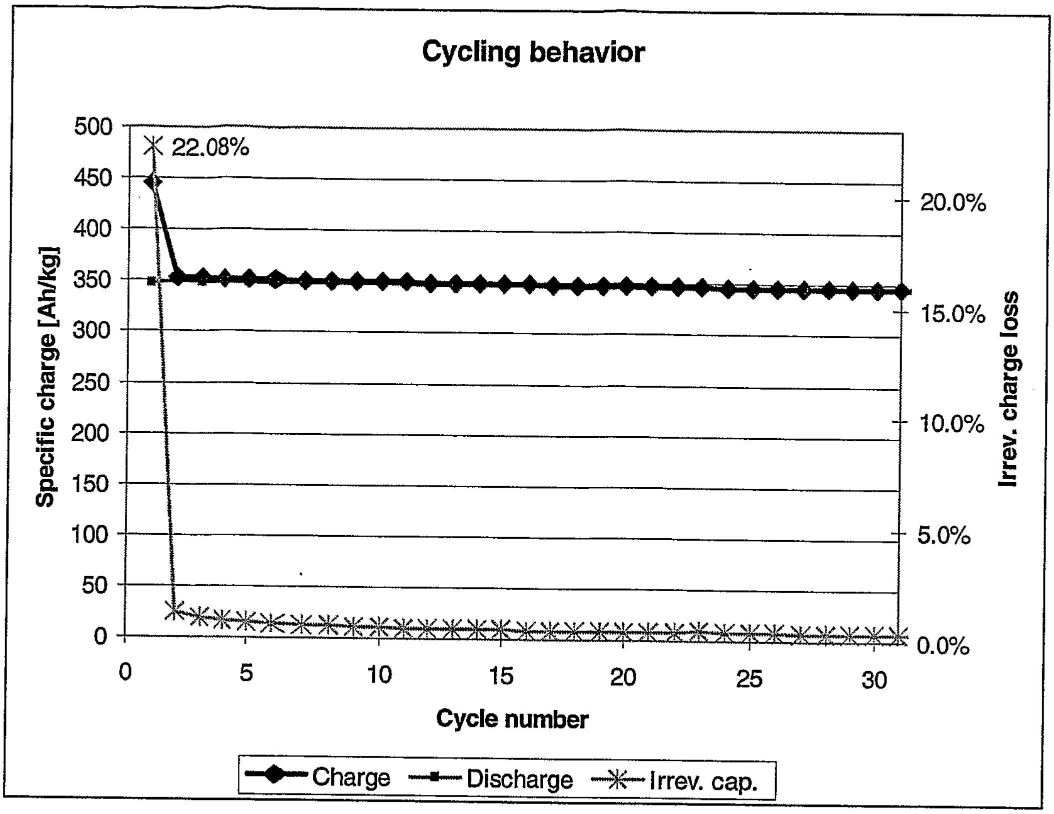

Fig. 3

C4-LP30Anilin1-LiW1 178%KS6

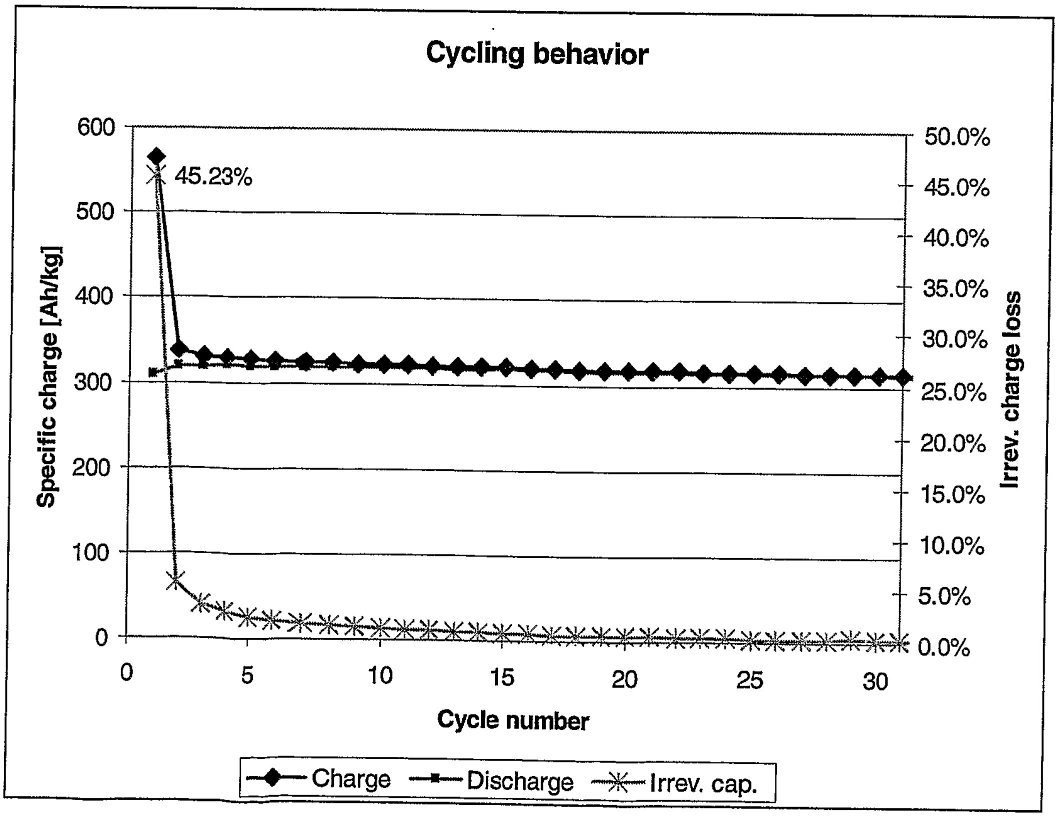

Fig. 4

B3-LP302pic1-LiW1178%KS6

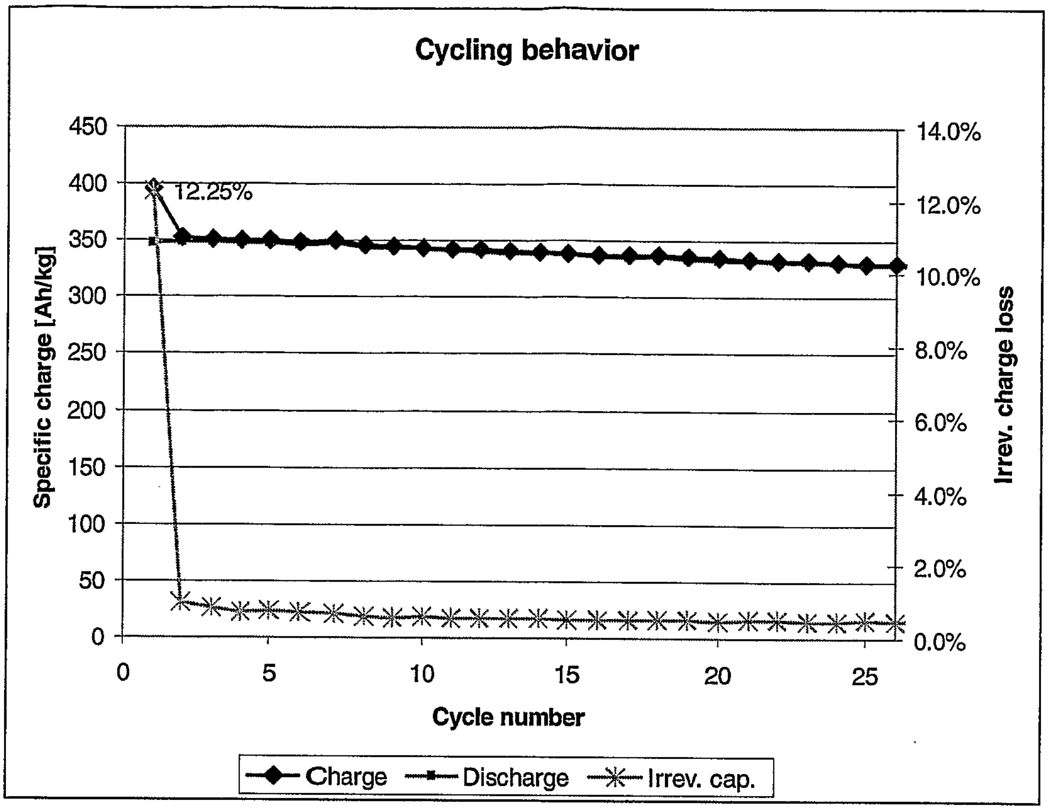

Fig. 5

A2-LP302pic1-LiW117+25SFG6

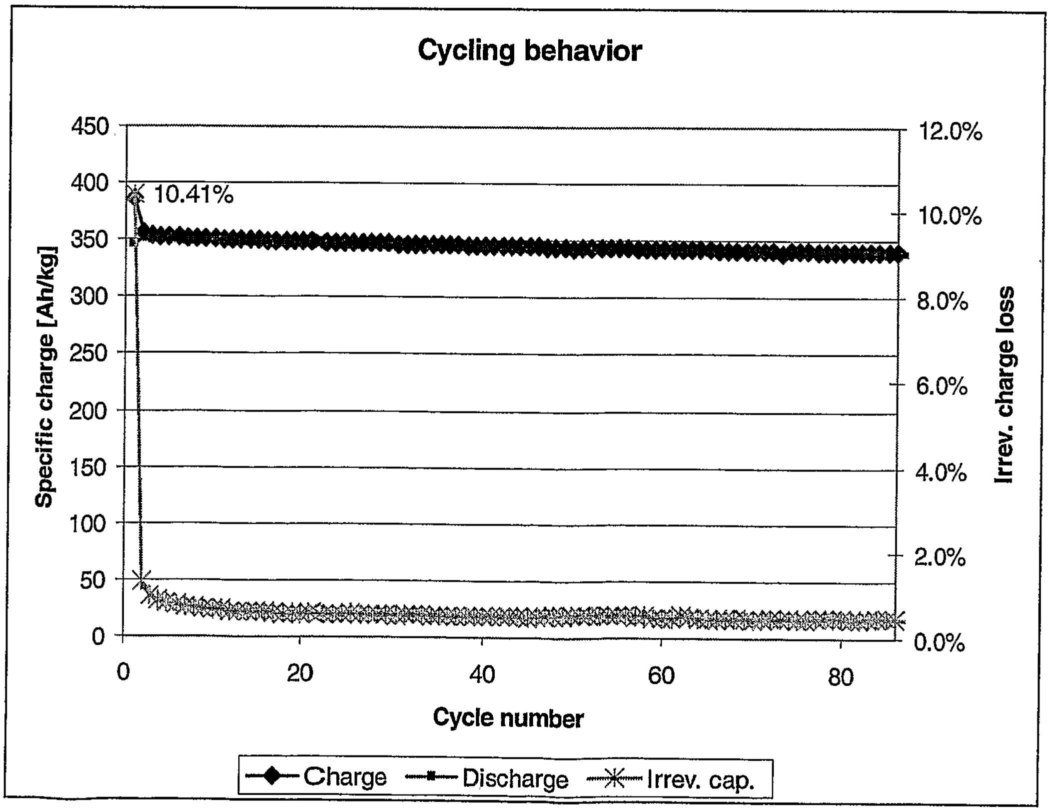

Fig. 6

A2-LP303pic1-LiW1178%KS6

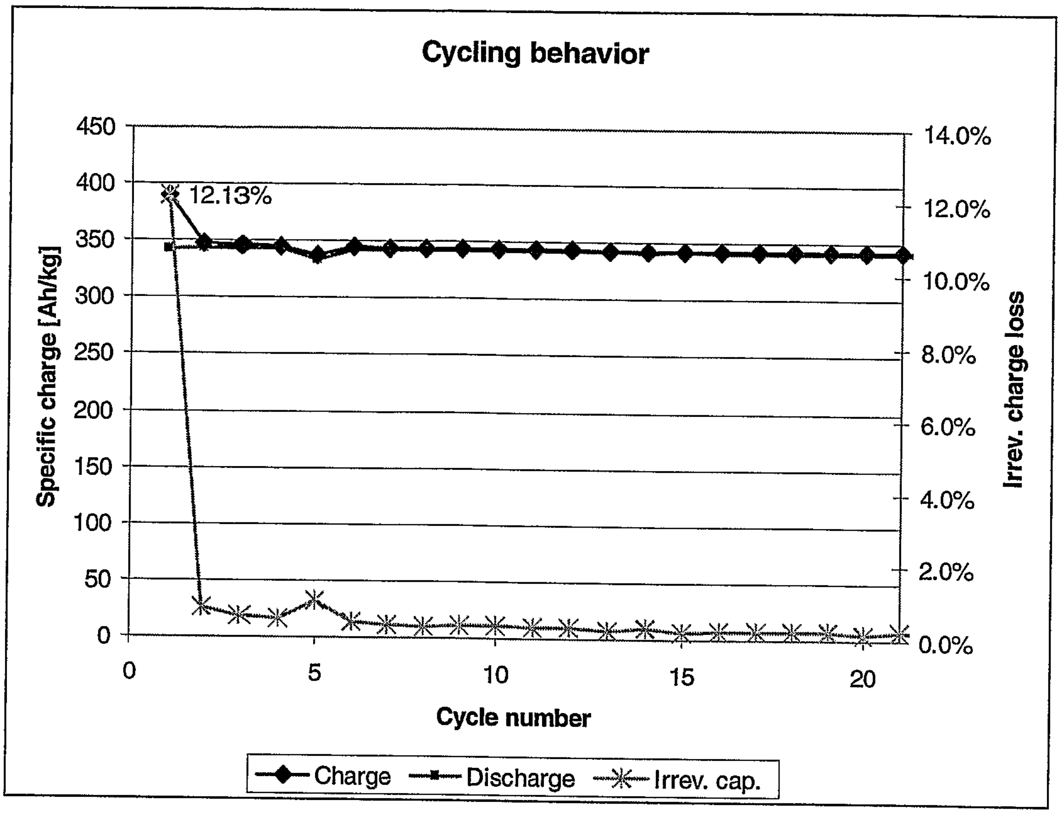

Fig. 7

B2-LP304vp1-LiW1178%KS6

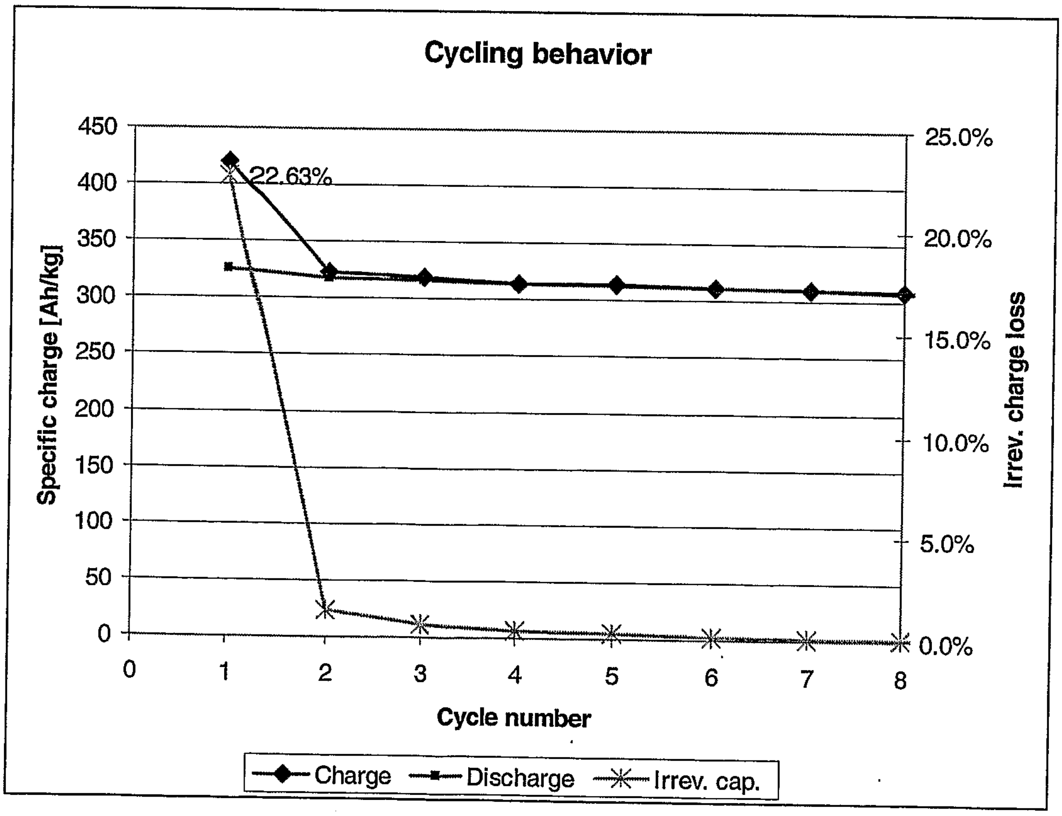

Fig. 8

B1-LP302vp1-LiW1178%KS6

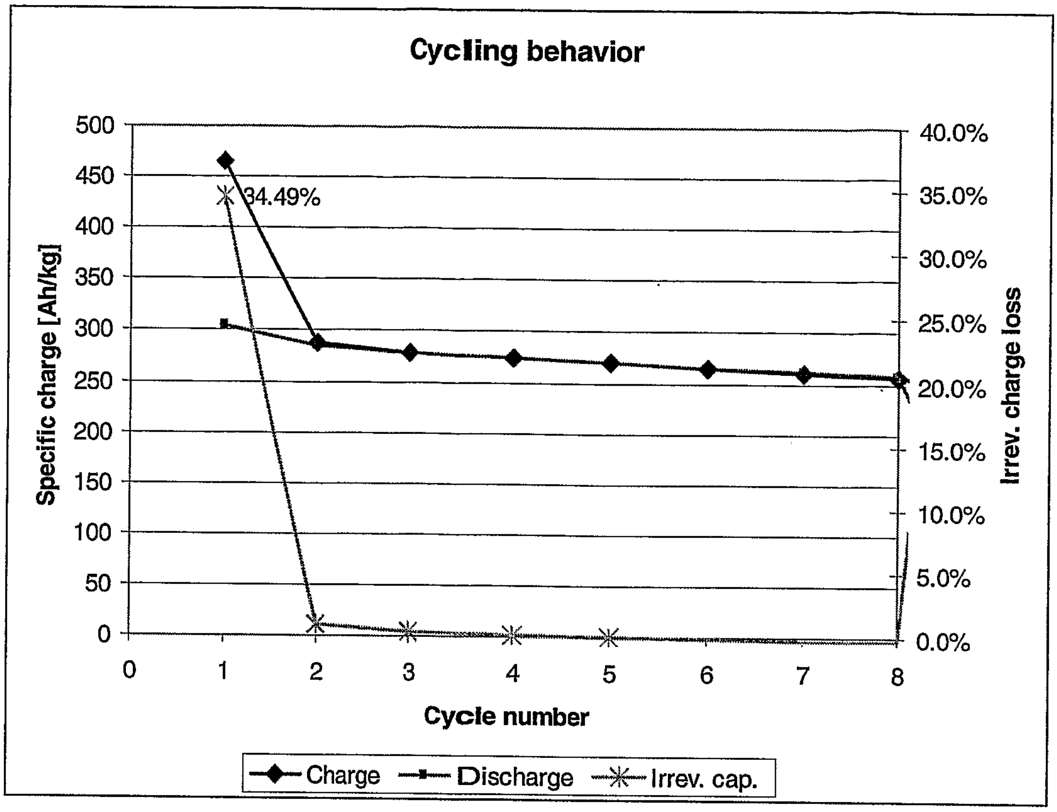

Fig. 9

A2-LP302vp(2-Vinylpyridin)02-LiW1178%KS6

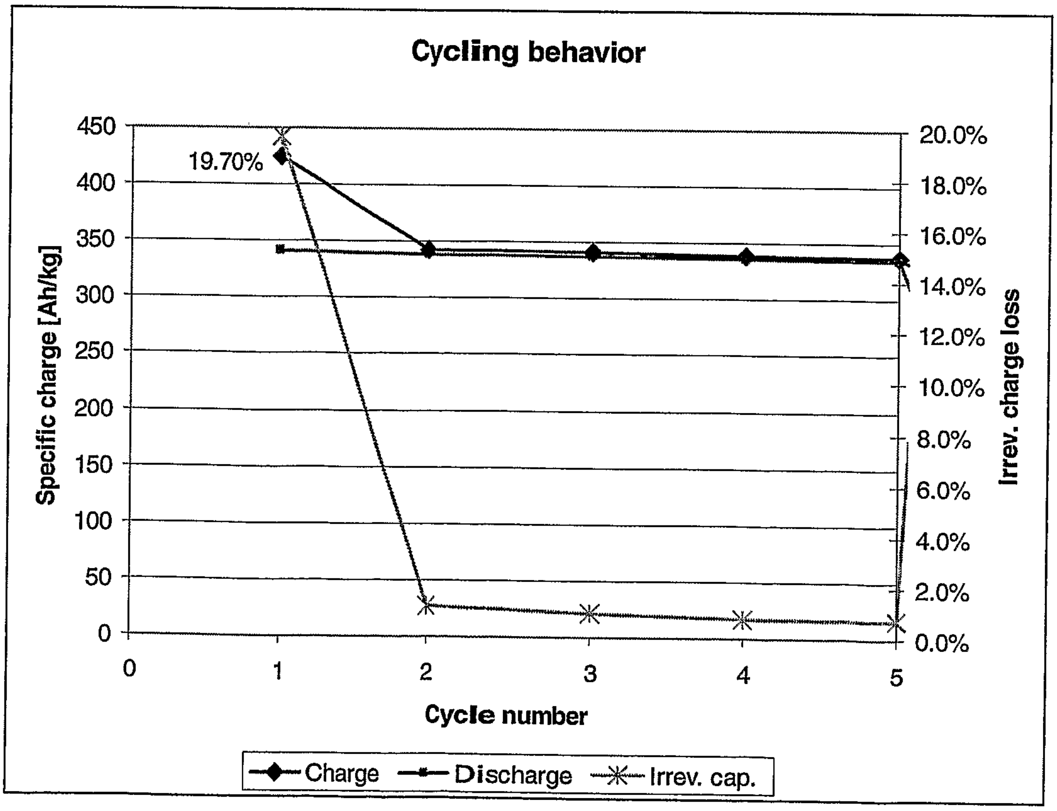

Fig. 10

C1-LP30pyrr02-LiW1178%KS6

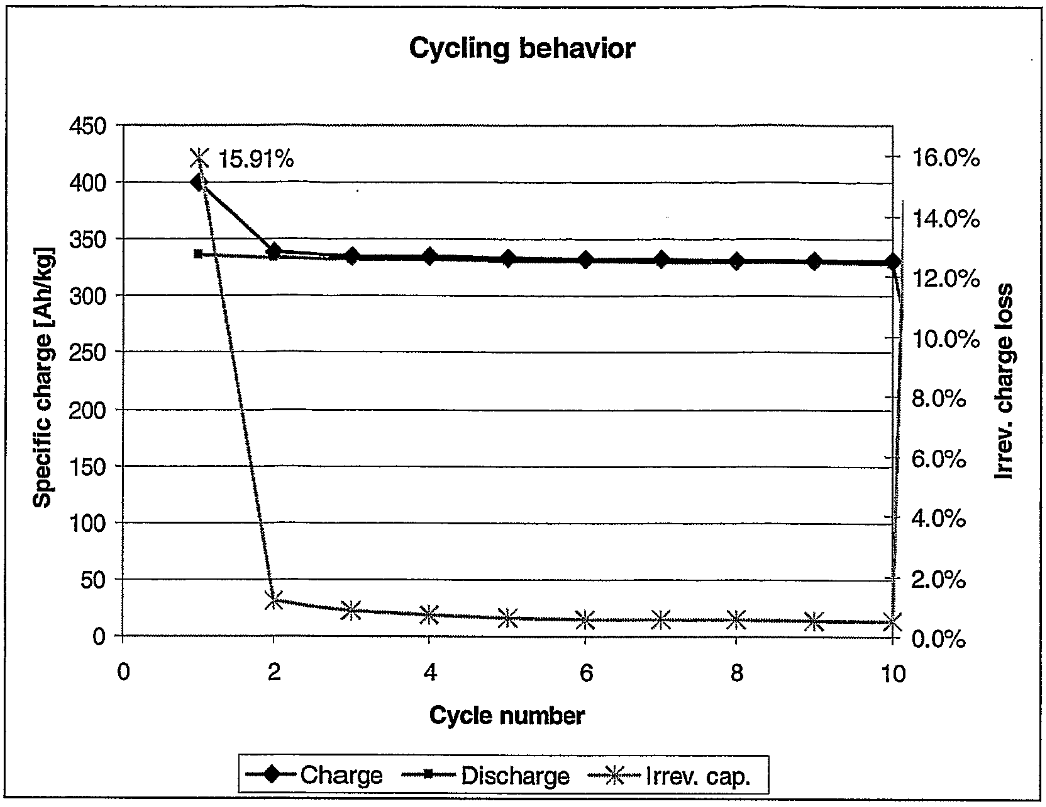

Fig. 11

A4-LP302m1pyrr1-LiW1178%KS6

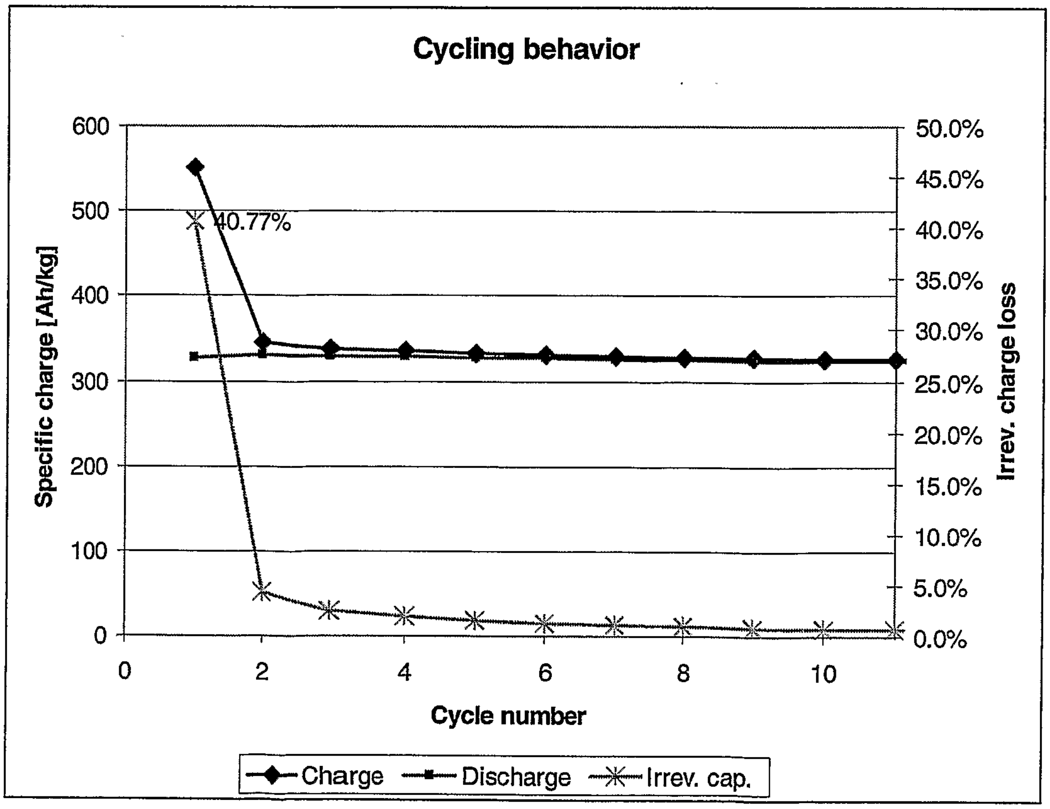

Fig. 12

A6-LP302m1pyrr3-LiW1178%KS6

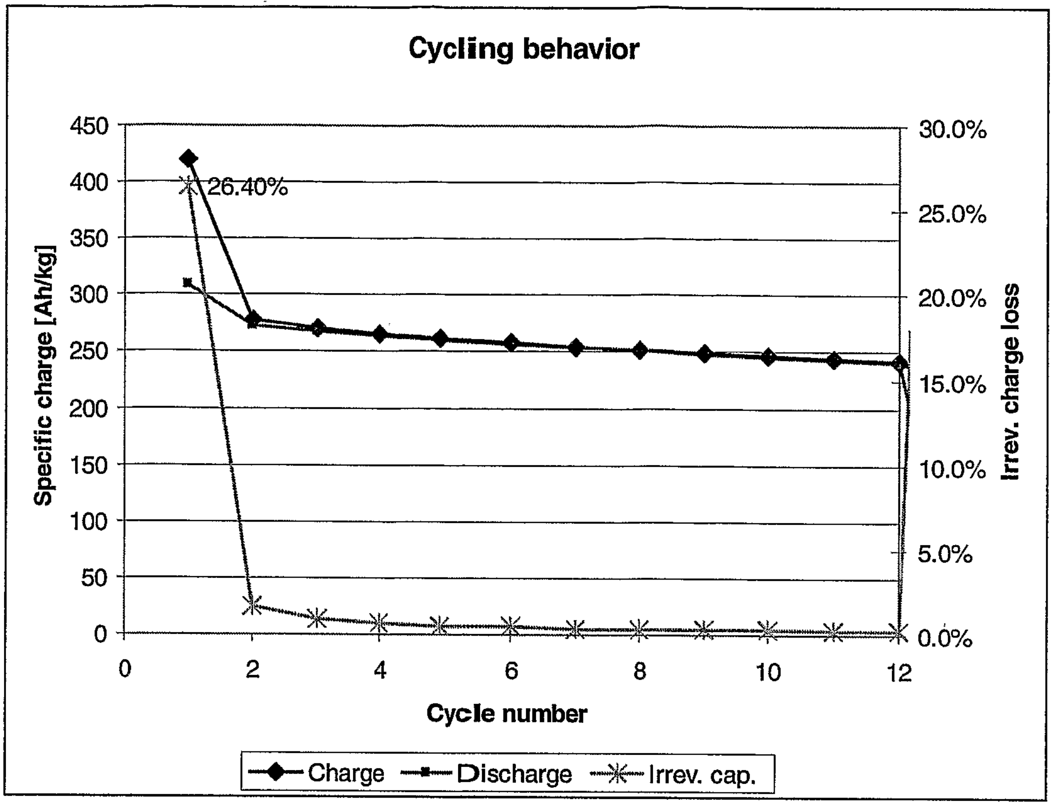

Fig. 13

B3-LP301v2pyrrolidinon-LiW1178%

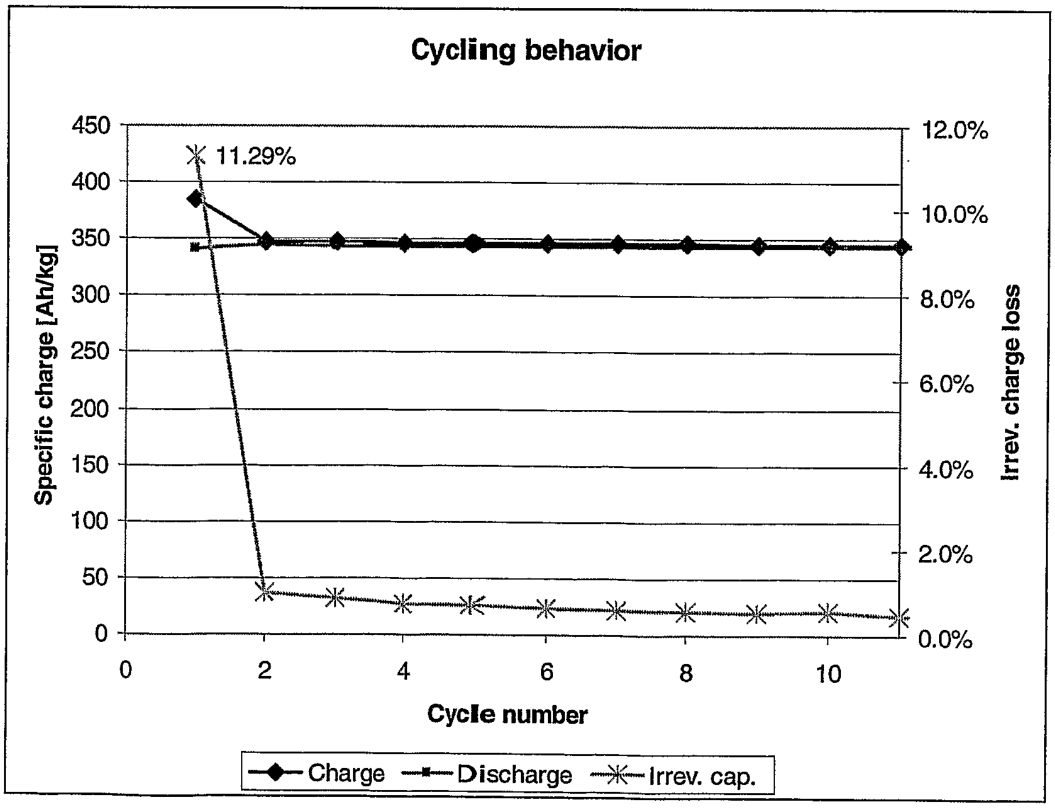

Fig. 14

A4-LP30DMPA(4-Dimethylaminopyridin)1-LiW1178%KS6

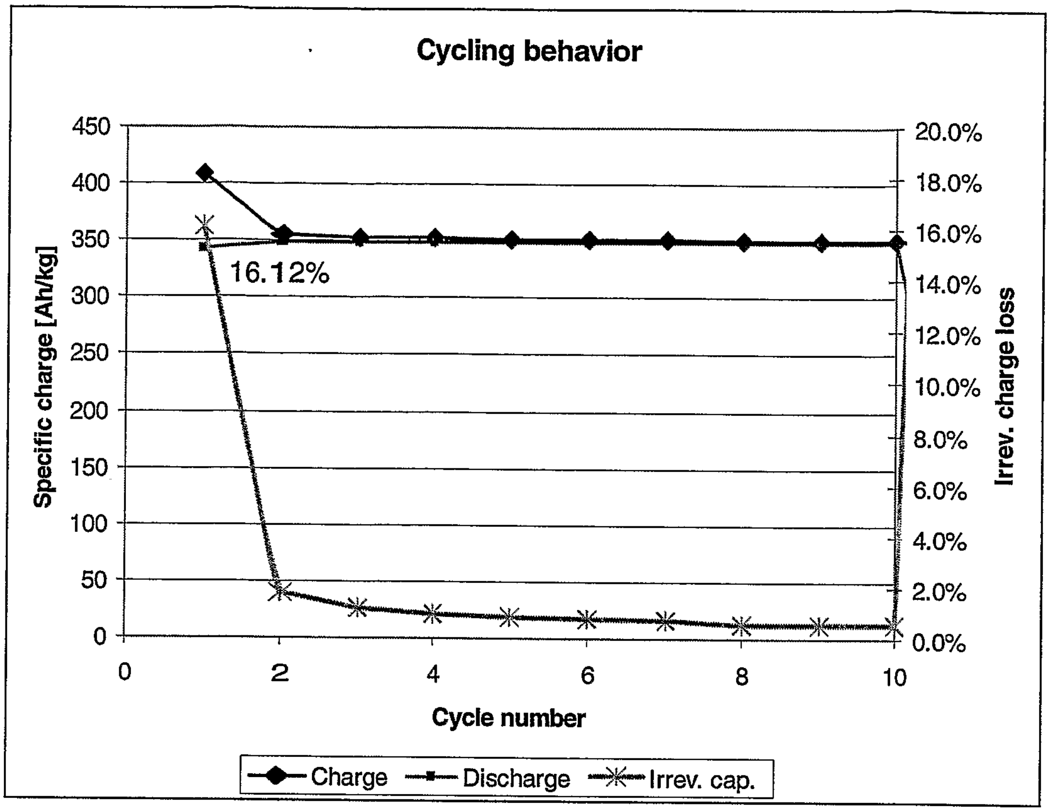

Fig. 15

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/014405

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 785 586 A (FUJI PHOTO FILM CO., LTD) 23 July 1997 (1997-07-23) * see p.4, 1.8 - 45, p.7, 1. 45 - 55, claims * the whole document	1-10
X	YOSHIHARU MATSUDA ET AL: "ORGANIC ADDITIVES FOR THE ELECTROLYTES OF RECHARGEABLE LITHIUM BATTERIES" 16 May 1989 (1989-05-16), JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, PAGE(S) 579-583 , XP000235220 ISSN: 0378-7753 * see p. 580, first par. * the whole document	1-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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International Application No
PCT/EP2004/014405

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 400 (E-569), 26 December 1987 (1987-12-26) & JP 62 160671 A (TOSHIBA CORP), 16 July 1987 (1987-07-16) abstract -----	1-10
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