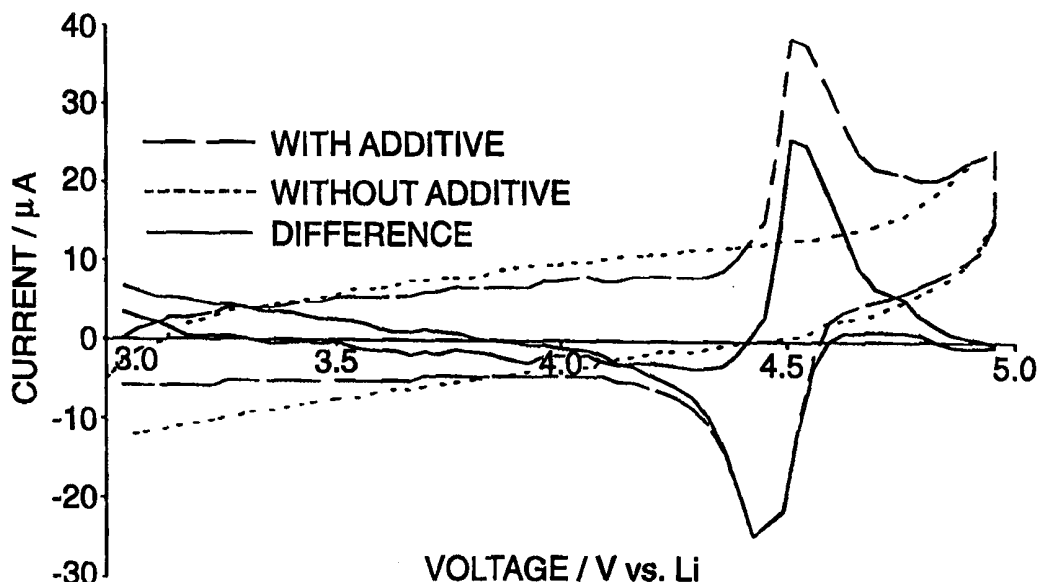




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: ELECTROLYTE FOR A RECHARGEABLE CELL



(57) Abstract

An electrolyte for use in a rechargeable cell whose charging voltage exceed 3.8 V includes a redox chemical comprising substituted aromatic molecules in which  $\alpha$  hydrogens are either absent, or are sterically stabilised against loss from the ionised form of the molecule. Such a chemical can act as a redox shuttle during overcharge, suppressing damage to the cell and preventing the deposition of metallic lithium during overcharge of a lithium ion cell, but does not affect normal operation of the cell either during charge or discharge. One such molecule is hexaethylbenzene.

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Electrolyte for a Rechargeable Cell

This invention relates to an electrolyte for a rechargeable cell, particularly but not exclusively a lithium cell or a lithium ion cell.

Rechargeable cells are known which incorporate an organic electrolyte with a lithium salt such as lithium hexafluorophosphate, a cathode of an insertion material such as titanium disulphide or lithium cobalt oxide into which lithium ions can be inserted, and an anode either of metallic lithium or a lithium alloy ('a lithium cell') or of a different insertion material ('a lithium ion cell') such as graphite. If such a cell is overcharged it may be degraded; this may result from oxidation of the organic solvent, or changes to the electrodes such as deposition of metallic lithium in a lithium ion cell. Overcharging may be prevented by monitoring the voltage of each cell in a battery and regulating it to remain below the voltage threshold at which degradation may occur.

A complementary or alternative approach is to incorporate a redox chemical into the electrolyte which is oxidised at a voltage above the normal cell voltage but below the voltage at which degradation occurs. For example US patent application 744 344 (W.K. Behl) refers to the use of lithium iodide (which is oxidised at about 2.8 V), and describes the use of lithium bromide (which is oxidised at about 3.5 V relative to lithium) as organic electrolyte additives to provide overcharge protection; EP 0 319 182 B (EIC Labs/Abraham et al) describes the use of metallocenes for this purpose, which have redox potentials relative to lithium in the range about 1.7 to 3.7 volts, such as ferrocene for which the redox potential is 3.05 to 3.38 V. However these redox

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chemicals are not suitable for use in cells where the normal charging cell voltage is above 3.8 volts.

According to the present invention there is provided  
5 an electrolyte for use in a rechargeable cell whose voltage exceeds 3.8 volts during charging, the electrolyte including a redox chemical comprising substituted aromatic molecules in which  $\alpha$  protons are either absent, or are stabilised by molecular geometry  
10 against loss from the ionised form of the molecule.

The term  $\alpha$  protons refers to protons attached to carbon atoms next to an aromatic ring. For example the aromatic molecules may be a substituted benzene of the  
15 general formula  $C_6R^1R^2R^3R^4R^5R^6$  in which:

- a)  $R^1$  to  $R^6$  are selected from trihalomethyl groups,  $C_2$  to  $C_{10}$  alkyl groups, or halogen-substituted  $C_2$  to  $C_{10}$  alkyl groups; or  
20  
b)  $R^1$  to  $R^5$  are as specified in (a), and  $R^6$  is H or a halogen.

In a preferred embodiment  $R^1$  to  $R^6$  are all  $C_2$  to  $C_5$   
25 alkyl groups, preferably ethyl groups.

The voltage at which such redox chemicals undergo oxidation varies with the nature of the substituents, but can have values between 3.8 and 5.0 volts relative to  
30  $Li/Li^+$ . The oxidised form, which is a cation, must be sufficiently stable that it can diffuse through the electrolyte to the other electrode where it is reduced

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back to its original, unionised, form before it undergoes any competing reactions.

The electrolyte will comprise other ingredients, in particular a salt, and an organic liquid or a polymer. For example it might comprise a solution of lithium hexafluorophosphate (1 molar) in a solvent comprising a mixture of organic carbonates such as ethylene carbonate, propylene carbonate, diethylcarbonate and/or dimethyl-  
10 carbonate. Alternatively it might comprise a polymer consisting principally of vinylidene fluoride, with a plasticizer such as propylene carbonate and a salt such as lithium perchlorate, which form a gel-like solid electrolyte. In either case the redox chemical must be  
15 sufficiently soluble in the other organic ingredients, and it must be able to diffuse through the thickness of the electrolyte.

The invention also provides a rechargeable cell including an electrolyte as specified above. In such a cell the active cathode material is typically  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ , or  $\text{LiMn}_2\text{O}_4$ , which operate at least partly in the range above 4.0 V, or mixtures of such oxides, or mixed oxides. Although the active anode material might be  
25 metallic lithium, the use of graphitic carbon (which can insert lithium to form  $\text{LiC}_6$ ) is preferred, as it avoids the potential hazards of metallic lithium.

The invention will now be further and more particularly described, by way of example only, and with reference to the accompanying drawings in which:

Figure 1 shows cyclic voltammograms for electrolyte with and without a redox chemical;

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Figure 2 shows graphically the variation of cell voltage with charge during the first charge/discharge cycle, for test cells with and without a redox chemical; and

5

Figure 3 shows graphically the variation of stored charge with cycle number for the said test cells, after repeated overcharging.

10 Referring to Figure 1, cyclic voltammetry was performed using an experimental cell with a carbon fibre electrode with a diameter of 7  $\mu\text{m}$ , and a lithium metal foil counter electrode which also acts as a reference electrode, in a 25  $\text{cm}^3$  flask. The applied voltage between  
15 the electrodes was swept between 3 V and 5 V at a rate of 1 V/s and the current amplified and measured. In both tests the electrolyte was a mixture of organic carbonates such as propylene carbonate and diethyl carbonate (PC, DEC) with 1 mole/litre of  $\text{LiPF}_6$ . In one test  
20 hexaethylbenzene was added at 0.01 mol/litre as additive, but not in the other.

The graph shows as broken lines the variations of current with voltage for the two tests, and as a solid  
25 line the difference between the two currents. It is evident from the difference that there is an oxidation peak at around 4.5 V, and that this is associated with a reduction peak at about the same voltage on the reverse sweep. This reverse peak shows that the oxidation of the  
30 hexaethylbenzene is reversible, and that the oxidised (cationic) form is stable for at least about 1 s in this electrolyte.

Test cells were made using carbon coated onto copper  
35 foil as anode, and  $\text{LiCoO}_2$  and carbon coated onto aluminium

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foil as cathode, the coatings including polyvinylidene fluoride (PVdF) as a binder and being on both sides of each of the foils. Electrical connection to the foils was obtained by removing the coating over a small area and spot welding an aluminium tag to the aluminium foil and a nickel tag to the copper foil. Rectangular strips of anode and cathode material were then wound into a spiral with sheets of separator material between them, and encased in a metal can with an insulator on the base. The cells each had a theoretical capacity of 1400 mAh. Liquid electrolytes similar to those used in the voltammetry tests were then used to fill the cells, under a partial vacuum to preventing gas bubbles remaining. In half the cells the organic carbonate/LiPF<sub>6</sub> electrolyte had no additive, and in the other cells hexaethylbenzene was also included at a concentration between 0.005 mol/litre and 0.1 mol/litre; in the cell A whose behaviour is shown in Figures 2 and 3 the hexaethylbenzene was 0.058 mol/litre.

20

Referring to Figure 2 the first charge and discharge cycles are shown for a cell A with the additive, and for a cell B without. This cycle was performed at the C/10 rate, that is 140 mA, between voltage limits of 2.75 V and 4.2 V, and with a 2 hour hold at 4.2 V. The graphs show that the additive has little effect on the cell behaviour during the first cycle.

The cells A and B were then subjected to 11.5 charge and discharge cycles at 270 mA between 2.75 V and 4.2 V, so they ended up charged. Cell B's capacity after charging gradually decreased from 115% of its theoretical value to 106%, and its current efficiency gradually increased from about 94.5% to about 97%. Cell A behaved similarly, its capacity after charging decreasing from

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about 113% to 107%, and its current efficiency increasing from about 98.3% to a plateau at around 99.3%.

The cells A and B were then overcharged, cycling at  
5 270 mA between voltage limits of 4.0 V and 5.0 V for a period of 18 hours. Cell B experienced 250 cycles, and cell A experienced 150 cycles. After overcharging the cells, the voltage limits of 2.75 V and 4.2 V were then reimposed. Referring to Figure 3 this shows graphically  
10 the cell capacity for these subsequent cycles for the cells A and B; for cell A the capacity on charging is slightly higher than that on discharging, whereas for cell B the capacity on discharging was slightly higher. Cycling of cell B was terminated after 12 cycles, whereas  
15 cell A experienced over 200 cycles.

It is evident from the results shown in Figure 3 that the presence of the redox additive, hexaethylbenzene, in the electrolyte of cell A markedly  
20 enhanced the performance of the cell when it had been overcharged. Whereas the capacity of cell B after repeated overcharging was reduced to less than 5% of its theoretical value, the cell A had lost much less of its capacity.

25

Similar tests have been carried out with other cells with and without this redox additive. The results described above, showing that in normal operation the additive does not degrade cell performance, have been  
30 obtained consistently. The performance of cells during and after overcharge have not been as consistent, and appear to depend at least partly on how the overcharge is brought about. In particular where cells were overcharged to the 5.0 V limit directly from the  
35 discharged state (2.75 V), it appears that the extent of

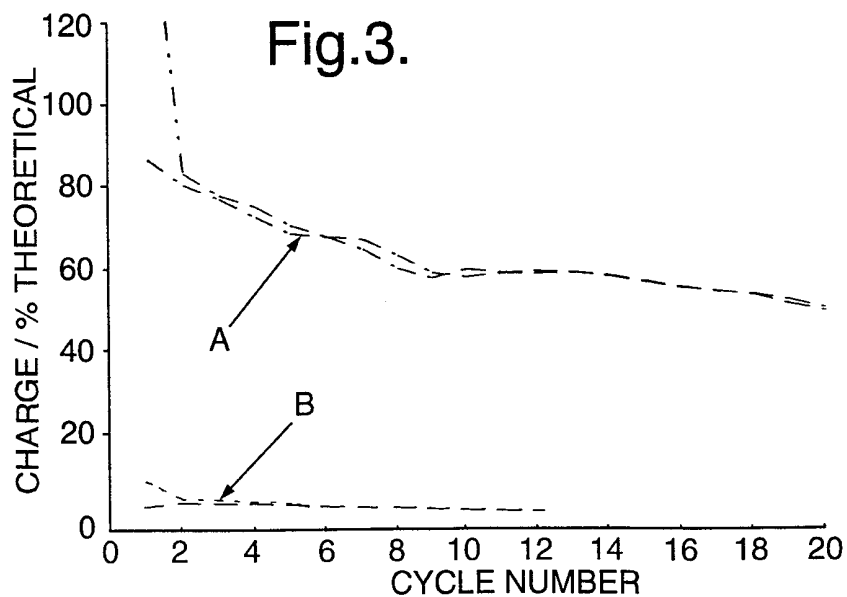
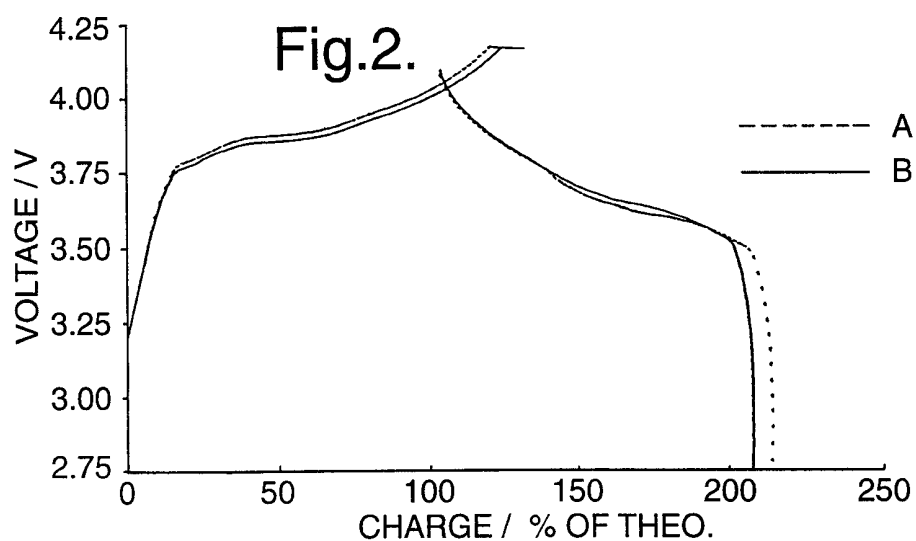
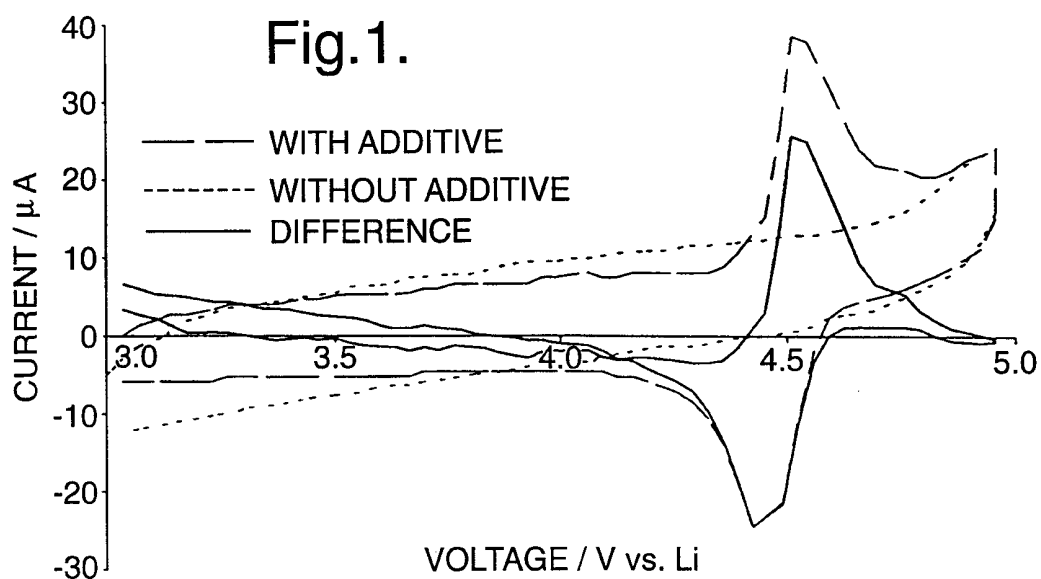


overcharge (expressed as a percentage of the theoretical charge) is an important consideration.

Claims

1. An electrolyte for use in a rechargeable cell whose voltage exceeds 3.8 volts during charging, the  
5 electrolyte including a redox chemical comprising substituted aromatic molecules in which  $\alpha$  protons are either absent, or are stabilised by molecular geometry against loss from the ionised form of the molecule.
- 10 2. An electrolyte as claimed in Claim 1 wherein the aromatic molecules comprise a substituted benzene of the general formula  $C_6R^1R^2R^3R^4R^5R^6$  in which:
- a)  $R^1$  to  $R^6$  are selected from trihalomethyl groups,  
15  $C_2$  to  $C_{10}$  alkyl groups, or halogen-substituted  $C_2$  to  $C_{10}$  alkyl groups; or
- b)  $R^1$  to  $R^6$  are as specified in (a), and  $R^6$  is H or  
20 a halogen.
3. An electrolyte as claimed in Claim 2 wherein  $R^1$  to  $R^6$  are all  $C_2$  to  $C_5$  alkyl groups.
4. An electrolyte as claimed in Claim 3 wherein  $R^1$  to  $R^6$   
25 are all ethyl groups.
5. An electrolyte as claimed in any one of the preceding Claims also comprising a lithium salt in solution in an organic solvent.
- 30 6. An electrolyte as claimed in Claim 5 wherein the solvent comprises at least one organic carbonate.

7. An electrolyte as claimed in any one of the preceding Claims also comprising an organic polymer, so forming a gel-like solid.
- 5 8. A rechargeable cell including an electrolyte as claimed in any one of the preceding Claims.
9. A rechargeable cell as claimed in Claim 8 including an anode comprising carbon, a cathode comprising an oxide  
10 of a transition metal, such that lithium ions can be reversibly intercalated into both the carbon of the anode and the oxide of the cathode, the anode and the cathode being separated by the electrolyte.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/02416

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01M10/40 H01M10/42

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 6 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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 746 050 A (SONY CORP) 4 December 1996	1,5,6,8,9
A	see page 3, line 7 - page 6, line 4 see page 7, line 12 - page 10, line 15; claims 1-5	2-4,7
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A	see abstract	2
X	EP 0 740 359 A (SONY CORP) 30 October 1996  see the whole document	1,5,6,8,9
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☒ Further documents are listed in the continuation of box C.

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International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	<p>CHA C S ET AL: "POLYPYRIDINE COMPLEXES OF  IRON USED AS REDOX SHUTTLES FOR OVERCHARGE  PROTECTION OF SECONDARY LITHIUM BATTERIES"  JOURNAL OF POWER SOURCES,  vol. 54, no. 2, 1 April 1995, pages  255-258, XP000542229  see the whole document</p> <p style="text-align: center;">---</p>	1
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