

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number
WO 01/29920 A1

(51) International Patent Classification: **H01M 6/18,**
10/40

Thomas, J. [US/US]; 1062 65th Street, Oakland, CA 94608 (US). ROSS, Philip, N., Jr. [US/US]; 103 Alta Mesa Court, Moraga, CA 94556 (US).

(21) International Application Number: PCT/US00/28975

(22) International Filing Date: 18 October 2000 (18.10.2000)

(74) Agent: SARTORIO, Henry, P.; Lawrence Berkeley National Laboratory, Patent Dept., One Cyclotron Road, MS 90-1121, Berkeley, CA 94720 (US).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): JP, KR, US.

(30) Priority Data:
60/160,391 18 October 1999 (18.10.1999) US

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(71) Applicant (*for all designated States except US*): THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 12th floor, 1111 Franklin Street, Oakland, CA 94607 (US).

Published:
— With international search report.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): RICHARDSON,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/29920 A1

(54) Title: SHUTDOWN AND REDOX SHUTTLE ADDITIVES FOR BATTERIES

(57) Abstract: A group of shutdown additives are provided in the electrolyte of rechargeable batteries or electrochemical storage or secondary cells. The additives are low molecular weight organic aromatic compounds, and function to prevent overcharging of the cell. Some of the additives also function as redox shuttle additives at less severe overcharging conditions. These additives can be used in any rechargeable battery utilizing a non-aqueous or solid polymer electrolyte and a positive electrode which is fully charged at about 4 V vs. Li/Li⁺. These include batteries for consumer electronics, communications, power tools, electric vehicles, and load leveling.

Shutdown and Redox Shuttle Additives for Batteries

Related Applications

This application claims priority of Provisional Application Ser. No. 60/160,391 filed 10/18/99, which is herein incorporated by reference.

Government Rights

The United States Government has rights in this invention pursuant to Contract No. DE-AC03-76SF00098 between the United States Department of Energy and the University of California.

Background of the Invention

The invention relates to rechargeable batteries, and more particularly to shutdown additives and redox shuttle additives for overcharge protection in rechargeable batteries.

Reliable and inexpensive overcharge protection for multi-cell lithium (and other) battery stacks is a major obstacle to commercialization of these promising systems in electric vehicles and other high voltage applications. Overcharging not only can reduce rechargeable capacity and cell life, but can also create hazardous conditions. Even moderate overcharging of transition metal oxide cathodes often leads to structural and compositional changes in the oxide matrix which have significant effects on their subsequent cycling behavior.

The redox shuttle approach to overcharge protection employs an electrolyte additive that acts as an internal current shunt when the charging potential exceeds a characteristic onset potential for the additive. The ability of certain organic aromatic compound additives to extend cell life in transition metal oxide lithium solid polymer electrolyte cells under conditions of moderate to severe overcharging has been demonstrated, as illustrated in U.S. Patent 6,004,698 to Richardson et al. Other redox shuttle additives have been reported for both polymer electrolyte, as described by F. Tran-

Van et al., *Electrochim. Acta*, 44, 2789 (1999), and 4 volt lithium ion cells, as shown in U.S. Patent 5,763,119 to Adachi.

Overcharging of batteries can create hazardous conditions, leading to explosion, fire, and/or release of toxic materials. External protection mechanisms that stop charging when a voltage, temperature, or internal pressure limit is reached are currently in use, but these are subject to failure or abuse (such as using a charger designed for a different battery). Redox shuttle additives provide an internal, automatic overcharge protection mechanism that allows charging current to pass through the cell without overcharging it. The ability of such additives to extend cell life in lithium and lithium ion cells under conditions of moderate to severe overcharging has been demonstrated. However, for many applications, the issue of safety takes precedence over the desire for cell life extension. A mechanism that renders the battery harmless on overcharging is acceptable even though it ends its useful life. Thus "shutdown" additives that achieve this goal are desired. Some of these may act as redox shuttles under moderate overcharge conditions and as shutdown additives when the overcharge conditions are more severe. Both redox shuttle and shutdown additives may be present in the same cell.

Summary of the Invention

Accordingly it is an object of the invention to provide shutdown additives for rechargeable batteries.

It is also an object of the invention to provide shutdown additives for rechargeable batteries that also act as redox shuttle additives at lower overcharge conditions.

It is another object of the invention to provide shutdown additives, which may also act as redox shuttle additives, for rechargeable lithium or lithium ion batteries, particularly 4 V lithium ion batteries.

The invention is a group of shutdown additives for the electrolyte of rechargeable batteries or electrochemical storage or secondary cells, and the rechargeable batteries or electrochemical storage cells with these additives. The additives are low molecular weight organic aromatic compounds, and function to prevent overcharging of the cell. When one or more of the additives is added to the electrolyte of a rechargeable cell, it will

be oxidized at the positive electrode at a potential specific to the additive(s). The product of this oxidation increases the resistance of the cell by means of polymerization, precipitation, electrolyte depletion, chemical reaction, or other mechanism. This prevents further charging of the cell, thereby preventing development of unsafe conditions.

Some of the additives also function as redox shuttle additives at less severe overcharging conditions. When one or more of them is added to the electrolyte of a rechargeable cell, it is oxidized at the positive electrode to its respective radical cation at certain potentials. The cation diffuses through the electrolyte to the negative electrode, where it is reduced to its original neutral state. This allows the additive(s) to transport an electrical charge through the cell without damage to the cell under conditions that would, in the absence of the additive(s), cause it to lose capacity or fail. Under more severe overcharging conditions, the cation transport through the electrolyte is insufficient, and the additives are oxidized at the positive electrode to shut off the cell.

These additives could find use in any rechargeable battery utilizing a non-aqueous or solid polymer electrolyte and a positive electrode which is fully charged at about 4 V vs. Li/Li^+ . These include batteries for consumer electronics, communications, power tools, electric vehicles, and load leveling.

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of a rechargeable battery or electrochemical cell.

Fig. 2 is a graph of the onset potentials of two shutdown additives of the invention.

Fig. 3 is a graph of the onset potentials of seven shutdown/redox shuttle additives of the invention compared to two prior art additives.

Fig. 4 is a graph of the onset potentials of seventeen shutdown/redox shuttle additives of the invention.

Detailed Description of the Invention

The invention applies to rechargeable batteries or electrochemical storage cells, e.g. lithium and lithium ion batteries, of the type which are well known in the art, e.g. as

described in U.S. Patents 6,004,698 and 5,763,119, which are herein incorporated by reference. The materials of which the standard parts of the batteries or cells of the invention are made, as well as the configuration of the battery or cell, can be found in these and other references.

Fig. 1 illustrates a battery or cell 12 that is formed within a nonreactive outer case or shell 12 with an optional insulating inner lining 14 inside case 12 that form sidewalls of battery 12. A negative electrode current collector 20 is positioned against one sidewall of battery 12, and a negative electrode 24, which forms the negative electrode material, is positioned next to and in contact with negative electrode current collector 20. Alternatively, negative electrode 24 and negative electrode current collector 20 may form a unitary structure, referred to as negative electrode 24. Similarly, a positive electrode current collector 36 is positioned against an opposed sidewall of battery 12, and a positive electrode 32, which forms the positive electrode material, is positioned next to and in contact with positive electrode current collector 36. Alternatively, positive electrode 32 and positive electrode current collector 36 may form a unitary structure, referred to as positive electrode 32.

Between negative electrode 24 and positive electrode 32 is solid polymer electrolyte 28, which is ionically conducting and also serves as an insulator or separator between the negative electrode 24 and positive electrode 32. In some batteries it may be possible that the electrolyte is liquid. In accordance with the invention, electrolyte 28 includes the shutdown or shutdown/redox shuttle additives of the invention.

The shutdown (SD) and shutdown/redox shuttle (SD/RS) additives of the invention have common structural features including an aromatic ring and electro-withdrawing substituents which give them high oxidation potentials and stabilize the resulting oxidized species. They fall into several structural subcategories. Some additives can be considered to be members of more than one of these subgroups.

Category A: halogenated benzenes and naphthalenes

Category B: substituted methoxybenzenes

Category C: substituted benzodioxoles

Category D: alkyl polyethers

Category E: substituted nitrogen-containing heterocycles

The following compounds in Table I act as cell shutdown additives:

Table I

SD #	Compound Name	CAS No.	Onset Potential	Category
1	3,5-difluoroanisole	9334-10-3	4.45	A,B
2	1,3,5-trimethoxybenzene	621-23-8	4.00	B
3	2-methoxyethyl ether	111-96-6	5.20	D
4	tri(ethylene glycol) dimethyl ether	112-49-2	5.20	D
5	tetra(ethylene glycol) dimethyl ether	143-24-8	5.25	D
6	1,2,4-trifluorobenzene	367-23-7	5.20	A
7	1,2,3,4-tetrafluorobenzene	551-62-2	5.15	A
8	2,4,6-trimethoxypyrimidine	13106-85-9	4.50	E
9	2,6-dimethoxy-1,4-benzoquinone	530-55-2	5.10	B
10	2,4-dimethoxybenzonitrile	4107-65-7	4.50	B

The onset potential graphs for the first two additives in Table I (SD 1, SD 2) are shown in Fig. 2.

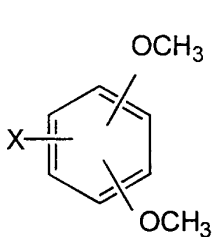
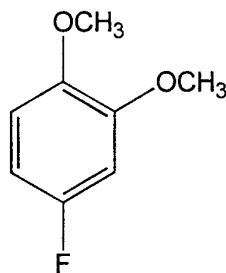
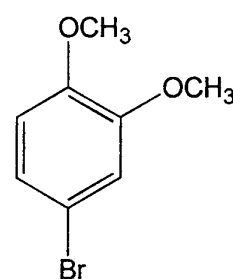
In addition, the following additives in Table II can act both as redox shuttles under moderate overcharge conditions, and as cell shutdown additives when subjected to more severe overcharging:

Table II

SD/RS#	Compound Name	CAS No.	Onset Potential	Category
LBNL 1	1,2-difluoro-4,5-dimethoxybenzene	203059-80-7	4.20	A,B
LBNL 2	1,4-difluoro-2,5-dimethoxybenzene	199866-90-5	4.20	A,B
LBNL 3	3,4-dimethoxybenzonitrile	2024-83-1	4.50	B
LBNL 4	piperonylnitrile	4421-09-4	4.52	C
LBNL 5	5-chloro-1,3-benzodioxole	7228-38-8	4.25	C
LBNL 6	5-bromo-1,3-benzodioxole	2635-13-4	4.27	C
LBNL 7	5-nitro-1,3-benzodioxole	2620-44-2	4.57	C
LBNL 8	1,2-dimethoxy-4-nitrobenzene	709-09-1	4.55	B
LBNL 9	3,4,5-trimethoxybenzonitrile	1885-35-4	4.40	B

LBNL 10	octafluoronaphthalene	313-72-4	4.90	A
LBNL 11	2,3-dimethoxybenzonitrile	5653-62-3	4.50	B
LBNL 12	3,5-dimethoxybenzonitrile	19179-31-8	4.45	B
LBNL 13	2,3,4-trimethoxybenzonitrile	43020-38-8	4.50	B
LBNL 14	1,2,3-trimethoxybenzene	634-36-6	4.46	B
LBNL 15	1,2,4-trimethoxybenzene	135-77-3	3.72	B
LBNL 16	3,4-difluoroanisole	115144-40-6	4.57	A,B
LBNL 17	pentafluoroanisole	389-40-2	5.05	A,B
LBNL 18	1,2,4,5-tetrafluorobenzene	327-54-8		A
LBNL 19	1,2,3-trifluorobenzene	1489-53-8		A
LBNL 20	1,3,5-trifluorobenzene	372-38-3		A
LBNL 21	1,2,3,5-tetrafluorobenzene	2367-82-0		A
LBNL 22	2,3,4-trifluorobenzonitrile	143879-80-5		A
LBNL 23	2,3,6-trifluorobenzonitrile	136514-17-5		A
LBNL 24	3,4,5-trifluorobenzonitrile	134227-45-5		A

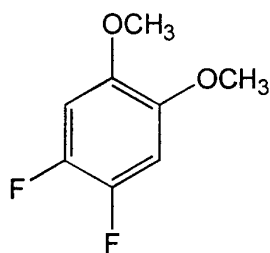
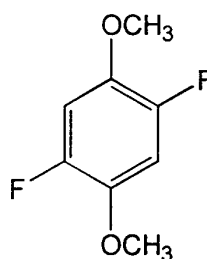
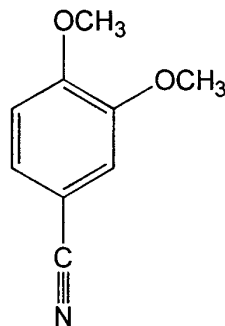
This invention provides new additives for batteries or electrochemical storage cells, particularly for 4 volt cells incorporating liquid or preferably polymer electrolytes. The prior art redox shuttle additives by Sony researchers described in U.S. Patent 5,763,119 are dimethoxybenzenes with a single halide substituent, having molecular structure "a" shown below, where X is a halogen, e.g. fluorine (SONY 1) or bromine (SONY 2).

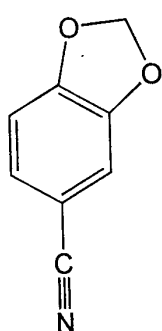
**a****SONY 1****SONY 2**

They have onset potentials ranging from 3.93 to 4.10 V vs. Li/Li^+ . The onset potentials for the two best-performing SONY additives are shown in Fig. 3, labelled SONY 1 and SONY 2. While SONY 2 is capable of providing some overcharge protection in lithium cobalt cells, a significant capacity penalty is incurred due to an

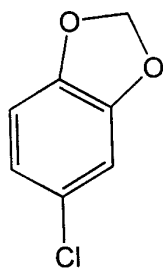
inability to fully charge the cells before the onset potential is reached. Similar limitations would apply to their use in lithium manganese oxide or lithium nickel oxide cells.

Seven additives of the present invention (LBNL 1 – 7 in Table II, with molecular structures shown below) are also included in the onset potential graph of Fig. 3. LBNL 1 and LBNL 2 differ from additives described in U.S. Patent 5,763,119 in being difluoro-substituted dimethoxybenzenes rather than monohalo-compounds. LBNL 3 is also a dimethoxybenzene, but it contains no halogen, having a nitrile group in a position para to a methoxy- group. LBNL 4 - 7 are 4-substituted 1,2-(methylenedioxy)benzenes. The structures of LBNL 8 – 17 are also shown below. The LBNL additives have redox shuttle onset potentials of about 4.25 V or higher. Lithium manganese oxide cells containing these additives can be charged to their full normal capacity at 4.2 V. These cells are protected from overcharging and maintain their original discharge capacities for at least five cycles under conditions of severe overcharging (50% greater charge capacity than normal).

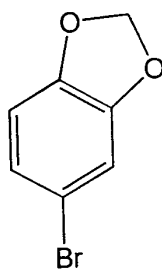
**LBNL 1****LBNL 2****LBNL 3**



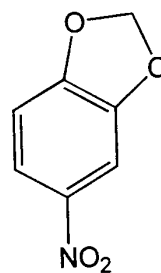
LBNL 4



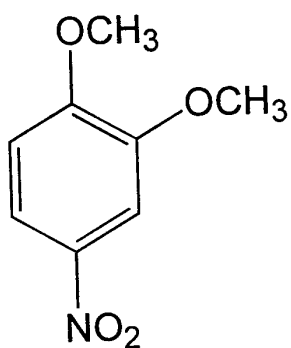
LBNL 5



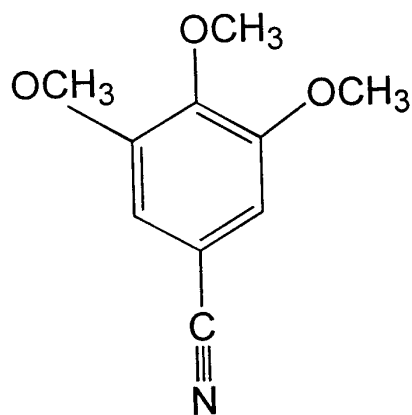
LBNL 6



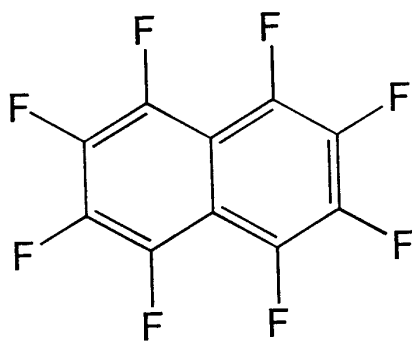
LBNL 7



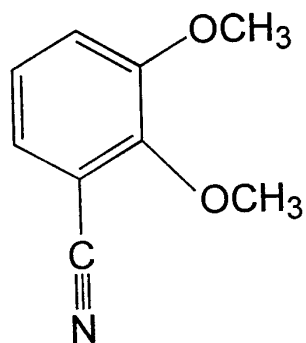
LBNL 8



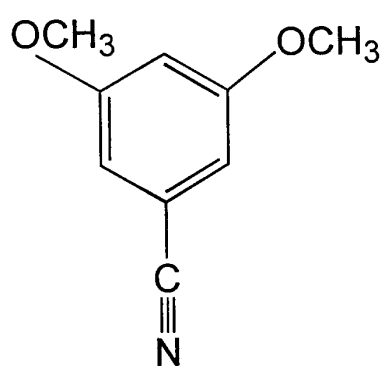
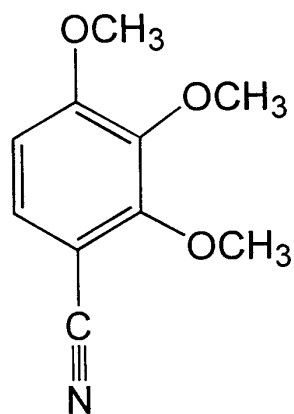
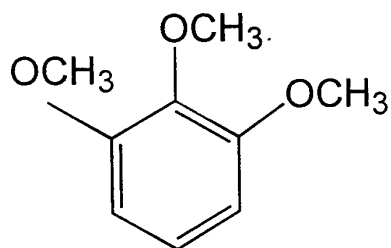
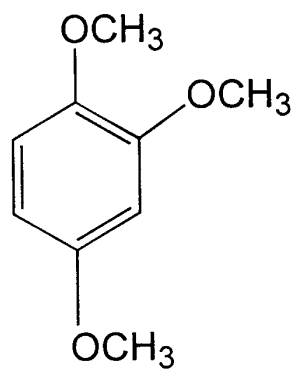
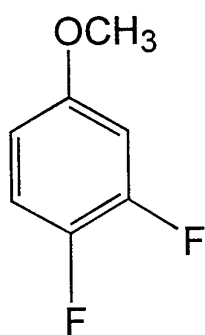
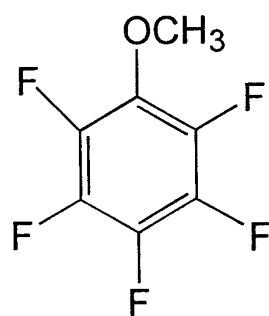
LBNL 9



LBNL 10



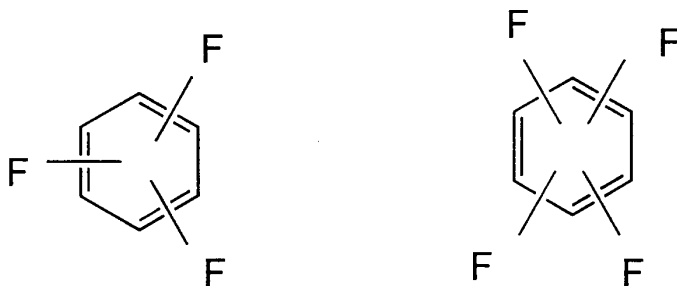
LBNL 11

**LBNL 12****LBNL 13****LBNL 14****LBNL 15****LBNL 16****LBNL 17**

The onset potentials of seventeen shutdown/redox shuttle additives (LBNL 1 – 17 in Table II) are shown in Fig. 4.

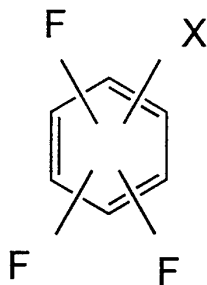
The additives of the invention fall within the general subgroups of Categories A – E, with certain exclusions, and are more specifically identified as follows.

Category A includes halogenated benzenes without any methoxy groups (it also can include halogenated benzenes with methoxy groups, but these will be discussed under category B). The halogenated benzenes include benzenes with only halogen substituents, such as trifluorobenzene and tetrafluorobenzene; there are preferably at least three halogen substituents. Various isomers of the tri- and tetra- fluorobenzenes are included in Tables I and II (SD 6, LBNL 19, LBNL 20; SD 7, LBNL 18, LBNL 21). The structures of these compounds are as follows:

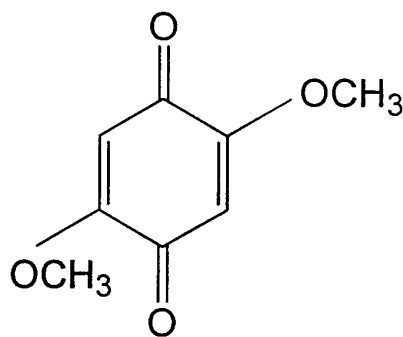
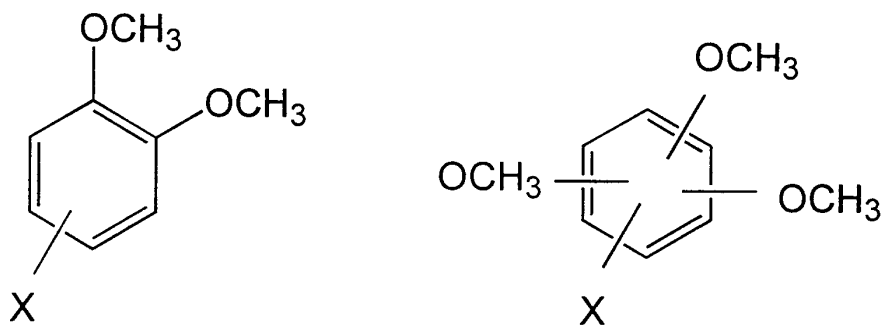


Also included in Category A are halogenated naphthalenes, such as octafluoronaphthalene (LBNL 10).

The halogenated benzenes can also include benzenes with halogens and other (non-methoxy) substituents, such as trifluorobenzonitrile (LBNL 22-24), which have the following structure where X is another substituent, e.g. nitrile:



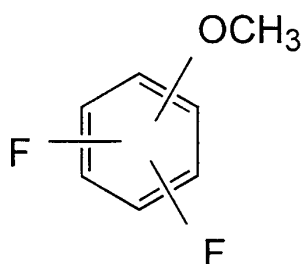
Category B includes substituted methoxybenzenes with no halogens. There are again preferably at least three substituents. These additives include benzenes with only methoxy groups, such as trimethoxybenzene (SD 2, LBNL 14-15), and benzenes with methoxy groups and other (non-halogen) substituents, such as dimethoxybenzonitrile (SD 10, LBNL 3, LBNL 11-12), dimethoxynitrobenzene (LBNL 8), trimethoxybenzonitrile (LBNL 9, LBNL 13), and the related compound dimethoxybenzoquinone (SD 9). The structures of these compounds are as follows, where X is a (non-halogen) substituent such as nitro- or nitrile group:



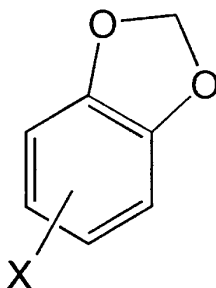
2,6-dimethoxy-1,4-benzoquinone

Category B also includes substituted methoxybenzenes with halogens (which overlaps with Category A since they would also be halogenated benzenes). However, this group of halogenated methoxybenzene additives excludes dimethoxybenzenes with a

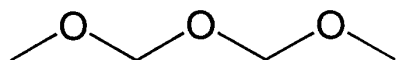
single halogen substituent (which are shown in U.S. Patent 5,763,119). This group of additives does include halogenated anisoles (benzenes with a single methoxy group), such as difluoroanisole (SD 1, LBNL 16) and pentafluoroanisole (LBNL 17), and also includes dimethoxybenzenes with at least two halogen substituents, such as the previously described difluorodimethoxybenzenes (LBNL 1-2). The structure of a halogenated anisole is as follows:



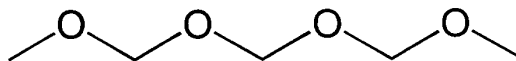
Category C is the substituted benzodioxoles or methylenedioxybenzenes, illustrated below, where X is a substituent. These include both halogenated compounds (LBNL 5-6) and nonhalogenated compounds (LBNL 4, LBNL 7) shown above.



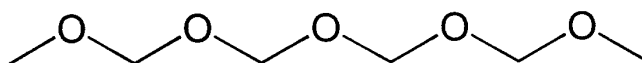
Category D is alkyl polyethers, such as methoxyethyl ether (SD 3) and tri- or tetra-(ethylene glycol) dimethyl ether (SD 4-5), illustrated below.



2-methoxyethyl ether

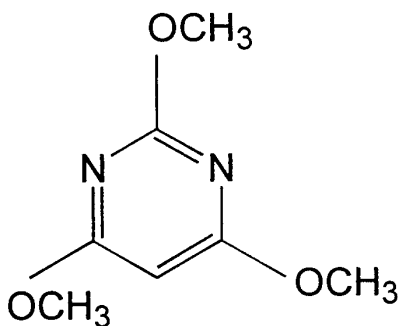


tri(ethylene glycol) dimethyl ether

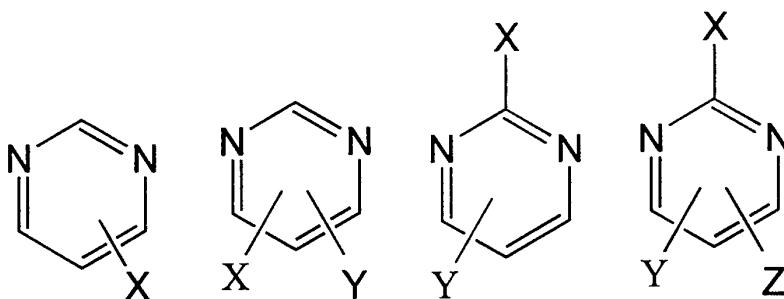


tetra(ethylene glycol) dimethyl ether

Category E is substituted nitrogen-containing heterocycles, such as trimethoxypyrimidine (SD 8), illustrated below along with generic substituted pyrimidines (X, Y, Z can be hydrogen).



2,4,6-trimethoxypyrimidine



The amount of additive can vary widely. The minimum is probably about 1 % by weight. The maximum can be very high. The additive could replace all of the solvent in some cases, though this might be prohibitively expensive. Typically, 1 molar solutions have been used for testing in complete cells. This is because the electrolyte is 1 molar Li salt, and is therefore depleted of Li when all of the additive is in the oxidized form. Adjustments (increases) to the Li salt concentration would probably be made in designing a cell that would incorporate a large amount of additive.

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

Claims

1. A battery or electrochemical storage cell, comprising a positive electrode, a negative electrode, an electrolyte between the positive and negative electrodes, and a shutdown additive in the electrolyte, wherein the shutdown additive is selected from:

- A. halogenated benzenes, without additional substituents, and with additional substituents but excluding methoxy substituents, and halogenated naphthalenes,
- B. substituted methoxybenzenes, without additional substituents, and with additional substituents, including halogens, but excluding monohalodimethoxybenzenes,
- C. substituted benzodioxoles,
- D. alkyl polyethers,
- E. substituted nitrogen containing heterocycles.

2. The battery or cell of Claim 1 wherein the additive is a halogenated benzene without additional substituents, a halogenated benzene with additional substituents but excluding methoxy substituents, or a halogenated naphthalene.

3. The battery or cell of Claim 2 wherein the additive is selected from trifluorobenzene, tetrafluorobenzene, trifluorobenzonitrile, and octafluoronaphthalene.

4. The battery or cell of Claim 1 wherein the additive is a substituted methoxybenzene without additional substituents, a substituted methoxybenzene with additional substituents excluding halogens, or a substituted methoxybenzene with additional halogen substituents but excluding monohalodimethoxybenzenes.

5. The battery or cell of Claim 4 wherein the additive is selected from trimethoxybenzene, dimethoxybenzonitrile, trimethoxybenzonitrile, dimethoxynitrobenzene, difluoroanisole, pentafluoroanisole, and difluorodimethoxybenzene.

6. The battery or cell of Claim 1 wherein the additive is a substituted benzodioxole.
7. The battery or cell of Claim 1 wherein the additive is an alkyl polyether.
8. The battery or cell of Claim 1 wherein the additive is a substituted nitrogen containing heterocycle.
9. The battery or cell of Claim 1 wherein the electrolyte is a solid polymer.
10. The battery or cell of claim 1 wherein the battery or cell is a lithium battery or cell.
11. The battery or cell of Claim 10 wherein the battery or cell is a 4 V lithium battery or cell.
12. A method of preventing overcharging of a battery or electrochemical storage cell, comprising providing a shutdown additive in the electrolyte of the battery or cell, wherein the shutdown additive is selected from: A. halogenated benzenes, without additional substituents, and with additional substituents but excluding methoxy substituents, and halogenated naphthalenes, B. substituted methoxybenzenes, without additional substituents, and with additional substituents, including halogens, but excluding monohalodimethoxybenzenes, C. substituted benzodioxoles, D. alkyl polyethers, E. substituted nitrogen containing heterocycles.
13. An electrolyte with additive composition for a battery or electrochemical storage cell, comprising an electrolyte and a shutdown additive in the electrolyte, wherein the shutdown additive is selected from: A. halogenated benzenes, without additional substituents, and with additional substituents but excluding methoxy substituents, and halogenated naphthalenes, B. substituted methoxybenzenes, without additional

substituents, and with additional substituents, including halogens, but excluding monohalodimethoxybenzenes, C. substituted benzodioxoles, D. alkyl polyethers, E. substituted nitrogen containing heterocycles.

14. The composition of Claim 13 wherein the electrolyte is a solid polymer.

15. The composition of Claim 13 wherein the shutdown additive is selected from the additives listed in Tables I and II.

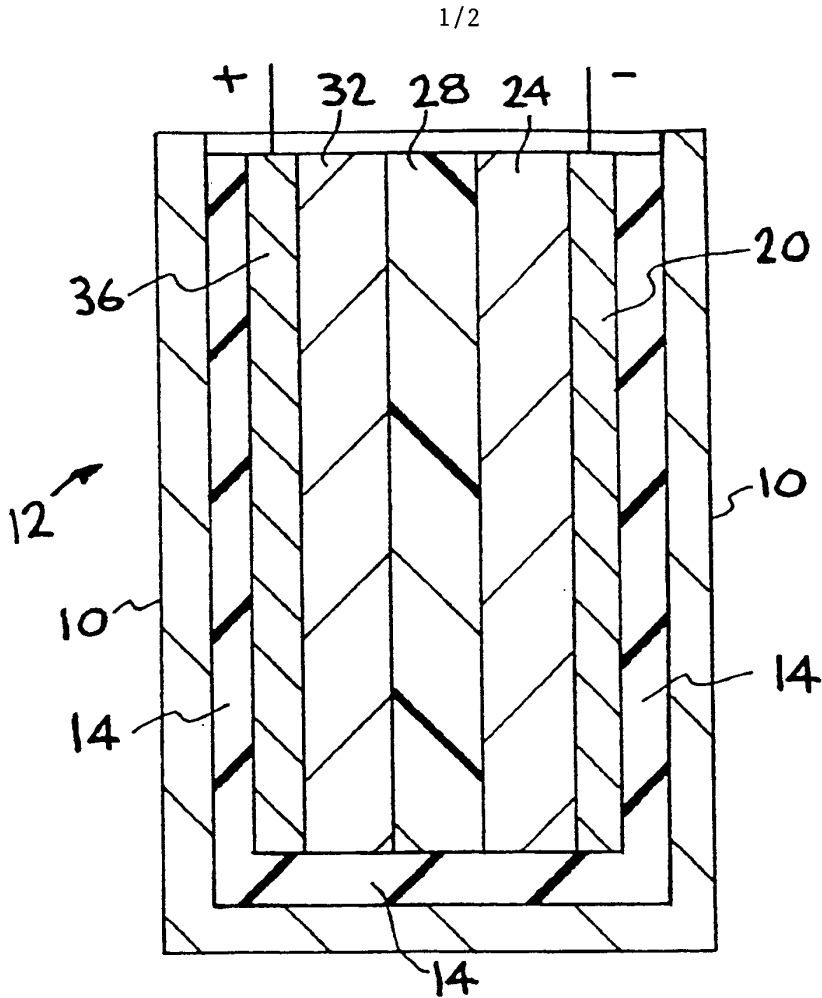


FIG. 1

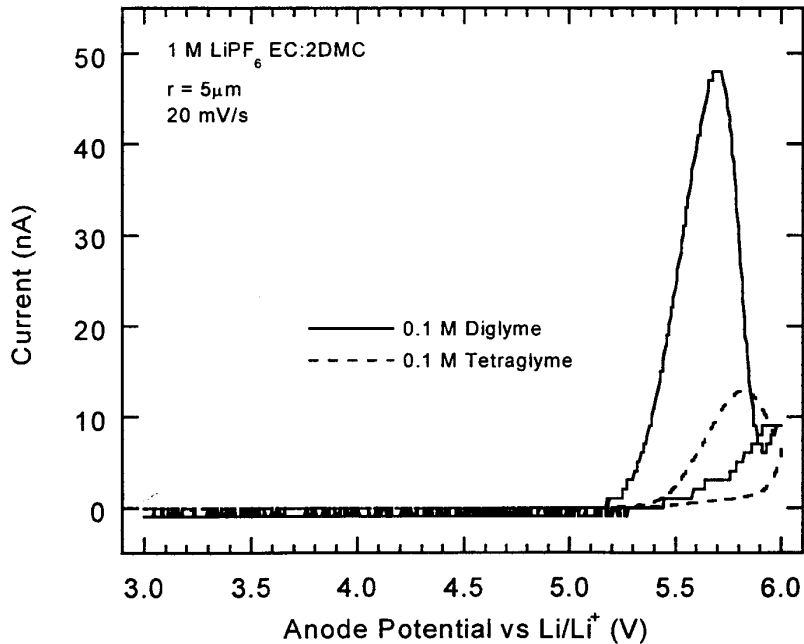


FIG. 2

2/2

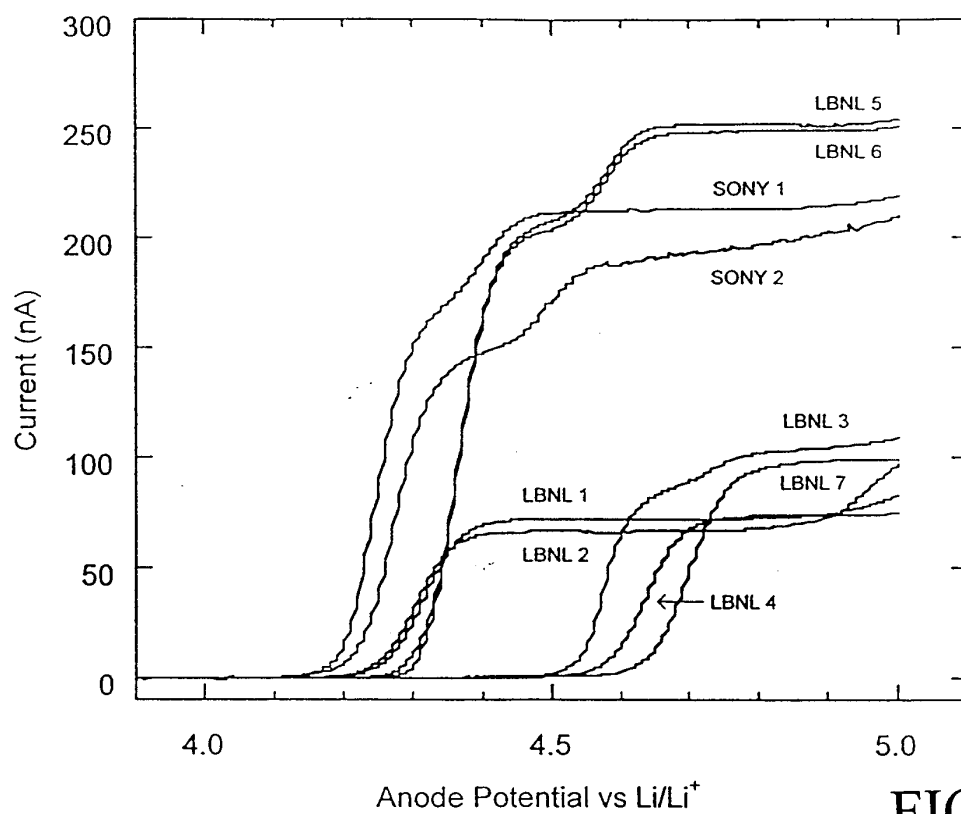


FIG. 3

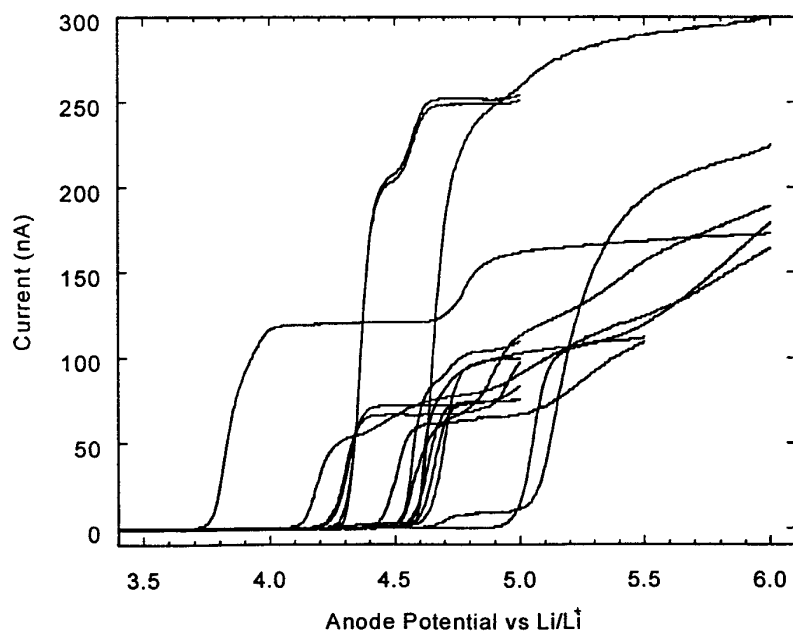


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/28975

A. CLASSIFICATION OF SUBJECT MATTER																						
IPC(7) : H01M 6/18, 10/40 US CL : 429/307, 231.95 ; 252/62.2 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) U.S. : 429/307, 231.95 ; 252/62.2																						
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 practicable, search terms used) Please See Continuation Sheet																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X, P	US 6,004,698 A (RICHARDSON et al) 21 December 1999 (21.12.1999), column 4, lines 25-40, column 5, lines 31-40, column 6, lines 6-11, column 7, lines 49-66 and abstract.	1-2, 9-10, 12-14																				
X, P	US 6,045,952 A (KERR et al) 04 April 2000 (04.04.2000), column 2, lines 24-30, column 4, lines 65-67, and abstract.	1-2, 9-11																				
X	US 4,801,359 A (JEANNE et al) 31 January 1989 (31.01.1989), column 22, lines 47-50.	13-14																				
X	US 5,789,585 A (LEE et al) 04 August 1998 (04.08.1998), column 4, lines 12-19, column 5, line 64 to column 6, line 56.	1, 7, 10, 12-13																				
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.																						
* Special categories of cited documents: <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>earlier application or patent published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																			
"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																			
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 28 December 2000 (28.12.2000)		Date of mailing of the international search report 18 JAN 2001																				
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230		Authorized officer Laura S Weiner Jean Proctor Paralegal Specialist Telephone No. 703-308-0661																				

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/28975

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claim Nos.: 15
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 15 has the phrase "selected from additives listed in Tables I and II". These additives need to be listed in the claim.
3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/28975

Continuation of B. FIELDS SEARCHED Item 3: EAST

search terms: additive, redox shuttle, overcharge protection, solid polymer electrolyte, benzene, methoxybenzene, benzodioxole, electrolyte, overcharging, battery, cell