



(86) Date de dépôt PCT/PCT Filing Date: 2001/01/26

(87) Date publication PCT/PCT Publication Date: 2001/08/02

(85) Entrée phase nationale/National Entry: 2001/09/21

(86) N° demande PCT/PCT Application No.: US 2001/002533

(87) N° publication PCT/PCT Publication No.: 2001/056101

(30) Priorités/Priorities: 2000/01/26 (60/178,177) US;
2000/01/26 (60/178,217) US; 2000/01/26 (60/178,241) US

(51) Cl.Int.⁷/Int.Cl.⁷ H01M 4/58

(71) Demandeur/Applicant:
LION COMPACT ENERGY, INC., US

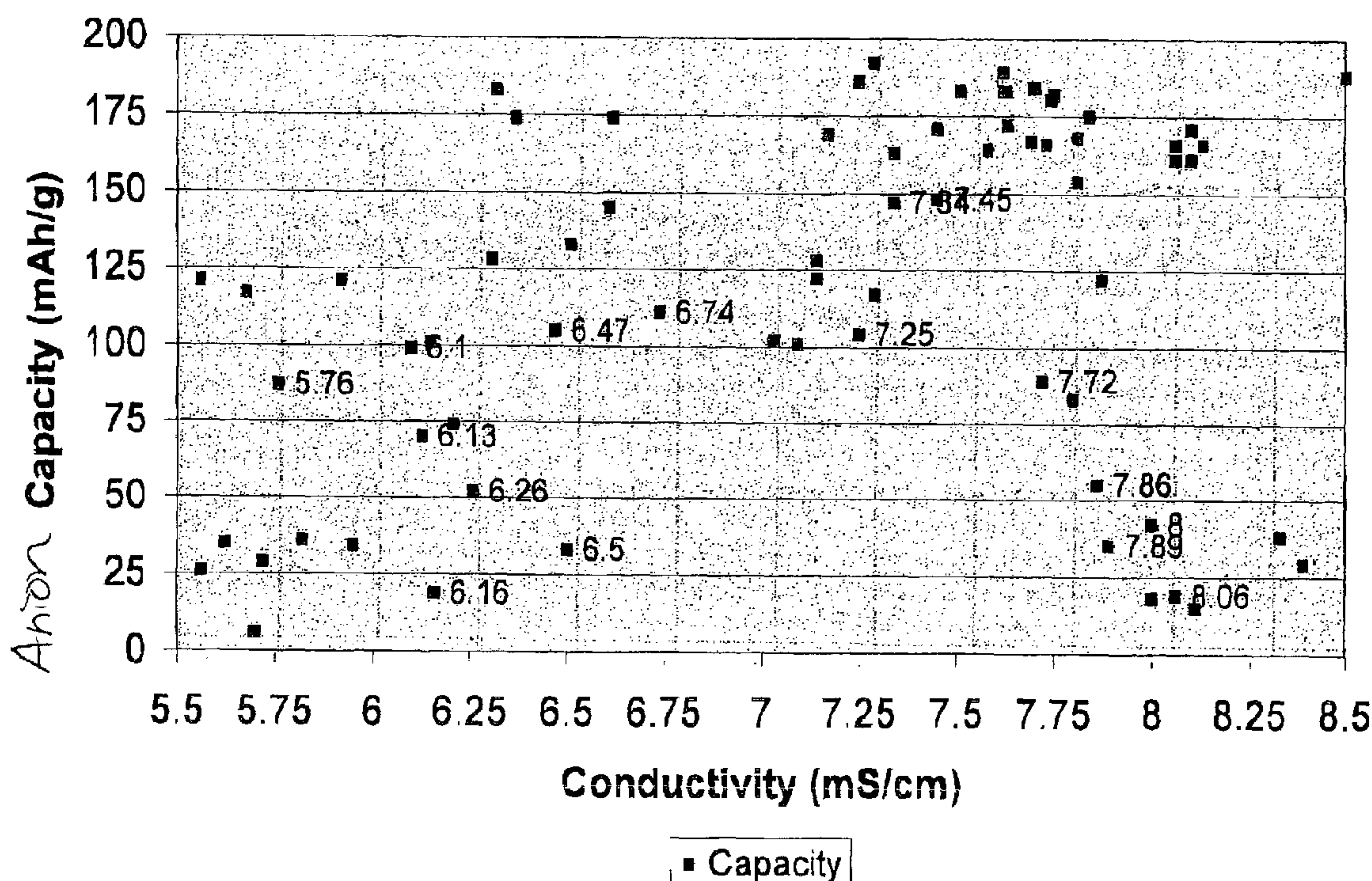
(72) Inventeurs/Inventors:
ORABONE, WILLIAM E., JR., US;
ELLIS, HEATHER N., US;
MACLEAN, GREGORY KENNETH, US;
HUANG, SUI-YANG, US;
LEWANDOWSKI, THONGKHANH P., US;
MASSARO, LISA MARIE, US

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : ELECTROLYTES POUR SYSTEME DE STOCKAGE D'ENERGIE A GRAPHITE DOUBLE

(54) Title: ELECTROLYTES FOR DUAL GRAPHITE ENERGY STORAGE SYSTEM

Elyte Characteristics



(57) Abrégé/Abstract:

There is provided an electrolyte recirculation system including a salt concentration monitor, a pump, and a salt reservoir. Also provided by the present invention is an electrolyte for use in a dual graphite cell, the electrolyte being made of a solvent that dissolves at least 15 wt.% salt. There is also provided an electrolyte for use in a dual graphite cell, the electrolyte stable above 5 V. Also provided is an electrolyte for use in a dual graphite cell, the electrolyte including a multiple solvent electrolyte that dissolves in at least 15 wt.% LiClO₄.

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 August 2001 (02.08.2001)

PCT

(10) International Publication Number
WO 01/56101 A1

(51) International Patent Classification⁷: **H01M 4/58**

(21) International Application Number: PCT/US01/02533

(22) International Filing Date: 26 January 2001 (26.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/178,241 26 January 2000 (26.01.2000) US
60/178,217 26 January 2000 (26.01.2000) US
60/178,177 26 January 2000 (26.01.2000) US

(71) Applicant (for all designated States except US): **LION COMPACT ENERGY, INC.** [US/US]; 721 Pershing Street, Midland, MI 48640 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MASSARO, Lisa, Marie** [US/US]; 3808 E. Hubbard, Midland, MI 48642 (US). **LEWANDOWSKI, Thongkhahn, P.** [US/US];

6605 Scenic Drive South, Saginaw, MI 48603 (US). **HUANG, Sui-Yang** [US/US]; 6336 Singletree Way, Pleasanton, CA 94588 (US). **MACLEAN, Gregory, Kenneth** [US/US]; 8451 Whipporwhill Drive, Apt. F, Indianapolis, IN 46256 (US). **ELLIS, Heather, N.** [US/US]; 134 1/2 Ashman, Midland, MI 48640 (US). **ORABONE, William, E., Jr.** [US/US]; 5717 Slaxmoor, Midland, MI 48640 (US).

(74) Agents: **KOHN, Kenneth, I.** et al.; Kohn & Associates, Suite 410, 30500 Northwestern Highway, Farmington Hills, MI 48334 (US).

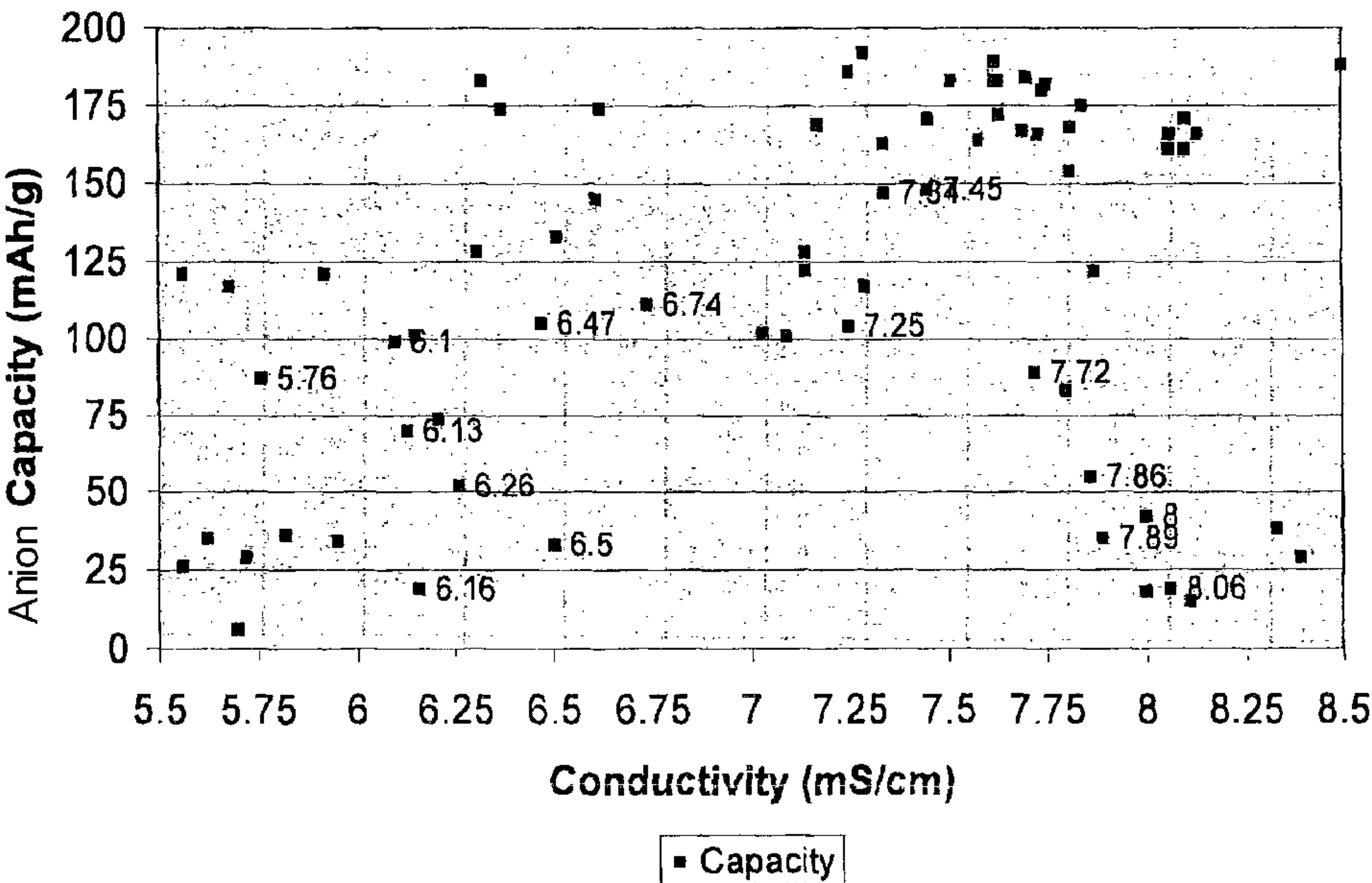
(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European

[Continued on next page]

(54) Title: ELECTROLYTES FOR DUAL GRAPHITE ENERGY STORAGE SYSTEM

Elyte Characteristics



(57) Abstract: There is provided an electrolyte recirculation system including a salt concentration monitor, a pump, and a salt reservoir. Also provided by the present invention is an electrolyte for use in a dual graphite cell, the electrolyte being made of a solvent that dissolves at least 15 wt.% salt. There is also provided an electrolyte for use in a dual graphite cell, the electrolyte stable above 5 V. Also provided is an electrolyte for use in a dual graphite cell, the electrolyte including a multiple solvent electrolyte that dissolves in at least 15 wt.% LiClO₄.

WO 01/56101 A1



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

Published:

— with international search report

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.

ELECTROLYTES FOR DUAL GRAPHITE ENERGY STORAGE SYSTEM**BACKGROUND OF THE INVENTION**

5

1. FIELD OF THE INVENTION

The present invention relates to energy storage cells. More specifically, the present invention relates to dual graphite energy storage
10 cells.

2. DESCRIPTION OF RELATED ART

The nature of dual graphite energy storage systems require that
15 an electrolyte be chosen specifically for it's use. The carbonaceous material and electrolyte chosen for dual graphite systems are used strictly to intercalate and deintercalate both cations and anions at two different electrodes. The ions are strictly drawn out of the electrolyte solution for intercalation, and never from one electrode to the other. The cations migrate
20 and intercalate into one electrode at the same time the anions migrate and intercalate into the other electrode. The reverse process also occurs simultaneously. This explains why many skilled in the art refer to this technology as dual intercalating. Dual graphite, or dual intercalating, energy

storage systems are not dependent upon an electrochemical reaction. These systems also blur the lines of what are commonly used terms of anode or cathode. Instead, those skilled in the art of dual graphite systems refer to the electrodes as “anion intercalating fiber” and “cation intercalating fiber”.

5

The materials used in dual graphite systems are chosen with different requirements than seen in much of the prior art. United States Patent Number 5,993,997, for instance, describes the use of a carbon compound material capable of occluding and discharging lithium (or doping/de-doping) which is then shuttled to the negative electrode composed mainly of a carbon material that intercalates and deintercalates the lithium in opposition to the reaction occurring at the opposite electrode. This patent is typical of the prior art. The common rechargeable energy storage systems, such as Li-ion, NiCd, and NiMH, do require an electrochemical reaction as the technology basis. The dual graphite energy storage system is very different as described previously. It is easy to see why, while still referred to as a battery, dual graphite systems do not fit the well known, and well used, term of “an electrochemical cell”, and in fact, while the ability to store energy does fit the definition of a battery, the dual graphite systems do not adhere to the stricter more detailed definitions of batteries that most in the battery art are familiar with using.

10

15

20

In the prior art, solvents to be used in electrolytes for dual graphite cells were mostly chosen for application testing because they were common in the battery industry for other technologies. Only United States Patent Numbers 4,830,938, and 4,865,931, and the references to Dahn et al., 2000, 5 and Steel et al., 2000, attempt to test and explain electrolytes in a full dual graphite cell that uses the technology in the same format as a true dual graphite cell with both electrodes made from carbonaceous material. Other references in the prior art refer to the dual intercalating/graphite system. However, these references fail to test usefulness and neglect to discuss 10 theories on electrolyte uses in a full dual graphite cell. Instead testing and resulting assumptions were based on half cell configurations, and testing was performed on properties, such as stability and capacity, in an exclusionary format.

15 The electrolytes and carbonaceous materials used in dual graphite systems require a unique selection process that is inherent with the technology, since all cell component requirements are interdependent. Through extensive testing, the inventors have proven that the results of individual half cells do not predict the final result of a full dual graphite cell. All 20 components in the dual graphite technology are interdependent, including the cation intercalating carbon fiber, the anion intercalating carbon fiber, and the electrolyte which is composed of an ionizable salt and its concentration, and

the solvent. Therefore, the results of the prior art are not indicative of results in a full dual graphite cell.

Energy storage, especially in dual graphite systems, is greatly enhanced by the proper selection of electrolytes. Increasing the electrolyte capabilities means that less volume and weight of the material can be required to achieve more energy storage. This in turn increases the entire device's energy density giving the device more energy per weight and volume. In addition, less total solvent material in the device reduces the total cost of device. Through an understanding of relatively concentrated electrolytes and specifically designed test procedures, the vast options of solvents is reduced to a few reasonable options for use in a dual intercalating/graphite energy storage system. It would therefore be useful to determine additional solvents and solutions that can be used as electrolytes for dual graphite cells.

Additionally, since each of the components of a dual graphite cell are interdependent, it is imperative that the right amounts of each are found in the cell. An improper balance can both limit the functionality of the dual graphite cell and potentially inhibit all dual graphite cell function. While it is imperative to maintain this balance, there is also concern with limiting the weight of the dual graphite cell. This can only occur by limiting the amount of components which are included in the dual graphite cell.

Various references in the prior art have offered suggestions for overcoming these obstacles. For example, United States Patent Numbers 5,061,578, to Kozuma et al., 5,340,667, to Stinson et al., and 5,543,243, to Brecht all disclose recirculation patterns for batteries. However, all of these patents disclose recirculation methods for maintaining proper volume of electrolytes within the battery. There is no disclosure of a system for monitoring the concentration of electrolytes within the battery. While the patents disclose methods for maintaining the proper volume of electrolytes in the battery, they do not disclose a method for limiting the amount of electrolyte and accordingly do not limit the weight of the battery.

It would therefore be useful to develop a system for maintaining proper electrolyte concentrations in a battery. It would also be useful to develop a method for limiting the weight of batteries.

SUMMARY OF THE INVENTION

According to the present invention, there is provided an electrolyte recirculation system including a salt concentration monitor, a pump, and a salt reservoir. Also provided by the present invention is an electrolyte for use in a dual graphite cell, the electrolyte being made of a solvent that dissolves greater than 15 wt% salt. There is also provided an

electrolyte for use in a dual graphite cell, the electrolyte being made of a solvent which is stable above 5 V. Also providing is an electrolyte for use in a dual graphite cell, the electrolyte including a multiple solvent electrolyte that dissolves in at least 15 wt% LiClO_4 .

5

DESCRIPTION OF THE DRAWINGS

Other advantages of the present invention are readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing wherein:

10

Figure 1 is a graph showing electrolyte characteristics by the anion capacity versus conductivity of the electrolytes.

15

DETAILED DESCRIPTION OF THE INVENTION

Generally, the present invention provides an electrolyte recirculation system for maintaining proper electrolyte concentration. The electrolyte recirculation system includes a salt concentration monitor, a pump and a salt reservoir.

20

The dual graphite system requires specific electrolytes for optimal results. While a wide range of options exist, extensive appropriate testing,

theoretical design, and other factors help to design an electrolyte that is most appropriate for the dual graphite system. Testing for any, or any number of, properties is always performed using a complete dual graphite cell or battery system with a design of experiment in place. Data analysis is accomplished
5 through extensive statistical analysis and patterns thus seen where possible. The other factors involved are those set by the inventors as reasonable constraints for consumer goods and performance criteria. These include items such as safety, salt dissolution capability, conductivity, voltage stability, and high capacity (anionic and cationic). Therefore, salts chosen for use in
10 dual graphite electrolytes must be readily ionizable, at least relatively voltage stable, dissolvable in the chosen solvent to a minimum of 15 wt% (depending upon cell design), and intercalatable. Also, the solvents chosen for use in dual graphite electrolytes must support the above needs of the salt, in addition to itself having a voltage stability that is appropriate for the dual
15 graphite system.

In-depth studies of salts, solvents, and electrolytes (salt + solvent) have been performed by numerous entities, while the knowledge on high concentration electrolytes, 1M solutions and greater, in terms of precise
20 structure is still relatively unknown in the art. The use of some simple models is beneficial when relating these high concentration electrolytes to use in a dual graphite system.

Dipole moments and numerous other physical properties of solvents have been considered to explain the behavior of low concentration, less than 1M, electrolytes. However, low concentration electrolytes have multiple interactions that make the physical chemistry difficult to pinpoint and anion capacity is rarely the focus.

A pattern has been found in electrolytes with salt concentrations of 25 weight percent and greater. At these high concentrations, single solvents and the interactions with the salts to provide anion intercalation have been shown to be tied very closely to the solvent dipole moment and the electrolyte conductivity. Following a few easily measurable or calculable physical properties there is provided a model that can be run on any candidate solvent to determine if the solvent has the ability to give the desired capacity results without having to spend time, money and materials to test every imaginable solvent in a dual graphite cell. The single solvent electrolyte systems that have been proven to provide dual graphite capacity for anion and cation intercalation must meet the following qualifications.

1. Only solvents that dissolve at least 25wt% salt are used for capacity and conductivity measurements.

2. Acyclic solvents with dipole moments of less than 2.0 dynes, which are measured or calculated using the DelRe model or CNDO open shell model, that when blended with the salt have a conductivity of greater than 0.5mS/cm. Examples of acyclic solvents include, but are not limited to,

dimethyl carbonate, dimethyl sulfite, methyl acetate, and ethyl methyl carbonate.

3. Cyclic solvents with dipole moments between 7.0 and 4.5 dynes, are measured or calculated using the DelRe model or CNDO open shell model,
5 that when blended with the salt have a conductivity of greater than 2.0mS/cm.

Examples of cyclic solvents include, but are not limited to, sulfolane, glycol sulfite, and propylene carbonate.

4. Benzene based compounds studied to date have no dual graphite capacity, in compounds such as pyridine (PY) and toluene (TL) these cyclic
10 solvents fall out of the required dipole moment requirements (PY's is around 2 dynes and TL is around 1 dyne). Other benzene base compounds, such as nitrobenzene (NB), do not dissolve the required amount of salt.

When a new sample is investigated, a structure is drawn with some
15 modeling software (such as ChemSW ®) and the dipole moment is calculated or it can be experimentally measured. If the dipole moment does not meet the requirements for the structure type, it is not pursued as a capacity enhancing solvent or capacity additive for dual graphite system electrolytes. If the dipole moment does meet the requirements for the structure type, a
20 small electrolyte sample is prepared and conductivity measured. A dual graphite cell is built for capacity measurement only if the requirements are met. Capacity enhancing solvents for dual graphite cells meet these requirements: acyclic compounds have <2D dipole, >0.5mS/cm conductivity

and are able to solubilize at least 25wt% salt; cyclic solvents have 4.5 to 7D dipole, >2mS/cm conductivity, and do not contain a benzene ring and be able to solubilize at least 25wt% salt.

5 Trends can also be seen in carbonate solvent compounds and dual graphite anion capacity. Longer chain acyclic carbonates produce less capacity, lower conductivity, and have lower voltage stability than their shorter acyclic counterparts.

10 Various additives can be mixed in small portions with the single solvent compounds described above without detrimentally affecting the capacity performance. Additives, including non-flammable additives like TEPO (triethylphosphate), or conductive additives like PN (propionitrile); while none of these additives meet the model requirements for capacity enhancement as
15 single solvents themselves, nor do they achieve reasonable capacity upon testing, when used as additives in 10wt% or less quantities are not detrimental to the capacity measured in the supporting solvent (i.e. SL alone measures at least 160mAh/g capacity and when 10wt% TEPO is added to the SL the capacity is the same). In fact they can occasionally improve capacity
20 achieved in the supporting solvent.

Additional patterns in dual graphite capacity data are seen in multiple solvent blends. For example, binary blends of one acyclic and one cyclic

carbonate provide reasonable capacity at all blend ratios. One example is EC:DMC (ethylene carbonate:dimethyl carbonate) with blends from 10:90 to 90:10 by weight with 15wt% LiClO₄ achieving over 100mAh/g capacity, the preferred ratio being 50:50 with capacities over 180mAh/g. Another binary blend pattern is that of two cyclic carbonates mixed together. One example is EC:PC (PC=propylene carbonate) 10:90 by weight with 15wt% LiClO₄ achieving at least 160mAh/g anion capacity; other blends from 10:90 to 90:10 also achieve over 100mAh/g capacity.

Another binary blend pattern involves the use of a binary solvent blend using a sulfone, such as sulfolane (SL), or a cyclic carbonate, such as ethylene carbonate, in combination with an ester, such as methyl acetate (MA). While all ratios of these binary blends give dual graphite capacity, the ratio of two parts sulfone or cyclic carbonate to one part ester by weight is the most desirable.

Other preferred binary blends for a dual graphite/intercalation cell include: sulfone and carbonate blends (i.e. SL:PC at 25:75 to 75:25, or SL:DMC at 35:65, or Ethyl Methyl Sulfone:DMC at 50:50), sulfone and nitrile blends (i.e. SL:PN at 90:10), cyclic ester and carbonate blends (i.e. gamma-butyrolactone:DMC at 50:50).

Many examples of higher order blends for use in the dual graphite cell also exist. They are composed of the following types of compounds: ethers, such as diethyl or 2-methoxyethyl); amides (like dimethyl acetamide or dimethyl formamide); esters including cyclic esters (for example GBL) cyclic carbonates or acyclic carbonates; nitriles (for example, propionitrile or 3-methoxypropionitrile); sulfones (for example, sulfolane, ethyl methyl sulfone, 3-methyl sulfolane, ethyl isopropyl sulfone, etc.); sulfoxides (such DMSO); sulfites (such as dimethyl sulfite); ketones (such as MEK); and furans (for example, THF or dioxane). Organophosphates (such as TEPO). The most preferred solvents are EC, PC, DMC, DEC, GBL, SL, EMS, MSL, EMC, MA, TEPO, and GS. The least preferred solvents are MEK, MIPK, MF, EA, DMS, DG, DEE, MTHF, and BST.

There are several tertiary blends of special interest for capacity in dual graphite cells. They include various ratio blends of SL:EC:DMC (especially 6:70:24), EC:DMC:TEPO (especially 67:28:5), EC:DMC:GLN (especially 49:49:2), SL:MA:PC (15:15:70); EC:PC:MA (9:76:15); SL:MA:DMC (15:15:70); EMC:PC:MA (9:67:24); and EC:PC:TEPO (19:76:5).

Another pattern seen in all electrolytes with conductivities between about 6.2 and about 7.7mS/cm is that they consistently achieve anion capacities greater than 100Ah/g. This is shown in Figure 1.

Electrolytes with high anodic voltages have always been of interest in electrochemical batteries. Dual graphite systems also require high voltage stability. Higher anodic voltage stability provides the dual graphite systems with less solvent degradation which increases cycle life of a cell, and allows
5 for higher possible charge voltages increasing various cell performances such as energy density by increasing the midpoint voltage on discharge. Testing of voltage stability in an electrolyte for use in a dual graphite cell must occur in a dual graphite cell. These test cells then have a graphite working electrode and a graphite counter electrode, while the reference electrode used is lithium
10 metal. This test set up portrays the true activities of cell components in a dual graphite environment. Anion intercalation voltages depend upon the anion used; they are generally between 3.9 and 4.9V in a dual graphite system, this is therefore the minimum voltage stability that makes a solvent useful.

15 The following single solvents with at least 25wt% salt are representative of appropriate voltage stability materials: PC (5V), EC (>5.5V), DMC (4.9V), SL(>5.5V), GS(4.6V), DEE (5.3V), GBL(5.5V). The solvents listed are representative of compounds of that class; for instance DEC & DMC are both acyclic carbonates and both are stable to 4.9V. As is the case with
20 capacity, additives of 10 wt% or less can be used with single solvents without detrimental affects on stability.

Additional patterns in dual graphite voltage stability data are seen in binary solvent blends. For example, binary blends of one acyclic and one cyclic carbonate provide similar voltage stability results at all blend ratios. One example is EC:DMC (ethylene carbonate:dimethyl carbonate) with blends from 10:90 to 90:10 by weight with 15wt% LiClO₄ achieving approximately 4.9V, the preferred ratio being 90:10 with a stability of 5.3V. Another binary blend pattern is that of a mixture of 2 cyclic carbonates. One example is EC:PC 33:67 by weight with 15wt% LiClO₄ achieving at least 5.5V stability; other blends from 10:90 to 90:10 also achieve stability over 5V.

10

Another binary blend pattern example involves the use of a binary solvent blend using a sulfone, such as sulfolane (SL), or a cyclic carbonate, such as ethylene carbonate, in combination with an ester, such as methyl acetate (MA). While all ratios of these binary blends give voltage stability greater than 5V, the ratio of 2 parts sulfone or cyclic carbonate to 1 part ester by weight is the most desirable.

15

Other preferred blends for a dual graphite/intercalation cell with reasonable stability include, but are not limited to: sulfone and carbonate blends (i.e. SL:PC at 25:75 to 75:25, or SL:DMC at 35:65, or Ethyl Methyl Sulfone:DMC at 50:50), sulfone and nitrile blends (i.e. SL:PN at 90:10), cyclic ester and carbonate blends (i.e. gamma-butyrolactone:DMC at 50:50),

20

EC/PC/TEPO (19:76:5), EC/PC/MA (9:76:15), PC/TEPO (50:50), SL/EC/DMC (6:70:24), and EMC/PC/MA (9:67:24).

The most preferred salts for use in dual graphite systems are, in order of preference, LiClO₄, LiPF₆, LiBF₄, LiCF₃SO₃, or mixtures thereof. Least preferred salts are LiCF₃CO₂, LiAsF₆, LiCl, LiBr, LiI, LiSCN. The higher the salt concentration, the higher the possible dual graphite battery energy density. The preferred salt concentration in dual graphite cells is between 15wt% and saturation. The most preferred salt concentration range is from 15 to 40wt% of the electrolyte.

Another concern with regard to the energy storage cell is the total weight of the cell. It is therefore necessary to determine methods and mechanisms for limiting the weight of the cell. One method of maintaining electrolyte concentrations during charge and discharge, and to improve cell energy density is to remove the excess solvent from a dual graphite cell. This can be accomplished with an electrolyte recirculation system. To optimize a cell's energy density, all inactive materials have to be eliminated or reduced to minimize cell weight. In the dual graphite energy storage system, these materials include the current collector materials, separator, solvent, and packaging. The only active materials that contribute directly to cell capacity are the carbonaceous fibers and the salt. The largest inactive weight contributor is the solvent in the electrolyte solution, which is required to carry

the salt. Without a material to aid in ion transfer (such as an organic solvent, ionic liquid, gel, or polymer) the system does not work, since this is the mechanism for intercalation into the graphite materials. Reducing the solvent quantity, however, also means reducing the amount of salt. Otherwise, the salt can come out of solution or its concentration can be too high and thereby reducing the electrolyte conductivity. The more conductive the electrolyte, the more mobile the ions are.

In order to maximize the energy density of a cell; one has to maximize salt concentration and at the same time minimize solvent weight without any conductivity loss. To minimize the amount of solvent required to carry the salt, but still provide the cell with the appropriate amount of ions for intercalation, an electrolyte recirculation system can be used. This is a system that allows a cell to be continually cycled at the most conductive salt concentration. The recirculation system is designed to replenish and to remove the salt as needed to maintain maximum cell conductivity, which in turn minimizes cell resistance. This system requires a concentration monitor which monitors the salt concentration and allows salt to be removed or added to the electrolyte as needed using a pump. The system also requires that a salt reservoir be maintained which stores any unused salt. During charge, as the anions and cations are intercalating into the graphite fibers, salt concentration is reduced in the electrolyte, therefore the circulation system adds salt at that time. During discharge, as ions are deintercalating, the salt

concentration increases; therefore the circulation system removes the excess salt from the cell and stores it in the salt reservoir. This method reduces the required solvent weight, while maintaining optimal dual graphite cell conditions. One circulation system can be tied to one or multiple dual
5 graphite cells or batteries. The electrolyte recirculating system optimizes the cell capacity and the energy density of a dual graphite energy storage system, because the recirculation creates the most conductive salt concentrations without ever depleting the salt supply or ions in the energy storage device. The system replenishes and removes salt as needed to
10 maximize cell conductivity which in turn minimizes cell resistance.

Throughout this application, various publications, including United States patents, are referenced by author and year and patents by number. Full citations for the publications are listed below. The disclosures of these
15 publications and patents in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

The invention has been described in an illustrative manner, and it is to
20 be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation.

Obviously, many modifications and variations of the present invention

are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims, the invention can be practiced otherwise than as specifically described.

Insert Table 1 List of Solvent Abbreviations

AN	Acetonitrile
BST	1,4-Butane sultone
DEC	Diethyl Carbonate
DEE	Diethyl ether
DG	Diglyme (or 2-methoxyethyl ether)
DMA	Dimethyl acetamide
DMC	Dimethyl Carbonate
DME	Dimethoxyethane (or Glyme)
DMEU	Dimethyl-2-imidazolidinone (or Dimethylethylene urea)
DMF	Dimethyl formamide
DMS	Dimethyl sulfite
DMSO	Dimethylsulfoxide
EA	Ethyl acetate
EC	Ethylene Carbonate
EIS	Ethyl isopropyl sulfone
EMC	Ethyl methyl carbonate
EMS	Ethyl methyl sulfone
ESS	Ethyl sec-butyl sulfone
GBL	γ -Butyrolactone
GLN	Glutaronitrile
GS	Glycol sulfite
MA	Methyl Acetate
MEK	Methyl ethyl ketone
MF	Methyl Formate
MIPK	Methyl isopropyl ketone
MPN	3-Methoxypropionitrile
MSL	3-Methyl sulfolane
MTHF	2-Methyl tetrahydrofuran
NB	Nitrobenzene
NE	Nitroethane
NM	Nitromethane
NMO	N-methyl-2-oxazolidinone
NMP	N-methyl-2-pyrrolidinone
PC	Propylene Carbonate
PN	Propionitrile
PY	Pyridine
SL	Sulfolane
TEP	Triethylphosphite
TEPO	Triethylphosphate
THF	Tetrahydrofuran
TL	Toluene
TMSO	Tetramethylene sulfoxide
TMU	Tetramethyl urea

REFERENCES

U.S. Patent Documents

4,830,938	5/1989
4,865,931	9/1989
5,993,997	

Other References

- 1 Dahn, J.R. and Steel, J.A., Energy and capacity projections for practical dual-graphite cells, *Journal of The Electrochemical Society*, Vol. 147, No. 3, 2000, p899-901.
- 2 Steel, J.A. and Dahn, J.R., Electrochemical intercalation of PF6 into graphite, *Journal of The Electrochemical Society*, Vol. 147, No. 3, 2000, p892-898.
- 3 Santhanam, R. and Noel, M., Electrochemical intercalation of ionic species of tetrabutylammonium perchlorate on graphite electrodes. A potential dual-intercalation battery system, *Journal of Power Sources*, Vol. 56, 1995, p101-105.
- 4 Santhanam, R. and Noel, M., Electrochemical intercalation of cationic and anionic species from a lithium perchlorate-propylene carbonate system-a rocking-chair type of dual-intercalation system, *Journal of Power Sources*, Vol. 76, 1998, p147-152.
- 5 Noel, M., and Santhanam, R., Electrochemistry of graphite intercalation compounds, *Journal of Power Sources*, Vol. 72, 1998, p53-65.
- 6 Santhanam, R. and Noel, M., Influence of polymeric binder on the stability and intercalation/de-intercalation behaviour of graphite electrodes in non-aqueous solvents, *Journal of Power Sources*, Vol. 63, 1996, p1-6.
- 7 Santhanam, R. and Noel, M., Effects of solvents on the intercalation/de-intercalation behaviour of monovalent ionic species from non-aqueous solvents on polypropylene-graphite composite electrode, *Journal of Power Sources*, Vol. 63, 1996, p1-6.
- 8 Xu, Kang, et. al., Toward reliable values of electrochemical stability limits for electrolytes, *Journal of The Electrochemical Society*, Vol. 46, No. 11, 1999, p4172-4178.

CLAIMS

What is claimed is:

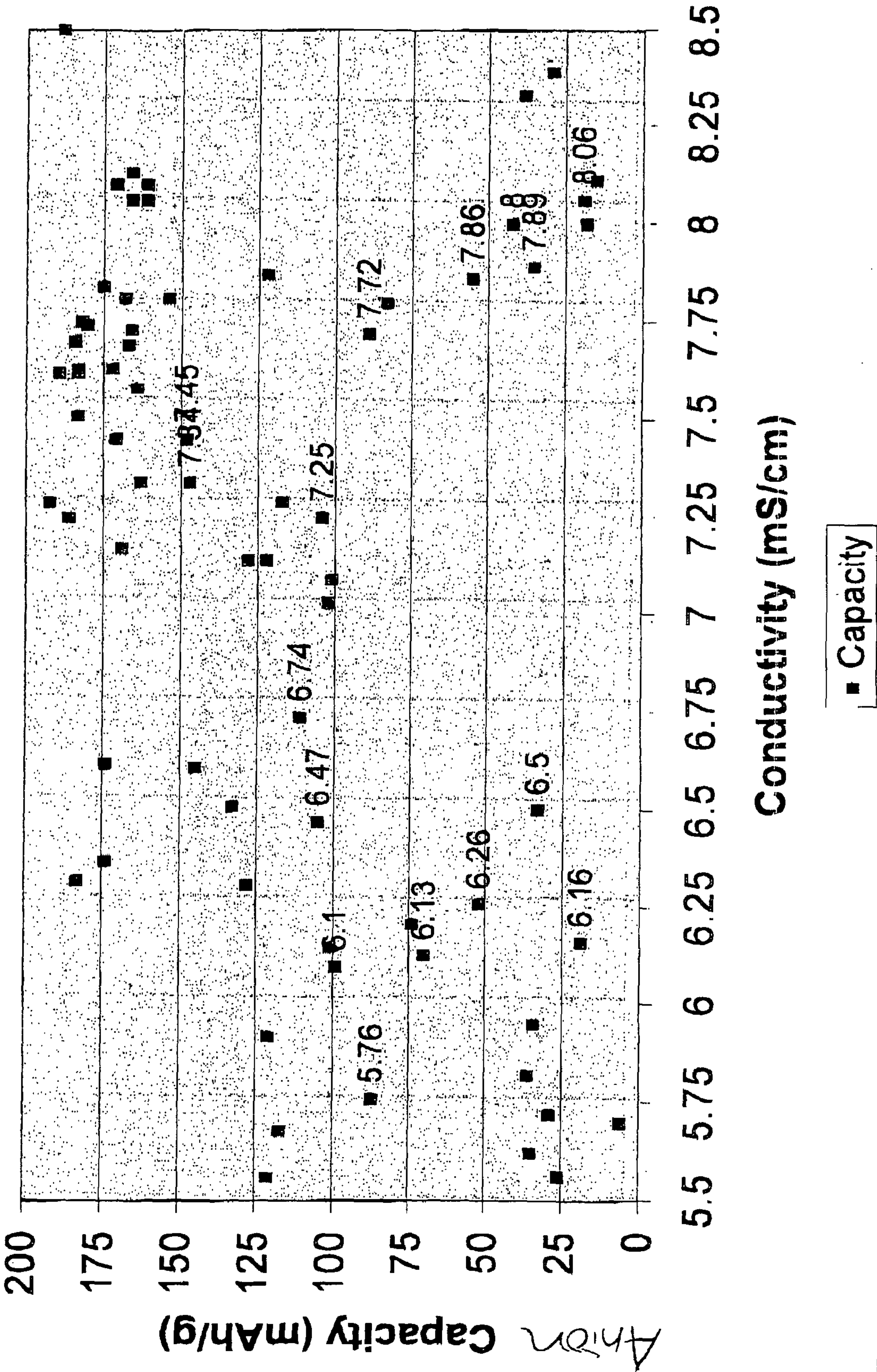
1. An electrolyte for use in a dual graphite cell, said electrolyte comprising a solvent that dissolves at least 25 wt% salt.
2. The electrolyte according to claim 1, wherein said solvent is an acyclic solvent.
3. The electrolyte according to claim 2, wherein said acyclic solvent has dipole movements of less than 2.0 dynes.
4. The electrolyte according to claim 2, wherein said acyclic solvent has a conductivity of greater than 0.5 mS/cm.
5. The electrolyte according to claim 3, wherein said acyclic solvent is selected from the group consisting essentially of dimethyl carbonate, dimethyl sulfite, methyl acetate, and ethyl methyl carbonate.
6. The electrolyte according to claim 1, wherein said solvent is a cyclic solvent.
7. The electrolyte according to claim 6, wherein said cyclic solvent has dipole movements in the range of 7.0 and 4.5 dynes.
8. The electrolyte according to claim 6, wherein said cyclic solvent has a conductivity of greater than 2mS/cm.
9. The electrolyte according to claim 8, wherein said cyclic solvent is selected from the group consisting essentially of sulfolane, glycol

sulfite, propylene carbonate, and ethylene carbonate.

10. An electrolyte for use in a dual graphite cell, said electrolyte comprising a solvent stable above 5 V.
11. An electrolyte recirculation system comprising:
 - a salt concentration monitor;
 - a pump; and
 - a salt reservoir.
12. An electrolyte for use in a dual graphite cell, said electrolyte comprising a multiple solvent electrolyte that dissolves at least 15 wt% LiClO_4 .
13. The electrolyte according to claim 12, wherein said multiple electrolyte solvent is made of a blend of at least two solvents selected from the group consisting essentially of ethers, amides, esters including cyclic esters, cyclic carbonates or acyclic carbonates, nitriles, sulfones, sulfoxides, sulfites, ketones, furans, and organophosphates.
14. The electrolyte according to claim 12, wherein said multiple electrolyte solvent is made of one acyclic carbonate or cyclic carbonate and one cyclic carbonate.
15. The electrolyte according to claim 12, wherein said binary solvent ranges from 10 parts carbonate:90 parts carbonate to 90 parts carbonate:10 parts carbonate.
16. The electrolyte according to claim 12, wherein said electrolyte is made of two parts sulfone or carbonate and one part ester.

17. The electrolyte according to claim 12, wherein said solvent is a blend of at least two solvents, said blend being selected from the group consisting essentially of SL:DMC (35:65), SL:EC:DMC (6:70:24), EC:DMC:TEPO (67:28:5), SL:MA:PC (15:15:70), EC:PC:MA (9:76:15), SL:MA:DMC (15:15:70), EC:PC:TEPO (19:76:5), EMC:PC:MA (9:67:24), and EC:DMC:GLN (49:49:2).
18. The electrolyte according to claim 12, wherein said electrolyte has a conductivity between 6.7 and 7.7 mS/cm.
19. The electrolyte according to claim 12, wherein said electrolyte includes a salt selected from the group consisting essentially of LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , and mixtures thereof in a concentration of at least 15wt%.

Elyte Characteristics



Elyte Characteristics

