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Smart et al.

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(45) **Date of Patent: Jun. 10, 2014**

(54) **LITHIUM-ION ELECTROLYTES WITH FLUOROESTER CO-SOLVENTS**

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Related U.S. Application Data

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(51) **Int. Cl.**
H01M 6/16 (2006.01)
H01M 6/04 (2006.01)

(52) **U.S. Cl.**
USPC **429/326**; 429/188; 429/189; 429/324

(58) **Field of Classification Search**
None
See application file for complete search history.

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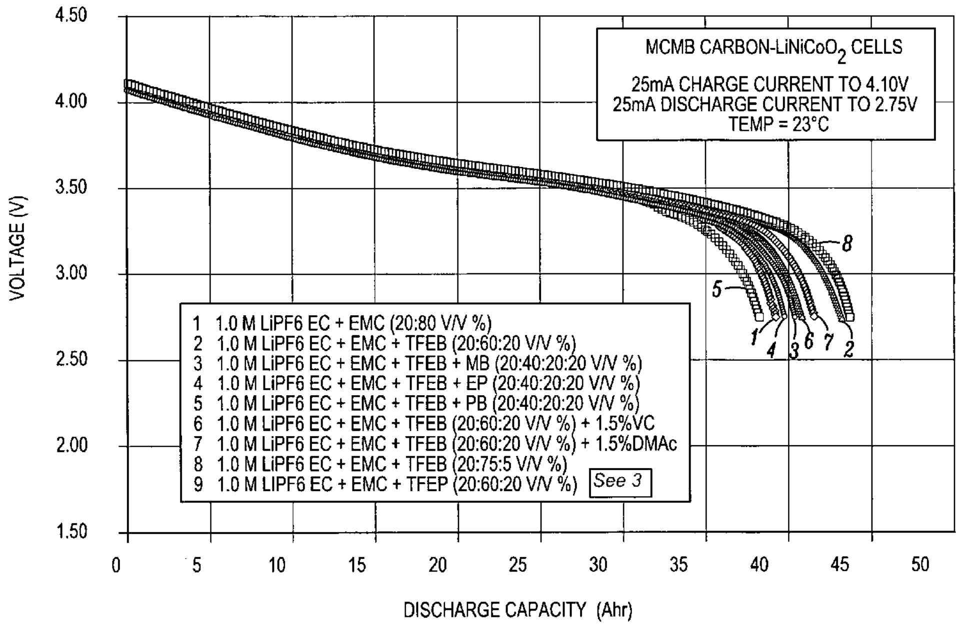
(57) **ABSTRACT**

An embodiment lithium-ion battery comprising a lithium-ion electrolyte of ethylene carbonate; ethyl methyl carbonate; and at least one solvent selected from the group consisting of trifluoroethyl butyrate, ethyl trifluoroacetate, trifluoroethyl acetate, methyl pentafluoropropionate, and 2,2,2-trifluoroethyl propionate. Other embodiments are described and claimed.

30 Claims, 10 Drawing Sheets



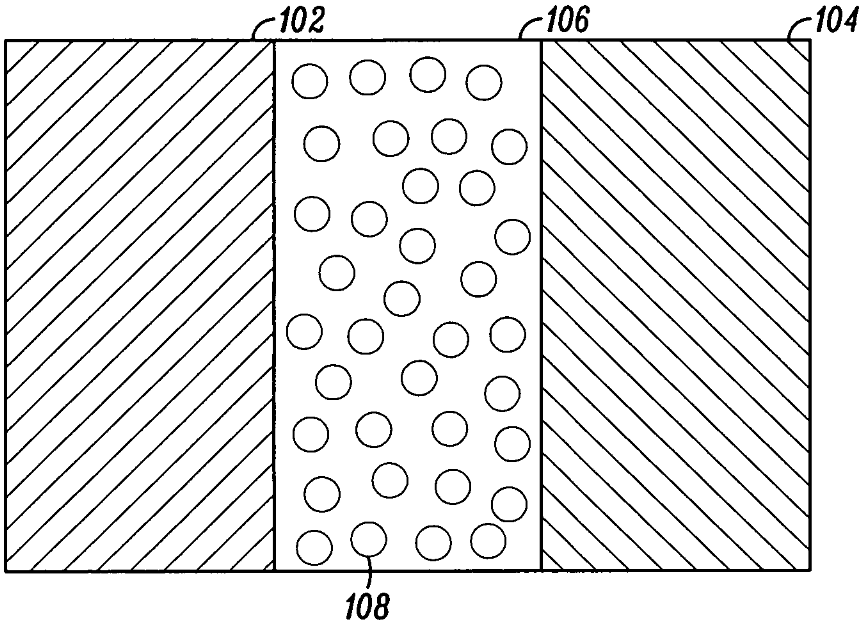


FIG. 1

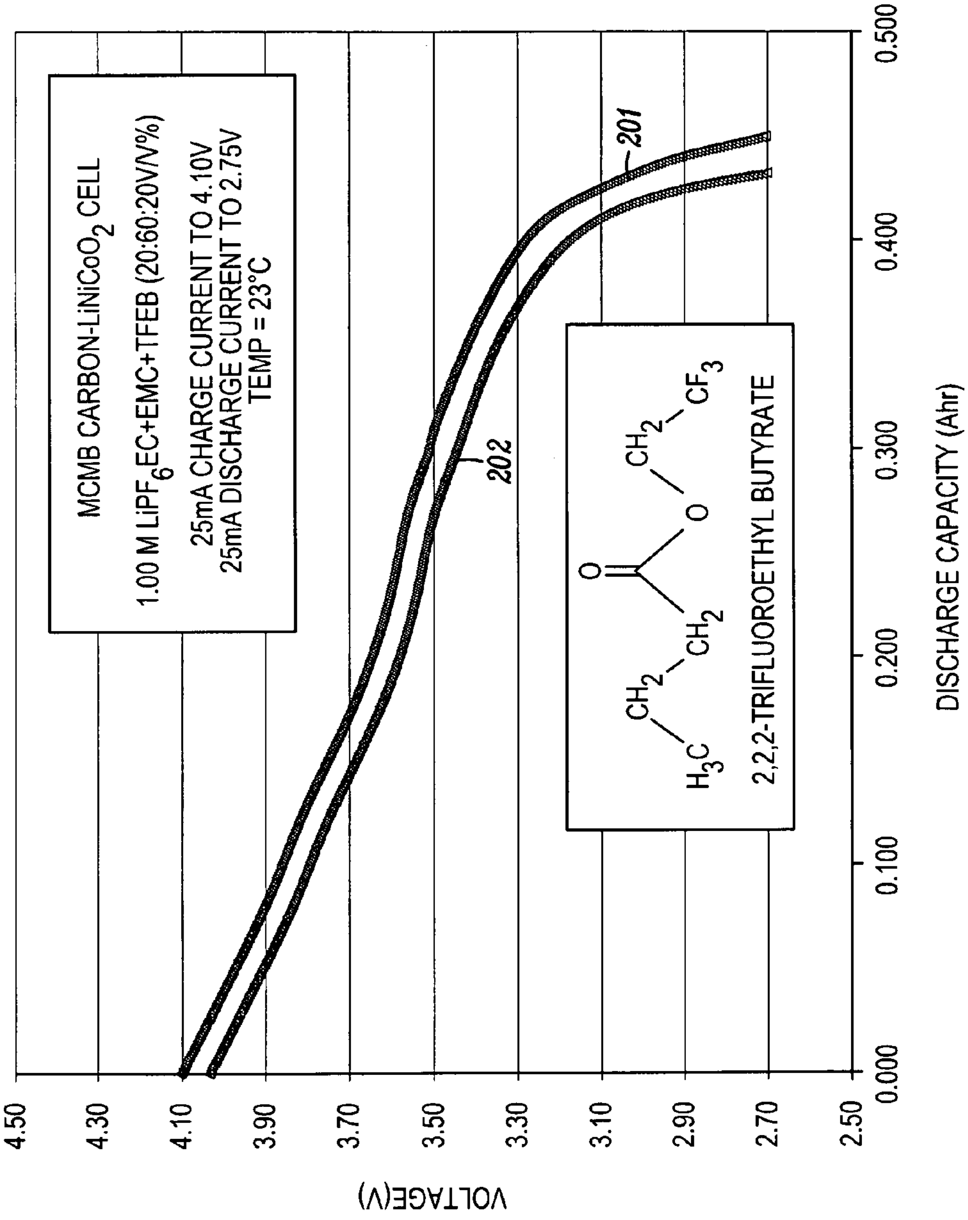

MCMB CARBON-LiNiCoO2 CELL
1.00 M LiPF6EC+EMC+TFEB (20:60:20V/V%)
25mA CHARGE CURRENT TO 4.10V
25mA DISCHARGE CURRENT TO 2.75V
TEMP = 23°C
201
202
H3C
CH2
CH2
O
O
CH2
CF3
2,2,2-TRIFLUOROETHYL BUTYRATE
VOLTAGE(V)
4.50
4.30
4.10
3.90
3.70
3.50
3.30
3.10
2.90
2.70
2.50
DISCHARGE CAPACITY (Ahr)
0.000
0.100
0.200
0.300
0.400
0.500

FIG. 2

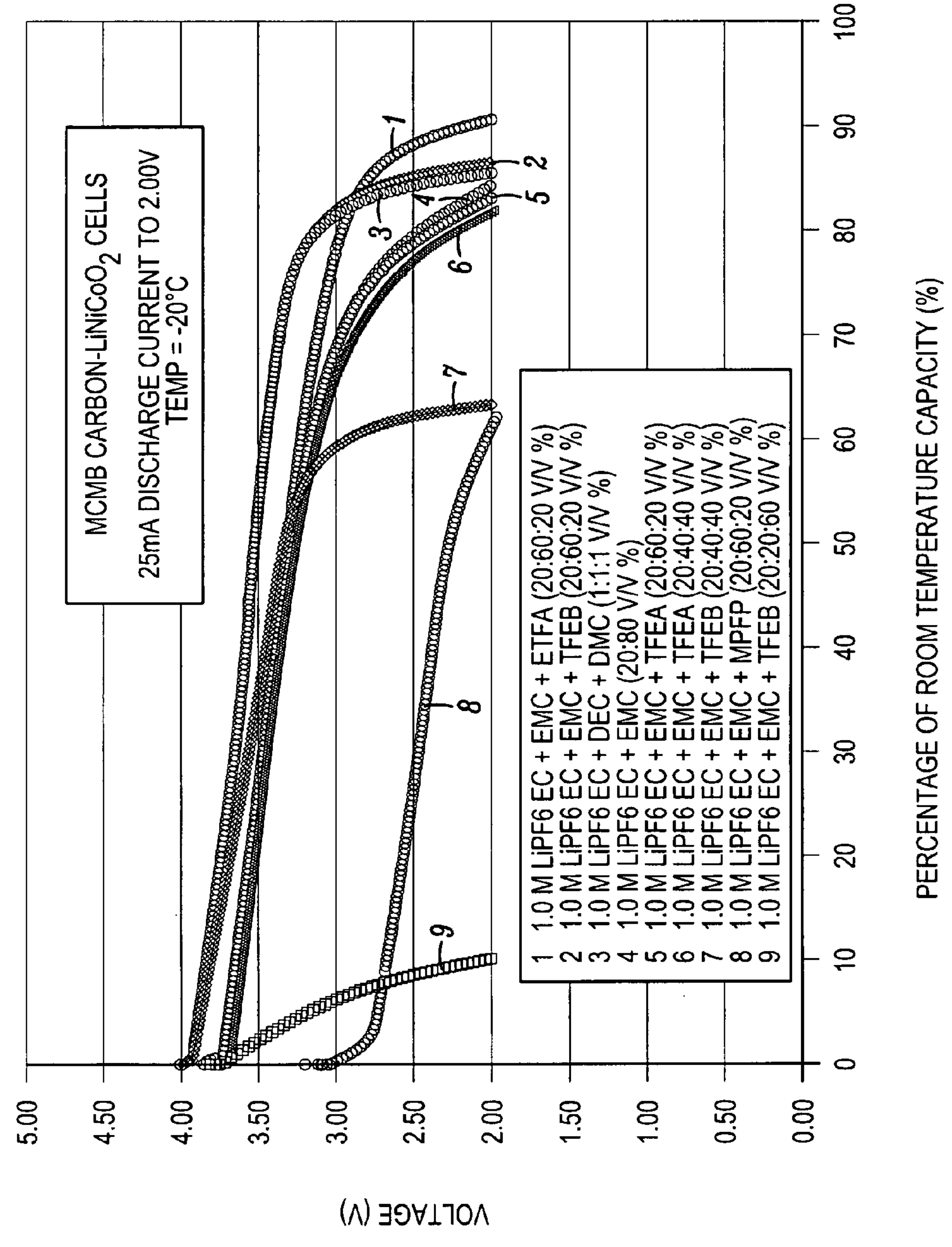

MCMB CARBON-LiNiCoO2 CELLS
25mA DISCHARGE CURRENT TO 2.00V
TEMP = -20°C
1 1.0 M LiPF6 EC + EMC + ETFA (20:60:20 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
3 1.0 M LiPF6 EC + DEC + DMC (1:1:1 V/V %)
4 1.0 M LiPF6 EC + EMC (20:80 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEA (20:60:20 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEA (20:40:40 V/V %)
7 1.0 M LiPF6 EC + EMC + TFEB (20:40:40 V/V %)
8 1.0 M LiPF6 EC + EMC + MPFP (20:60:20 V/V %)
9 1.0 M LiPF6 EC + EMC + TFEB (20:20:60 V/V %)
1
2
3
4
5
6
7
8
9
VOLTAGE (V)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
0
10
20
30
40
50
60
70
80
90
100

FIG. 3

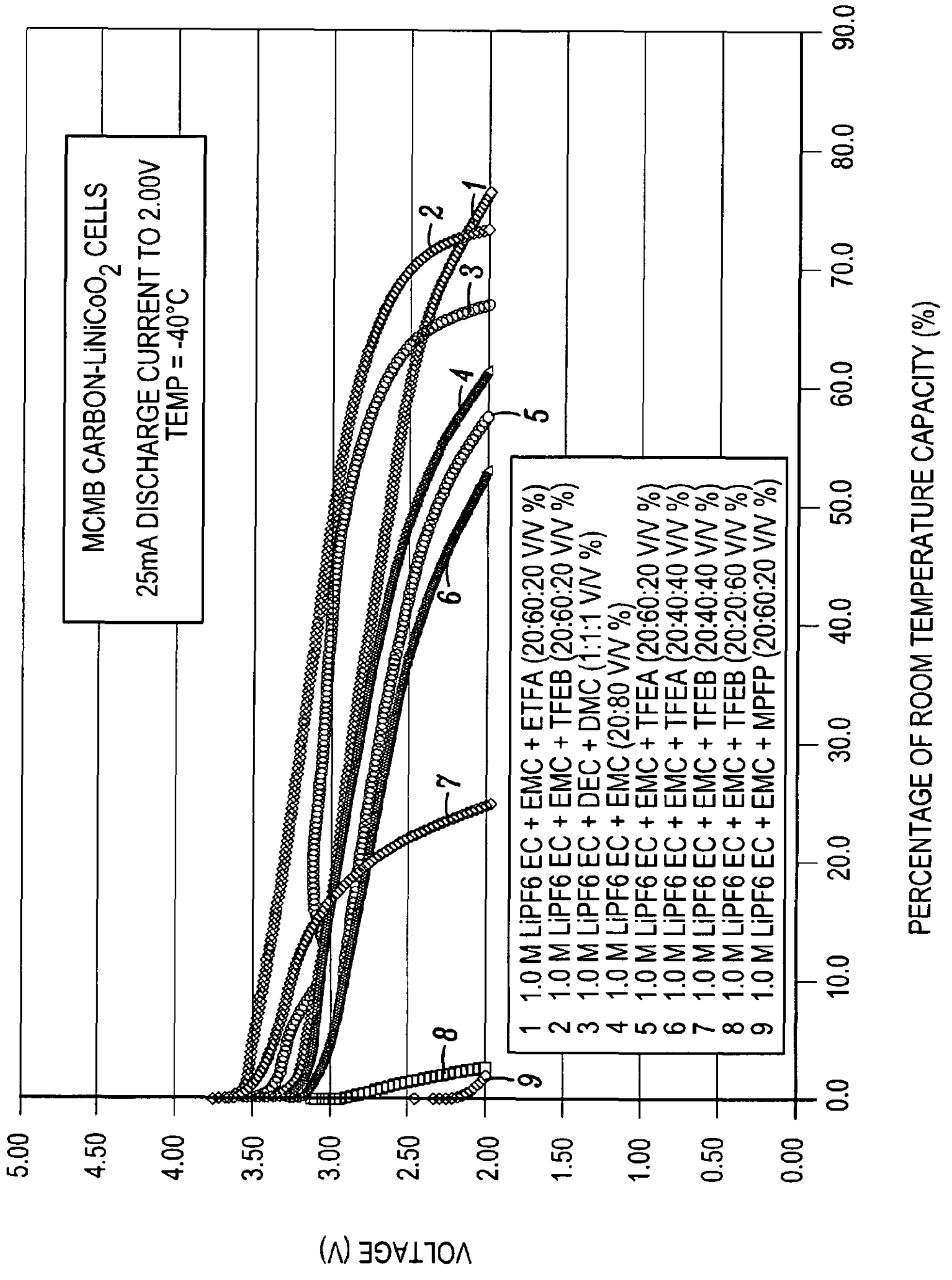

MCMB CARBON-LiNiCoO$_2$ CELLS
25mA DISCHARGE CURRENT TO 2.00V
TEMP = -40°C
1 1.0 M LiPF6 EC + EMC + ETFA (20:60:20 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
3 1.0 M LiPF6 EC + DEC + DMC (1:1:1 V/V %)
4 1.0 M LiPF6 EC + EMC (20:80 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEA (20:60:20 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEA (20:40:40 V/V %)
7 1.0 M LiPF6 EC + EMC + TFEB (20:40:40 V/V %)
8 1.0 M LiPF6 EC + EMC + TFEB (20:20:60 V/V %)
9 1.0 M LiPF6 EC + EMC + MPFP (20:60:20 V/V %)
1
2
3
4
5
6
7
8
9
VOLTAGE (V)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0

FIG. 4

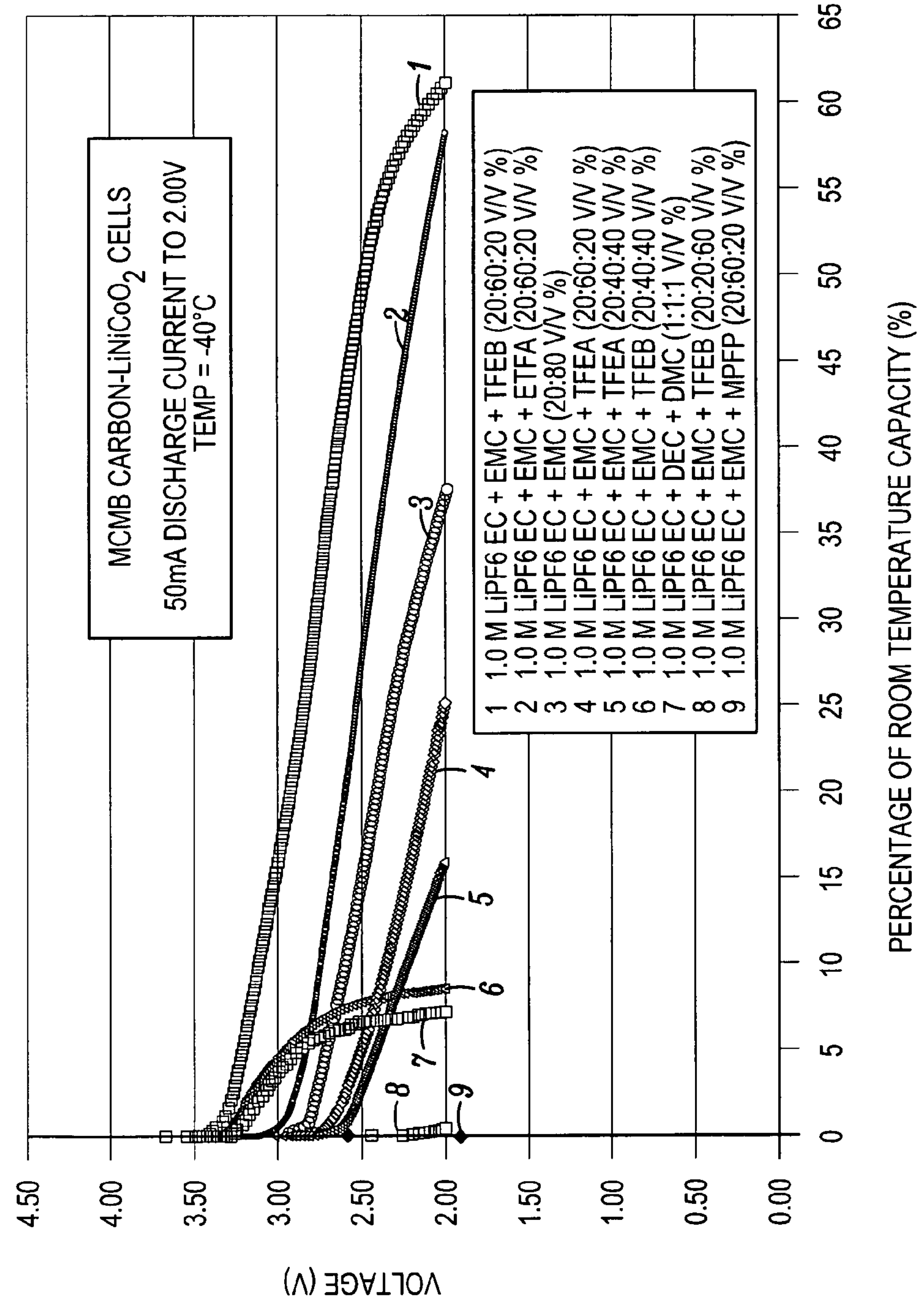

MCMB CARBON-LiNiCoO$_2$ CELLS
50mA DISCHARGE CURRENT TO 2.00V
TEMP = -40°C
1 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
2 1.0 M LiPF6 EC + EMC + ETFA (20:60:20 V/V %)
3 1.0 M LiPF6 EC + EMC (20:80 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEA (20:60:20 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEA (20:40:40 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEB (20:40:40 V/V %)
7 1.0 M LiPF6 EC + DEC + DMC (1:1:1 V/V %)
8 1.0 M LiPF6 EC + EMC + TFEB (20:20:60 V/V %)
9 1.0 M LiPF6 EC + EMC + MPFP (20:60:20 V/V %)
1
2
3
4
5
6
7
8
9
VOLTAGE (V)
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
0
5
10
15
20
25
30
35
40
45
50
55
60
65

FIG. 5

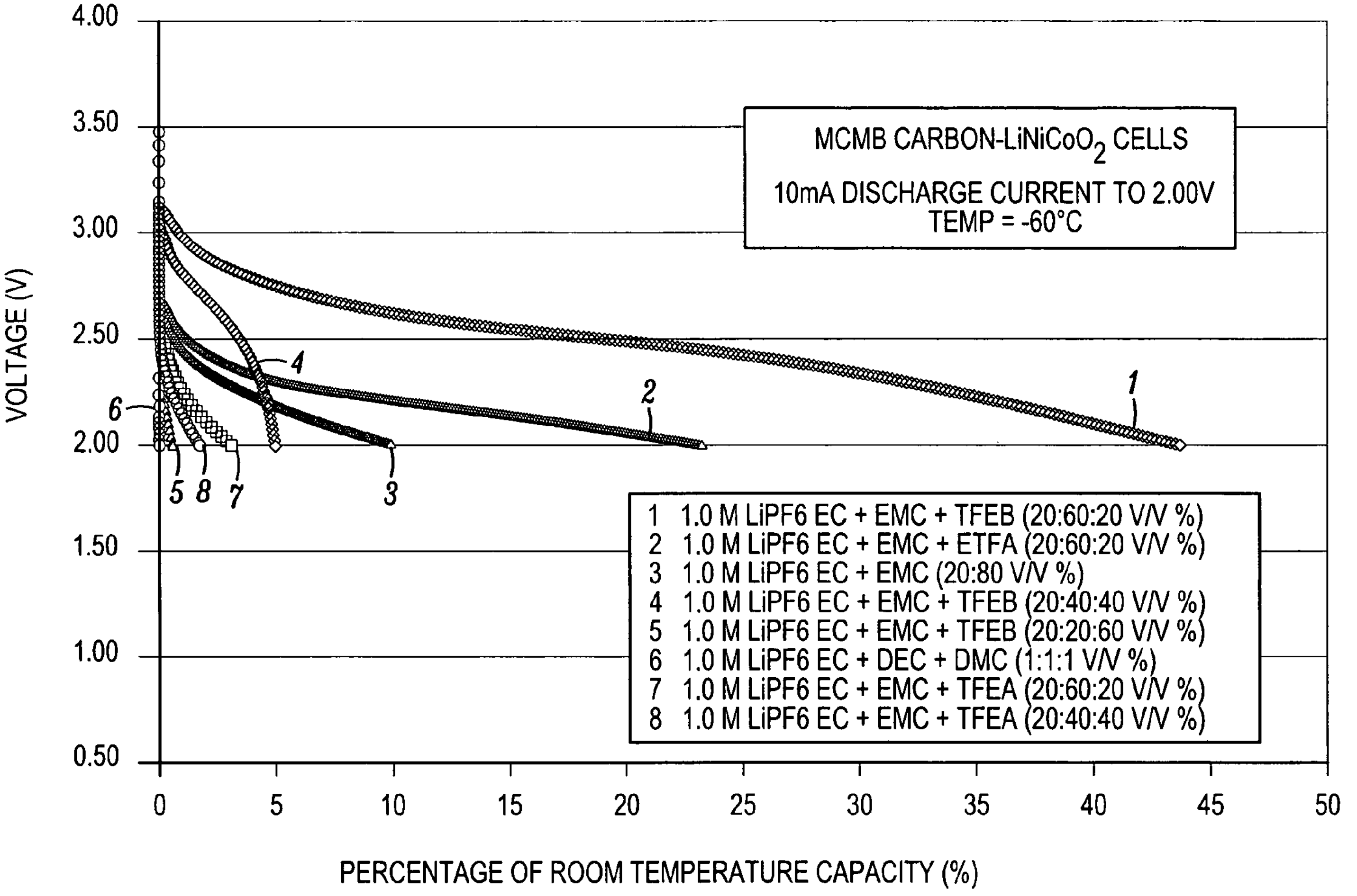

MCMB CARBON-LiNiCoO$_2$ CELLS
10mA DISCHARGE CURRENT TO 2.00V
TEMP = -60°C
VOLTAGE (V)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0
5
10
15
20
25
30
35
40
45
50
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
1
2
3
4
5
6
7
8
1 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
2 1.0 M LiPF6 EC + EMC + ETFA (20:60:20 V/V %)
3 1.0 M LiPF6 EC + EMC (20:80 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEB (20:40:40 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEB (20:20:60 V/V %)
6 1.0 M LiPF6 EC + DEC + DMC (1:1:1 V/V %)
7 1.0 M LiPF6 EC + EMC + TFEA (20:60:20 V/V %)
8 1.0 M LiPF6 EC + EMC + TFEA (20:40:40 V/V %)

FIG. 6

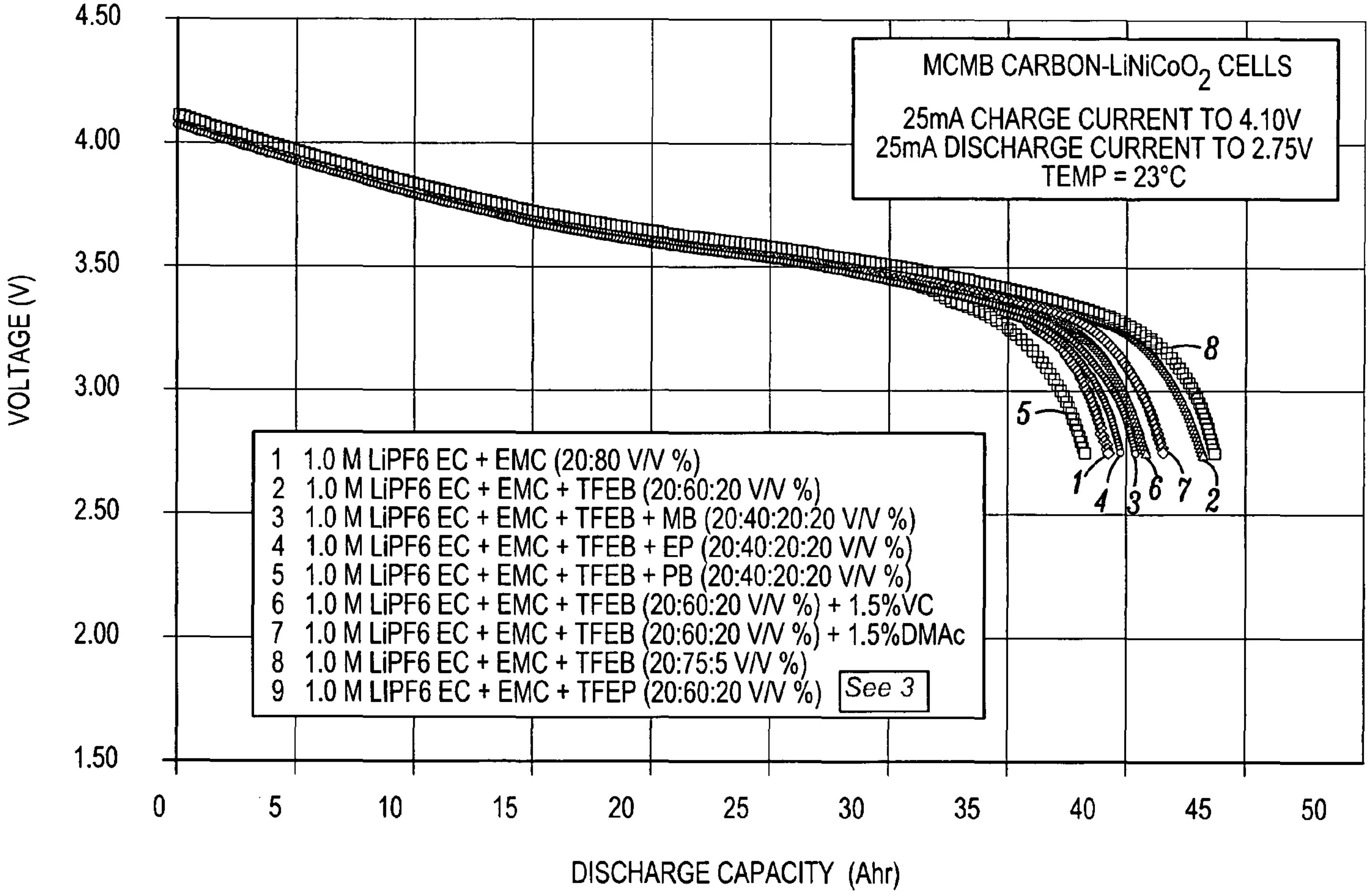

MCMB CARBON-LiNiCoO$_2$ CELLS
25mA CHARGE CURRENT TO 4.10V
25mA DISCHARGE CURRENT TO 2.75V
TEMP = 23°C
1 1.0 M LiPF6 EC + EMC (20:80 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
3 1.0 M LiPF6 EC + EMC + TFEB + MB (20:40:20:20 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEB + EP (20:40:20:20 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEB + PB (20:40:20:20 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%VC
7 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%DMAc
8 1.0 M LiPF6 EC + EMC + TFEB (20:75:5 V/V %)
9 1.0 M LiPF6 EC + EMC + TFEP (20:60:20 V/V %)
See 3
VOLTAGE (V)
4.50
4.00
3.50
3.00
2.50
2.00
1.50
DISCHARGE CAPACITY (Ahr)
0
5
10
15
20
25
30
35
40
45
50
8
5
1
4
3
6
7
2

FIG. 7

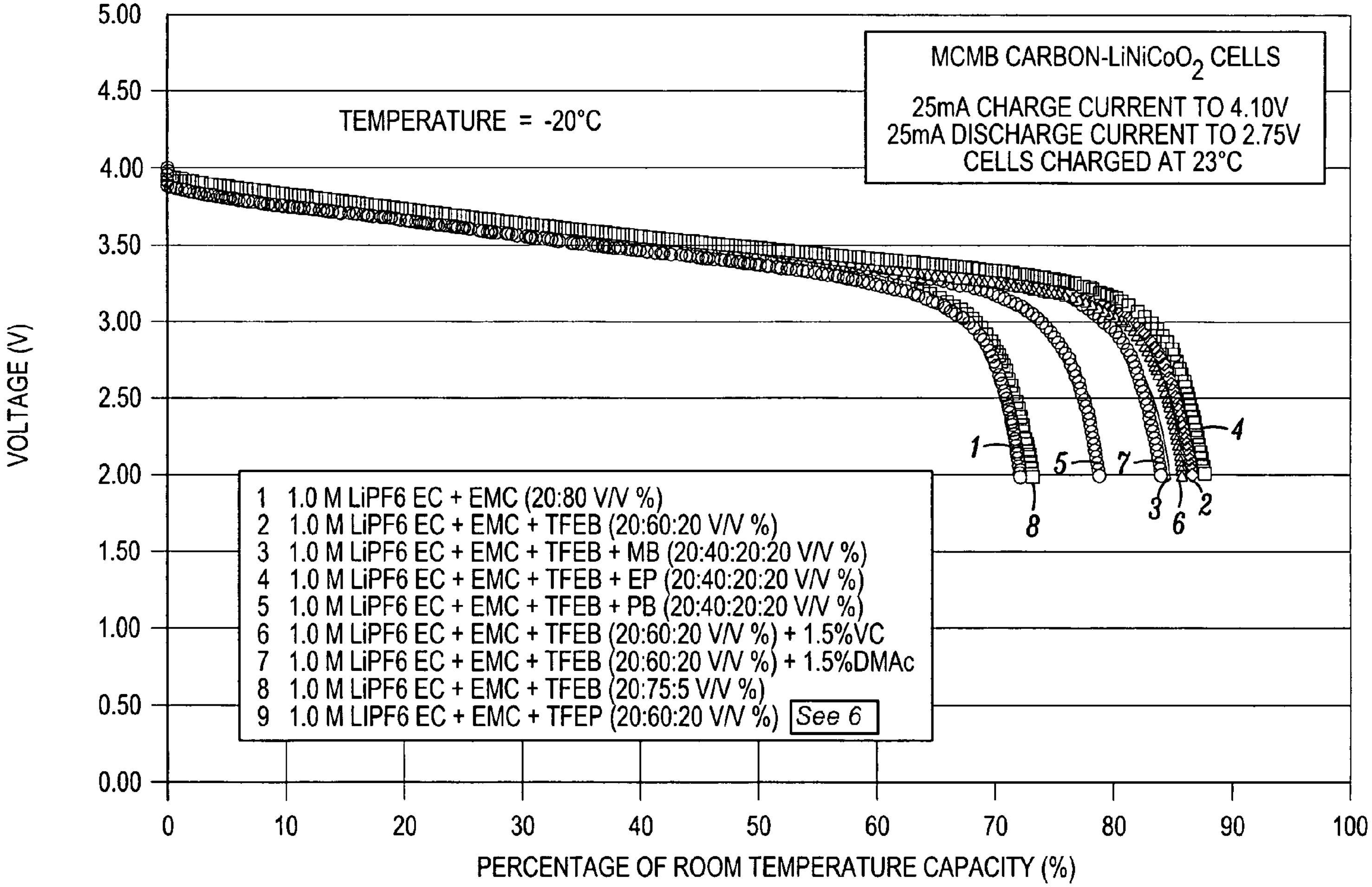

5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
VOLTAGE (V)
0
10
20
30
40
50
60
70
80
90
100
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
TEMPERATURE = -20°C
MCMB CARBON-LiNiCoO2 CELLS
25mA CHARGE CURRENT TO 4.10V
25mA DISCHARGE CURRENT TO 2.75V
CELLS CHARGED AT 23°C
1 1.0 M LiPF6 EC + EMC (20:80 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
3 1.0 M LiPF6 EC + EMC + TFEB + MB (20:40:20:20 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEB + EP (20:40:20:20 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEB + PB (20:40:20:20 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%VC
7 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%DMAc
8 1.0 M LiPF6 EC + EMC + TFEB (20:75:5 V/V %)
9 1.0 M LIPF6 EC + EMC + TFEP (20:60:20 V/V %) See 6
1
8
5
7
3
6
2
4

FIG. 8

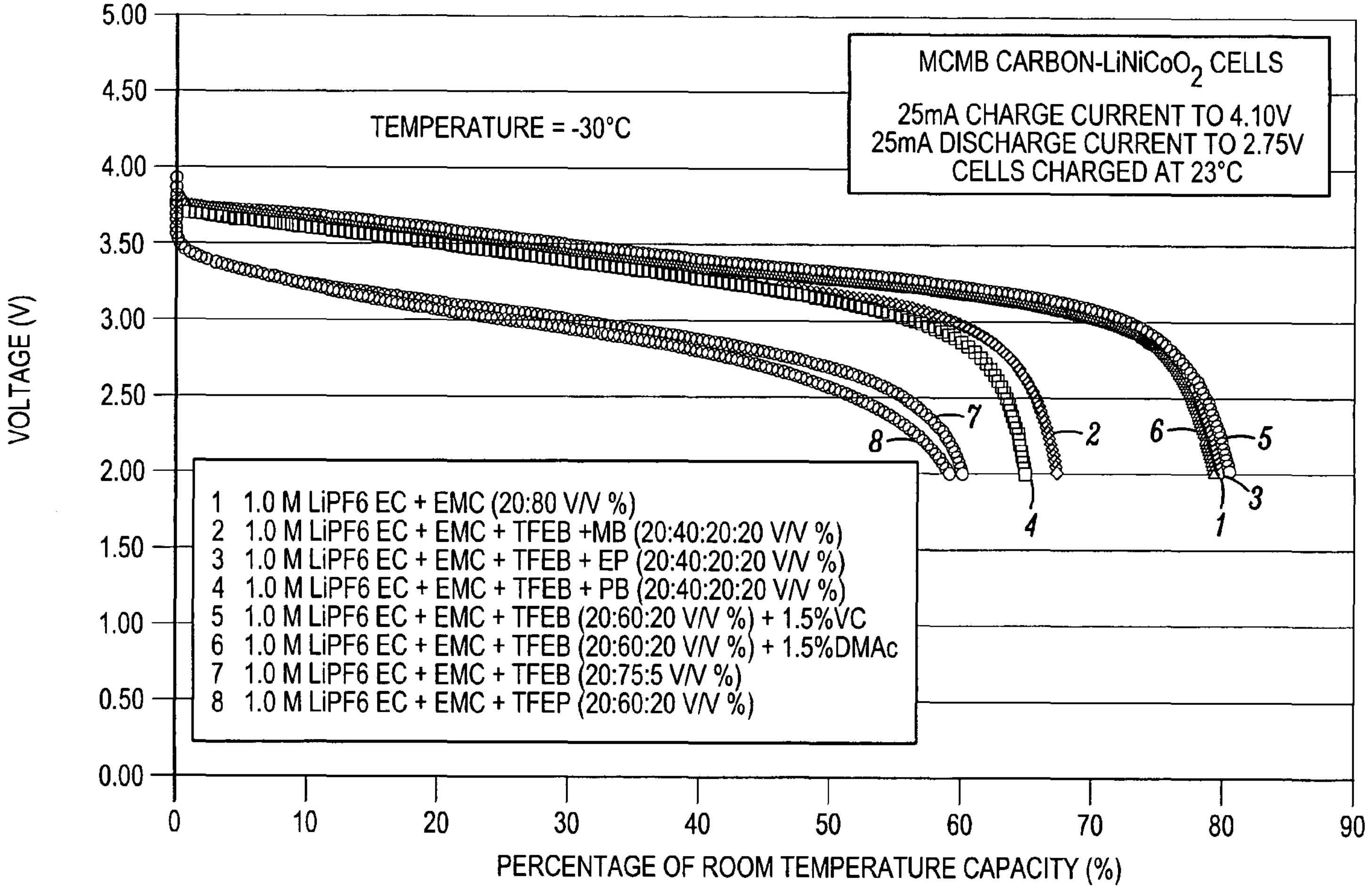

MCMB CARBON-LiNiCoO$_2$ CELLS
25mA CHARGE CURRENT TO 4.10V
25mA DISCHARGE CURRENT TO 2.75V
CELLS CHARGED AT 23°C
TEMPERATURE = -30°C
VOLTAGE (V)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
50
60
70
80
90
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
1 1.0 M LiPF6 EC + EMC (20:80 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB +MB (20:40:20:20 V/V %)
3 1.0 M LiPF6 EC + EMC + TFEB + EP (20:40:20:20 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEB + PB (20:40:20:20 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%VC
6 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%DMAc
7 1.0 M LiPF6 EC + EMC + TFEB (20:75:5 V/V %)
8 1.0 M LiPF6 EC + EMC + TFEP (20:60:20 V/V %)
7
8
2
4
6
5
3
1

FIG. 9

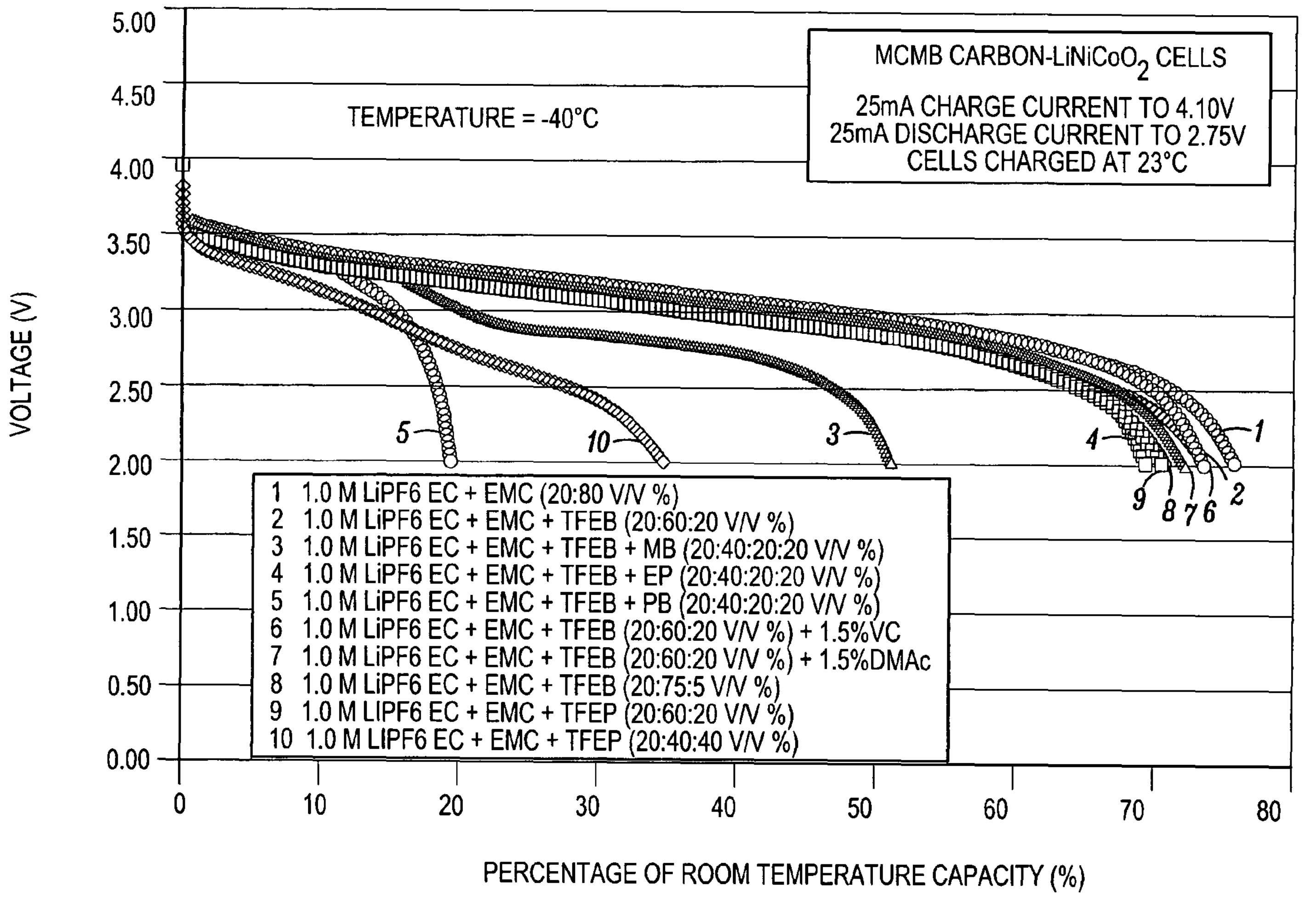

TEMPERATURE = -40°C
MCMB CARBON-LiNiCoO$_2$ CELLS
25mA CHARGE CURRENT TO 4.10V
25mA DISCHARGE CURRENT TO 2.75V
CELLS CHARGED AT 23°C
VOLTAGE (V)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PERCENTAGE OF ROOM TEMPERATURE CAPACITY (%)
0
10
20
30
40
50
60
70
80
5
10
3
4
1
2
6
7
8
9
1 1.0 M LiPF6 EC + EMC (20:80 V/V %)
2 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %)
3 1.0 M LiPF6 EC + EMC + TFEB + MB (20:40:20:20 V/V %)
4 1.0 M LiPF6 EC + EMC + TFEB + EP (20:40:20:20 V/V %)
5 1.0 M LiPF6 EC + EMC + TFEB + PB (20:40:20:20 V/V %)
6 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%VC
7 1.0 M LiPF6 EC + EMC + TFEB (20:60:20 V/V %) + 1.5%DMAc
8 1.0 M LiPF6 EC + EMC + TFEB (20:75:5 V/V %)
9 1.0 M LIPF6 EC + EMC + TFEP (20:60:20 V/V %)
10 1.0 M LIPF6 EC + EMC + TFEP (20:40:40 V/V %)

FIG. 10

LITHIUM-ION ELECTROLYTES WITH FLUOROESTER CO-SOLVENTS

PRIORITY CLAIM

This application claims the benefit of U.S. Provisional Application No. 60/897,316, filed 25 Jan. 2007.

GOVERNMENT INTEREST

The invention claimed herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

FIELD

The present invention relates to lithium-ion electrolytes, with application to lithium-ion batteries.

BACKGROUND

Future NASA missions to explore Mars, the Moon, and the outer planets, are expected to require rechargeable batteries that can operate over a wide temperature range (−60° C. to +60° C.) to satisfy the requirements of various applications, including landers, rovers, and penetrators. Some future applications typically may require high specific energy batteries that can operate at very low temperatures, while still providing adequate performance and stability at higher temperatures. In addition, many of these applications envisioned by the Exploration Systems Research and Technology (ESRT) program of NASA will require improved safety, due to their use by humans. The performance of currently known state-of-art lithium-ion systems is severely limited at temperatures below −40° C. and above +30° C. The limited performance at very low temperatures is believed to be due to poor electrolyte conductivity, poor lithium intercalation kinetics over the electrode surface layers, and poor ionic diffusion in the electrode bulk.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates a battery according to an embodiment.

FIGS. **2-10** illustrate discharge curves of embodiments.

DESCRIPTION OF EMBODIMENTS

In the description that follows, the scope of the term "some embodiments" is not to be so limited as to mean more than one embodiment, but rather, the scope may include one embodiment, more than one embodiment, or perhaps all embodiments.

FIG. **1** illustrates in a simplified pictorial fashion a portion of a lithium-ion battery according to an embodiment, comprising anode **102**, cathode **104**, and separator **106** with an electrolyte comprising lithium ions **108** that move through separator **106** from anode **102** to cathode **104** during a battery discharge, and from cathode **104** to anode **102** during a battery charge. For some batteries with a cylindrical form factor, another separator layer may be adjacent to cathode **104**, and all four layers may be wound into a cylindrical form. However, embodiments are not limited to any particular form factor.

For some embodiments, anode **102** comprises MCMB (Mesocarbon Microbeads) carbon, and cathode **104** comprises $LiNi_{0.8}CO_{0.2}O_2$ (lithium nickel cobalt oxide). Other embodiments may use other kinds of anodes or cathodes. For example, other embodiments may use cathodes comprising lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$), lithium iron phosphate ($LiPO_4$), and lithium nickel cobalt manganese oxide ($LiNiCoMnO_2$), and $LiFePO_4$ to name a few examples. As another example, the stoichiometries for nickel, cobalt, and manganese may vary, so that for some embodiments a cathode may comprise $LiMn_xO_4$ and $LiNi_yCo_zMn_uO_2$, where x, y, z, and u denote variable stoichiometries.

The lithium-ion electrolyte solution comprises a lithium salt, such as lithium hexafluoro phosphate ($LiPF_6$), dissolved into a co-solvent to provide a lithium-ion electrolytic solution (electrolyte). Other embodiments may use other types of lithium salt, such as lithium tetrafluoroborate ($LiBF_4$), lithium bis(oxalate) borate (LiBOB, or $LiB(C_2O_4)_2$), lithium hexafluoroarensate ($LiAsF_6$), lithium perclorate ($LiClO_4$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), and lithium bistrifluoromethanesulfonate sulfonyl imide ($LiN(SO_2CF_3)_2$), to name a few. Also, some embodiments may utilize a mixture of such lithium salts.

During discharge, the reaction $CLi_x \rightarrow C+Li^+ + xe^-$, where e^- denotes an electron, takes place at anode **102**, and the reaction $xLi^+ + xe^- + Li_{1-x}Ni_{0.8}Cu_{0.2}O_2LiNi_{0.8}CO_{0.2}O_2$ takes place at cathode **104** (for an embodiment with a cathode comprising $LiNi_{0.8}Cu_{0.2}O_2$). During charge, these reactions are reversed.

A number of ternary co-solvent embodiments were investigated comprising ethylene carbonate (EC), ethyl methyl carbonate (EMC), and a fluoroester (also referred to as fluorinated ester) solvent selected from the group consisting of 2,2,2-trifluoroethyl butyrate ($C_6H_9F_3O_2$ or $CH_3CH_2CH_2CO_2CH_2CF_3$), Chemical Abstract Services registry number CAS #371-27-7, abbreviated in these letters patent as TFEB; ethyl trifluoroacetate ($C_4H_5F_3O_2$, or $CF_3CO_2CH_2CH_3$), CAS #383-63-1, abbreviated in these letters patent as ETFA; 2,2,2-trifluoroethyl acetate ($C_4H_5F_3O_2$, or $CH_3CO_2CH_2CF_3$), CAS #406-95-1, abbreviated in these letters patent as TFEA; and methyl pentafluoropropionate ($C_4H_3F_5O_2$, or $CF_3CF_2CO_2CH_3$), CAS#378-75-6, abbreviated in these letters patent as MPFP. In particular, these co-solvents were blended in carbonate-based electrolytes to give the following electrolyte solutions:

1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %);
1.0 M $LiPF_6$ in EC+EMC+TFEB (20:40:40 v/v %);
1.0 M $LiPF_6$ in EC+EMC+TFEB (20:20:60 v/v %);
1.0 M $LiPF_6$ in EC+EMC+ETFA (20:60:20 v/v %);
1.0 M $LiPF_6$ in EC+EMC+TFEA (20:60:20 v/v %);
1.0 M $LiPF_6$ in EC+EMC+TFEA (20:40:40 v/v %); and
1.0 M $LiPF_6$ in EC+EMC+MPFP (20:60:20 v/v %).

A number of experimental glass wound (cylindrical) lithium-ion cells, with MCMB carbon anodes and $LiNi_{0.8}CO_{0.2}O_2$ cathodes, with Li metal reference electrodes, were fabricated to study the above listed electrolytes. Results of those experiments are provided in Table 1. The last two entries in Table 1 are electrolytes comprising 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %); and 1.0 M $LiPF_6$ in EC+DEC (diethyl carbonate)+DMC (dimethyl carbonate) (1:1:1 v/v %). These two electrolytes serve as baselines for comparison.

TABLE 1

Charge-discharge characteristics of experimental lithium-ion cells containing various electrolytes subjected to formation cycling.

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreverisible Capacity (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreverisible Capacity (1st-5th Cycle)	Couloumbic Efficiency (5th Cycle)
1.0 M LiPF6 EC + EMC (20:80 v/v %)	0.4216	0.3334	0.088	79.08	0.3341	0.3266	0.1241	97.76
1.0 M LiPF6 EC + DEC + DMC (1:1:1 v/v %)	0.47882	0.41059	0.068	85.75	0.41169	0.39789	0.1313	96.65
1.0 M LiPF6 EC + EMC + TFEA (20:60:20 v/v %)	0.39576	0.29202	0.104	73.79	0.31029	0.30345	0.1430	97.80
1.0 M LiPF6 EC + EMC + TFEA (20:40:40 v/v %)	0.42394	0.30787	0.116	72.62	0.32546	0.31174	0.2790	95.78
1.0 M LiPF6 EC + EMC + TFEB (20:60:20 v/v %)	0.51793	0.44202	0.076	85.34	0.43826	0.43123	0.1140	98.40
1.0 M LiPF6 EC + EMC + TFEB (20:40:40 v/v %)	0.53078	0.44252	0.088	83.37	0.44440	0.43290	0.1465	97.41
1.0 M LiPF6 EC + EMC + TFEB (20:20:60 v/v %)	0.42751	0.30552	0.122	71.47	0.29636	0.28616	0.1875	96.56
1.0 M LiPF6 EC + EMC + ETFA (20:60:20 v/v %)	0.48459	0.35629	0.128	73.53	0.34877	0.33726	0.1894	96.70
1.0 M LiPF6 EC + EMC + MPFP (20:60:20 v/v %)	0.48023	0.29415	0.186	61.25	0.21281	0.18844	0.3255	88.55

As shown in Table 1, all cells displayed good reversibility at room temperature and minimal reactivity during the formation cycling, with the exception of the cell containing the MPFP-based electrolyte. The high coulombic efficiency and comparable irreversible capacity losses are indirectly related to the overall stability of the solutions and the electrode filming characteristics. Note that the fluoroester-based solutions do not display deleterious effects that may limit the reversible capacity or may hinder the kinetics of the lithium intercalation and de-intercalation processes. In some cases, some cells displayed much higher efficiencies and lower cumulative irreversible capacity losses, such as the cells containing TFEB in low proportion, compared with the comparable baseline solution.

Of the electrolytes listed above, the embodiment formulations comprising 1.0 M LiPF$_6$ in EC+EMC+TFEB (20:60:20 v/v %) and 1.0 M LiPF$_6$ in EC+EMC+TFEA (20:60:20 v/v %) yielded the greatest improvements in terms of performance, resulting in improved low temperature performance and greater high temperature resilience. As shown in FIG. **2**, good reversibility was observed with the cell containing the 1.0 M LiPF$_6$ EC+EMC+TFEB (20:60:20 v/v %) electrolyte, being comparable with the baseline 1.0 M LiPF$_6$ electrolyte formulation. In FIG. **2**, curve **201** shows voltage vs. discharge capacity (in Ampere-hour units) for the first discharge cycle, and curve **202** shows this relationship for the fifth discharge cycle. A 25 mA current was used to charge the cell to 4.10 V, and discharge was at 25 mA to 2.75 V, all at a room temperature of 23° C.

FIG. **3** provides discharge curves for the above listed electrolytes at a temperature of −20° C., for a 25 mA discharge current to 2.00 V. The key to the curves is shown as an inset in FIG. **3**. FIG. **3** shows good low temperature performance with the cells containing the ethyl trifluoroacetate (ETFA) and trifluoroethyl butyrate (TFEB) co-solvents when used in 20 vol % compared with the ternary carbonate baseline, with over 85% of the room temperature capacity being delivered at −20° C. using moderate rates (a discharge rate of approximately C/16). The performance enhancement of these electrolytes is more dramatic when compared to the binary baseline formulation of comparable EC-content, especially with respect to the degree of polarization observed with the TFEB-containing solution.

The cells were evaluated at the lower temperature of −40° C., as shown in FIG. **4**. Excellent performance was again obtained with the cells containing the ethyl trifluoroacetate (ETFA) and trifluoroethyl butyrate (TFEB) co-solvents with over 70% of the room temperature capacity being delivered at a discharge rate of approximately C/16. Again, for embodiments with the TFEB-containing electrolyte, much less polarization was observed compared to the baseline, with a higher operating voltage throughout the discharge.

FIG. **5** provides discharge curves for the cells evaluated at −40° C., but using higher discharge rates (corresponding to a discharge rate of about C/8). The cell containing the TFEB in 20 vol % proportion dramatically outperformed all other cells, displaying over a six-fold increase in capacity when compared to the ternary baseline electrolyte. This dramatic improvement, in terms of overall capacity delivered and the extent of polarization observed, was also observed relative to the binary baseline composition with comparable EC-content, clearly demonstrating a beneficial effect of the fluoroester co-solvent upon the low temperature performance. (So as not to obscure the axes and other curves, in FIG. **5** only a few data points are shown for curve **9**.)

FIG. **6** provides discharge curves evaluated at −60° C. using lower discharge rates (corresponding to a discharge rate of about C/30). The cell containing the TFEB in 20 vol % proportion again dramatically outperformed all other cells, displaying over a four-fold increase in capacity when compared to the binary baseline electrolyte. In contrast, the ternary baseline electrolyte delivered negligible capacity, since the higher EC-content present in this formulation results in lower ionic conductivity due to the higher viscosity at these temperatures.

As seen from FIGS. **2-6**, embodiments with ethyl trifluoroacetate (ETFA) and trifluoroethyl butyrate (TFEB) co-solvents have been demonstrated to result in enhanced performance at low temperature compared with all-carbonate-based electrolyte baseline formulations. These results are summarized in Tables 2A, 2B, and 2C. It is believed that these results may presumably be due to the favorable physical properties of the fluoroester co-solvents coupled with desirable film-forming characteristics at the electrode-electrolyte interface, resulting in improved lithium kinetics. This has been indirectly confirmed by electrochemical characterization of the cells, including electrochemical impedance spectroscopy, Tafel polarization measurements, and linear polarization measurements.

TABLE 2A

Low Temperature Discharge Performance of MCMB-LiNiCoO$_2$ cells comprising fluoroester-based electrolytes.

		1.0M LiPF6 EC + EMC + TFEB (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + TFEB (20:40:40 v/v %)		1.0M LiPF6 EC + EMC + TFEB (20:20:60 v/v %)		1.0M LiPF6 EC + EMC + TFEA (20:60:20 v/v %)	
TEMP	Current (mA)	Capacity (Ahr)	%	Capacity (Ahr)	%	Capacity (Ahr)	%	Capacity (Ahr)	%
23 C.	25	0.4312	100	0.4329	100	0.3035	100	0.3117	100
−20 C.	25	0.3718	86.23	0.2727	63.00	0.2519	83.02	0.2544	81.59
−20 C.	50	0.3528	81.82	0.2314	53.45				
−40 C.	25	0.3166	73.41	0.1064	24.57	0.1756	57.87	0.1657	53.17
−40 C.	50	0.2631	61.01	0.0364	8.40	0.0777	25.61	0.0518	16.61
−50 C.	25	0.2024	467.93	0.0347	8.02	0.0288	9.48	0.0208	6.66
−50 C.	50	0.0324	7.52	0.0155	3.58				
−60 C.	5	0.2723	63.14	0.1084	25.03	0.0633	20.88	0.0456	14.64
−60 C.	10	0.1918	44.47	0.0210	4.85	0.0091	2.99	0.0055	1.75
−60 C.	25	0.0209	4.85	0.0080	1.84	0.0006	0.21	0.0002	0.08

TABLE 2B

Low Temperature Discharge Performance of MCMB-LiNiCoO$_2$ cells comprising fluoroester-based electrolytes.

		1.0M LiPF6 EC + EMC + TFEA (20:40:40 v/v %)		1.0M LiPF6 EC + EMC + ETFA (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + MPFP (20:60:20 v/v %)	
TEMP	Current (mA)	Capacity (Ahr)	%	Capacity (Ahr)	%	Capacity (Ahr)	%
23 C.	25	0.3117	100	0.3373	100	0.1884	100
−20 C.	25	0.2544	81.59	0.3051	90.48	0.1158	61.44
−20 C.	50			0.2764	81.97	0.0681	36.11
−40 C.	25	0.1657	53.17	0.2580	76.49	0.0038	2.02
−40 C.	50	0.0518	16.61	0.1983	58.79	0.0001	0.03
−50 C.	25	0.0208	6.66	0.1221	28.31	0.0023	1.22
−50 C.	50			0.0088	2.03	0.0000	0.01
−60 C.	5	0.04567	14.64	0.1749	40.55	0.0000	0.02
−60 C.	10	0.0055	1.75	0.0822	19.07	0.0000	0.00
−60 C.	25	0.0002	0.08	0.0018	0.41	0.0000	0.01

TABLE 2C

Low Temperature Discharge Performance of MCMB-LiNiCoO$_2$ cells comprising fluoroester-based electrolytes.

		1.0M LiPF6 EC + EMC (20:80 v/v %)		1.0M LiPF6 EC + DEC + DMC (1:1:1 v/v %)	
TEMP	Current (mA)	Capacity (Ahr)	%	Capacity (Ahr)	%
23 C.	25	0.3266	100	0.3979	100
−20 C.	25	0.2751	84.21	0.3399	85.43
−20 C.	50			0.3272	82.24
−40 C.	25	0.2023	61.93	0.2659	66.82
−40 C.	50	0.1217	37.27	0.0282	7.09
−50 C.	25	0.0736	22.54	0.0102	2.56
−50 C.	50			0.0001	0.02
−60 C.	5	0.1345	41.17	0.0063	1.58
−60 C.	10	0.0315	9.66	0.0000	0.01
−60 C.	25	0.0021	0.65	0.0000	0.00

In addition to evaluating the low temperature performance of the cells, the high temperature resilience of the cells was tested by subjecting them to increasingly higher temperature storage periods. Each storage period consisted of storing the cells in a full state of charge for 10 days in an open circuit condition. Although it would be expected that the performance degradation is less pronounced if the cells are stored in a partial state of charge, a fully charged condition was selected for the test to accelerate any deleterious electrochemical electrolyte reactions. As illustrated in Tables 3A, 3B, and 3C, the cell containing the 1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %) electrolyte sustained the least amount of performance degradation as a result of the high temperature storage testing. For example, after being subjected to 10 days at 55° C., the TFEB-containing cells retained about 75% of the reversible capacity exhibited prior to the storage period, whereas the binary baseline formulation only delivered about 59% of their initial capacity.

TABLE 3A

Discharge performance of MCMB-$LiNiCoO_2$ cells comprising fluoroester-based electrolytes after being subjected to high temperature storage periods (55° C. to 65° C.).

			1.0M LiPF6 EC + EMC + TFEA (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + TFEA (20:40:40 v/v %)		1.0M LiPF6 EC + EMC (20:80 v/v %)	
			Ah	% of initial	Ah	% of initial	Ah	% of initial
Prior to	20 C.	25 mA	0.2810	100.00	0.2803	100.00	0.3032	100.00
Storage Tests		50 mA	0.26904	95.89	0.2633	93.91	0.2879	94.96
		100 mA	0.2591	92.23	0.2446	87.25	0.2695	88.90
After 10 Days	20 C.	Residual	0.1004	35.74	0.09550	19.61	0.1515	49.97
Storage at 55 C.		25 mA	0.1355	48.22	0.1084	38.68	0.1794	59.17
		50 mA	0.1233	43.87	0.0959	Q34.22	0.1713	56.50
		100 mA	0.1081	38.46	0.0764	27.25	0.1585	52.29

TABLE 3B

Discharge performance of MCMB-$LiNiCoO_2$ cells comprising fluoroester-based electrolytes after being subjected to high temperature storage periods (55° C. to 65° C.).

			1.0M LiPF6 EC + EMC + TFEB (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + TFEB (20:40:40 v/v %)		1.0M LiPF6 EC + EMCMPFP (20:60:20 v/v %)	
			Ah	% of initial	Ah	% of initial	Ah	% of initial
Prior to	20 C.	25 mA	0.3723	100.00	0.3589	100.00	0.1077	100.00
Storage		50 mA	0.3656	98.22	0.3513	97.87	0.0907	84.20
Tests		100 mA	0.3575	96.04	0.33760	93.89	0.0805	74.71
After 10	20 C.	Residual	0.2463	66.16	0.2053	57.19	0.0173	16.05
Days		25 mA	0.2815	75.63	0.2594	72.28	0.0635	58.91
Storage		50 mA	0.2740	73.61	0.2546	70.94	0.0580	53.83
at 55 C.		100 mA	0.2582	69.37	0.2413	67.24	0.0505	46.90
After 10	20 C.	Residual	0.1441	38.70	0.1078	30.04	0.0001	0.14
Days		25 mA	0.1724	46.32	0.1492	41.57	0.0350	32.50
Storage		50 mA	0.1566	42.05	0.1326	36.95	0.0298	27.63
at 60 C.		100 mA	0.1297	34.83	0.1018	28.35	0.0141	13.07
After 10	20 C.	Residual	0.0776	20.83	0.0140	3.90	0.0014	1.27
Days		25 mA	0.0860	23.09	0.0226	6.30	0.0124	11.47
Storage		50 mA	0.0451	12.10	0.0090	2.52	0.0032	2.93
at 65 C.		100 mA	0.0108	2.91	0.0046	1.29	0.0044	4.12

TABLE 3C

Discharge performance of MCMB-$LiNiCoO_2$ cells comprising fluoroester-based electrolytes after being subjected to high temperature storage periods (55° C. to 65° C.).

			1.0M LiPF6 EC + EMC + ETFA (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + TFEB (20:20:60 v/v %)	
			Ah	% of initial	Ah	% of initial
Prior to	20 C.	25 mA	0.2382	100.00	0.2624	100.00
Storage		50 mA	0.2267	95.15	0.2209	84.17
Tests		100 mA	0.2009	84.32	0.646	24.61
After 10	20 C.	Residual	0.0208	8.75	0.1117	42.57
Days		25 mA	0.1130	47.44	0.1505	57.34

TABLE 3C-continued

Discharge performance of MCMB-$LiNiCoO_2$ cells comprising fluoroester-based electrolytes after being subjected to high temperature storage periods (55° C. to 65° C.).

			1.0M LiPF6 EC + EMC + ETFA (20:60:20 v/v %)		1.0M LiPF6 EC + EMC + TFEB (20:20:60 v/v %)	
			Ah	% of initial	Ah	% of initial
Storage		50 mA	0.1004	42.13	0.1210	46.10
at 55 C.		100 mA	0.0803	33.71	0.0680	25.90
After 10	20 C.	Residual	0.00	0.00	0.0400	15.23
Days		25 mA	0.0281	11.81	0.0679	25.89
Storage		50 mA	0.0138	5.80	0.0386	14.69
at 60 C.		100 mA	0.0076	3.19	0.0127	4.85
After 10	20 C.	Residual	0.00	0.00	0.0038	1.43
Days		25 mA	0.0071	2.96	0.0081	3.08
Storage		50 mA	0.0042	1.76	0.0042	1.62
at 65 C.		100 mA	0.0024	0.99	0.0006	0.24

As described so far, a number embodiments comprising fluoroester-based co-solvents in Li-ion electrolytes, including trifluoroethyl butyrate (TFEB), ethyl trifluoroacetate (ETFA), trifluoroethyl acetate (TFEA), and methyl pentafluoropropionate (MPFP), were found to provide good performance over a wide range of temperatures. It is believed that these embodiments have good safety characteristics, due to their low flammability associated with their halogenated nature. Of the solvents described so far, trifluoroethyl butyrate (TFEB) was demonstrated to yield the best performance, with improved low temperature capability and high temperature resilience. In addition to the above-described embodiments, other embodiments utilizing TFEB as a co-solvent have been found by developing multi-component electrolytes which also contain non-halogenated esters, film forming additives, thermal stabilizing additives, and flame retardant additives.

Several factors may influence the low temperature performance of lithium-ion cells, including: lithium ion mobility in the electrolyte solution (electrolyte conductivity); cell design; electrode thickness; separator porosity; and separator wetting properties. Of these parameters, the electrolyte properties are presumably the most dominant, in that sufficient conductivity is a necessary condition for good performance at low temperatures. In designing electrolytes with high conductivity at low temperatures, the solvents should possess a combination of several critical properties, such as: high dielectric constant; low viscosity; and adequate coordination behavior; as well as appropriate liquid ranges and salt solubilities in the medium.

Some embodiments comprise a quaternary co-solvent that includes TFEB as well as other non-fluorinated ester co-solvents, such as methyl butyrate (MB), ethyl propionate (EP), and propyl butyrate (PB). These non-fluorinated esters may improve the low temperature performance, due to their low viscosity and melting points. Furthermore, some embodiments make use of vinylene carbonate (VC) in conjunction with fluorinated esters, with the intent of producing robust solid electrolyte interface (SEI) layers on the electrodes. VC has previously been reported to be an effective additive in improving the high temperature cycle life and storage characteristics, and is believed to sacrificially polymerize on the electrode surfaces, producing protective films preventing further electrolyte reaction at the interface.

In addition, some embodiments make use of dimethyl acetamide (DMAc) as an electrolyte additive in conjunction with fluorinated ester co-solvents, which has been demonstrated to be a thermal stabilizing agent, acting to reversibly bind with PF_5, preventing $LiPF_6$ and carbonate solvents from decomposition at high temperature. It is envisioned that the use of VC, DMAc, or both, may improve the life characteristics and high temperature resilience of electrolyte formulations that also contain fluorinated ester co-solvents, which may impart improved operating temperature range and safety.

Embodiments may also include other fluorinated ester co-solvents in addition to the ones previously investigated, such as 2,2,2-trifluoroethyl propionate (C5H7F3 or CH3CH2CO2CH2CF3), referred to as TFEP. These new electrolyte formulations were compared with the previously described solutions, namely 1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %) and 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %), which were treated as baseline solutions. Accordingly, the following electrolytic solutions were prepared and evaluated:

1.0 M $LiPF_6$ in EC+EMC+TFEB+MB (20:40:20:20 v/v %);

1.0 M $LiPF_6$ in EC+EMC+TFEB+EP (20:40:20:20 v/v %);

1.0 M $LiPF_6$ in EC+EMC+TFEB+PB (20:40:20:20 v/v %);

1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %)+1.5% VC;

1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %)+1.5% DMAc;

1.0 M $LiPF_6$ in EC+EMC+TFEB (20:75:5 v/v %);

1.0 M $LiPF_6$ in EC+EMC+TFEP (20:60:20 v/v %); and

1.0 M $LiPF_6$ in EC+EMC+TFEP (20:40:40 v/v %).

These were compared with 1.0 M $LiPF_6$ in EC+EMC+TFEB (20:60:20 v/v %) and 1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %), which served as baselines.

In addition to the embodiments described above, some embodiments comprising TFEB may also comprise flame retardant additives, such as triphenyl phosphate, triethyl phosphate, tributyl phosphate, and bis-(2,2,2-trifluoroethyl) methyl phosphonate, to reduce the flammability of the electrolytes.

Lithium-ion batteries with MCMB carbon anodes and $LiNi_{0.8}CO_{0.2}O_2$ cathodes were fabricated with the electrolytes listed above, and measurements related to the cells are provided in Table 4. As shown in Table 4, all cells with the formulations listed above displayed good reversibility at room temperature, and relatively minimal reactivity during the formation cycling. The high coulombic efficiency and comparable irreversible capacity losses are believed to be indirectly related to the overall stability of the solutions and the electrode filming characteristics.

Note that the fluoroester-based solutions do not display deleterious effects that limit the reversible capacity or hinder the kinetics of the lithium intercalation and de-intercalation processes. From the formation data, it may be observed that: the trifluoroethyl butyrate solutions appear to produce more desirable surface films compared with trifluoroethyl propionate, as suggested by the lower cumulative irreversible capacity losses and higher efficiency values; with regard to the quaternary formulations comprising non-fluorinated ester co-solvents, propyl butyrate displayed the most desirable filming attributes, suggesting enhanced stability compared to methyl butyrate and ethyl propionate; vinylene carbonate appears to be an effective film forming agent, leading to stable cells with low irreversible capacity loss and high efficiency; and DMAc appears to have some reactivity during the formation cycling.

TABLE 4

Charge-discharge characteristics of embodiment lithium-ion cells comprising various electrolytes subjected to formation cycling.

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreverisible Capacity (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreverisible Capacity (1st-5th Cycle)	Couloumbic Efficiency (5th Cycle)
1.0 M $LiPF_6$ EC + EMC (20:80 v/v %)	0.4682	0.4044	0.064	86.39	0.4013	0.3914	0.1136	97.53
1.0 M $LiPF_6$ EC + EMC + TFEB (20:60:20 v/v %)	0.51793	0.44202	0.076	85.34	0.43826	0.43123	0.1140	98.40
1.0 M $LiPF_6$ EC + EMC + TFEB (20:75:5 v/v %)	0.52311	0.44761	0.076	85.57	0.44588	0.43613	0.1238	97.81
1.0 M $LiPF_6$ EC + EMC + TFEB + MB (20:40:20:20 v/v %)	0.49027	0.41108	0.079	83.85	0.40770	0.39872	0.1261	97.80
1.0 M $LiPF_6$ EC + EMC + TFEB + EP (20:40:20:20 v/v %)	0.48521	0.40316	0.082	83.09	0.40625	0.39724	0.1282	97.78
1.0 M $LiPF_6$ EC + EMC + TFEB + PB (20:40:20:20 v/v %)	0.46187	0.39214	0.070	84.90	0.38955	0.38170	0.1128	97.99
1.0 M $LiPF_6$ EC + EMC + TFEB (20:60:20 v/v %) + 1.5% VC	0.49797	0.42529	0.073	85.40	0.41434	0.40711	0.1088	98.25
1.0 M $LiPF_6$ EC + EMC + TFEB (20:60:20 v/v %) + 1.5% DMAc	0.51540	0.43330	0.082	84.07	0.43093	0.41485	0.1553	96.27
1.0 M LiPF6 EC + EMC + TFEP (20:60:20 v/v %)	0.49419	0.41287	0.081	83.54	0.41866	0.40341	0.1518	96.36
1.0 M LiPF6 EC + EMC + TFEP (20:40:40 v/v %)	0.45809	0.37293	0.085	81.41	0.37525	0.35896	0.1604	95.66

FIG. **7** illustrates discharge curves for the above displayed electrolytes. In FIG. **7**, curves **3**, **4**, **6**, and **9** are very close to each other, and it may be difficult to distinguish them from each other. (Curve **9** is on top of curve **3**, and consequently the numeric label **9** is not shown among the curves.) As shown in FIG. **7**, good reversibility was observed with the cells comprising these electrolyte variations, when compared after the formation cycling. It should be noted that some variation in capacity was due to different electrode weights, and not electrolyte type.

FIG. **8** shows discharge curves at −20° C. Good low temperature performance was generally observed, and was somewhat comparable to the baseline all-carbonate electrolyte. The best performance at −20° C. was exhibited by the cell comprising the EC+EMC+TFEB+EP electrolyte, demonstrating that improved low temperature performance may be obtained with fluorinated and non-fluorinated ester blends, and it may be guessed that further optimization of multi-component carbonate and ester blended electrolytes may yield further improvement in low temperature performance.

When the cells described were evaluated at −30° C., as shown in FIG. **9**, good performance was again obtained with the cells comprising the fluorinated ester co-solvents. Note that the cells comprising the EC+EMC+TFEB (20:60:20) electrolyte with either VC or DMAc, or the EC+EMC+TFEB+EP (20:60:20) electrolyte, performed comparable to the baseline EC+EMC (20:80) electrolyte, with all cells providing about 79% to 80% of the room temperature capacity at −30° C. Many cells also performed well at −40° C., with about 69% to 74% of the room temperature capacity being delivered at a discharge rate of about C/16, as shown in FIG. **10**.

A number of test cells with lithium-ion electrolytes comprising fluorinated ester co-solvents, including trifluoroethyl butyrate (TFEB) and trifluoroethyl propionate (TFEP), were tested, with their performance described in this specification. These electrolytes were found to deliver good performance over a wide temperature range in experimental lithium-ion cells. The general approach taken in the development of these electrolyte formulations was to optimize the type and composition of the co-solvents in ternary and quaternary solutions, focusing upon adequate stability (e.g., EC content for anode passivation, and EMC content for lowering the viscosity and widening the temperature range, while still providing good stability), enhancing the inherent safety characteristics (incorporation of fluorinated esters), and widening the temperature range of operation (the use of both fluorinated and non-fluorinated esters). Furthermore, the use of electrolyte additives, such as VC (SEI promoter) and DMAc (thermal stabilizing additive), are envisioned to provide enhanced high temperature life characteristics. For some embodiments, the concentrations of VC and DMAc may be relatively low, such as for example in the range of 0.10% and 5.0% by weight. It is anticipated that embodiment electrolyte solutions may offer improved performance when incorporated into hermitically sealed, large capacity, prototype cells, especially if all electrolyte components are highly pure.

Various modifications may be made to the described embodiments without departing from the scope of the invention as claimed below. For example, other non-fluorinated ester co-solvents that may be used are: methyl propionate, methyl acetate, ethyl acetate, propyl acetate, ethyl butyrate, butyl butyrate, and propyl propionate. Furthermore, it should be appreciated that experimental results were described for embodiments with specific concentrations of the co-solvents, but embodiments are not limited to these specific concentrations. For example, for some embodiments the EC content may vary from 10% to 50%, the EMC content may vary from 10% to 80%, the fluorinated ester co-solvent content may vary from 5% to 80%, and the non-fluorinated ester co-solvent content may vary from 10% to 80%. Furthermore, for some embodiments the lithium salt concentration (e.g., $LiPF_6$) may vary from 0.50 M to 1.50 M.

These concentration ranges are merely given to provide examples, and some embodiments may have different ranges of concentrations. For example, the lithium salt concentration may be between 0.80 M and 1.20 M, where very low temperature performance benefits from the lower end of this range, and where more moderate temperature and high power applications may benefit from the higher end of this range. As another example, the concentration of the non-fluorinated esters may be in the range of 10% to 80%.

Throughout the description of the embodiments, various mathematical relationships are used to describe relationships among one or more quantities. These relationships are in practice not satisfied exactly, and should therefore be interpreted as “designed for” relationships. One of ordinary skill in the art may design various working embodiments to satisfy various mathematical relationships, but these relationships can only be met within the tolerances of the technology available to the practitioner.

Accordingly, in the following claims, it is to be understood that claimed mathematical relationships can in practice only be met within the tolerances or precision of the technology available to the practitioner, and that the scope of the claimed subject matter includes those embodiments that substantially satisfy the mathematical relationships so claimed.

What is claimed is:

1. A battery comprising:

an anode;

a cathode; and

a lithium-ion electrolyte comprising a solvent and a lithium salt dissolved in the solvent, the solvent comprising a combination of:

ethylene carbonate having a volume-volume percentage concentration varying from 10% to 50%;

ethyl methyl carbonate having a volume-volume percentage concentration varying from 10% to 80%; and

a fluorinated ester co-solvent having a volume-volume percentage concentration of at least 20% and up to 80%, wherein the combination is such that the battery retains greater capacity at a temperature of −20° C. or below, as compared to a battery comprising an all carbonate based electrolyte.

2. The battery as set forth in claim **1**, wherein the lithium salt has a molarity concentration varying from 0.50 M to 1.50 M.

3. The battery as set forth in claim **1**, the fluorinated ester co-solvent comprising one or more co-solvents selected from the group consisting of trifluoroethyl butyrate, ethyl trifluoroacetate, trifluoroethyl acetate, methyl pentafluoropropionate, and 2,2,2-trifluoroethyl propionate.

4. The battery as set forth in claim **1**,

the anode comprising one or more compounds selected from the group consisting of mesocarbon microbeads (MCMB), carbon, and graphite; and

the cathode comprising one or more compounds selected from the group consisting of $LiNiCoAlO_2$, $LiPO_4$, $LiMn_xO_4$, $LiFePO_4$, $LiNi_yCo_zMn_uO_2$, where x, y, z, and u denote variable stoichiometries.

5. The battery as set forth in claim **1**, the lithium salt comprising one or more salts selected from the group consisting of lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium bis(oxalato) borate (LiBOB, or $LiB(C_2O_4)_2$), lithium hexafluoroarensate ($LiAsF_6$), lithium perclorate ($LiClO_4$), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), and lithium bistrifluoromethanesulfonate sulfonyl imide ($LiN(SO_2CF_3)_2$).

6. The battery as set forth in claim **1**, the solvent further comprising one or more non-fluorinated ester co-solvents selected from the group consisting of methyl butyrate, ethyl propionate, propyl butyrate, methyl propionate, methyl acetate, ethyl acetate, propyl acetate, ethyl butyrate, butyl butyrate, and propyl propionate.

7. The battery as set forth in claim **6**, the one or more non-fluorinated ester co-solvents having the volume-volume percentage concentration varying from 20% to 80% and wherein:

the anode comprises carbon, and

the greater battery capacity is at temperatures of −40° C. and −60° C.

8. The battery as set forth in claim **6**, the solvent further comprising one or more electrolyte additives selected from the group consisting of vinylene carbonate and dimethyl acetamide.

9. The battery as set forth in claim **8**, the one or more electrolyte additives in the solvent having a concentration varying from 0.1% to 5.0% by weight.

10. The battery of claim **1**, wherein the anode comprises mesocarbon microbeads carbon.

11. The battery of claim **1**, wherein the fluorinated ester co-solvent is ethyl trifluoroacetate.

12. The battery of claim **1**, wherein the fluorinated ester co-solvent is trifluoroethyl butyrate.

13. The battery of claim **1**, wherein the combination is such that the battery retains greater reversible capacity after storage at 55° C. as compared to a battery comprising an electrolyte that is a binary baseline formulation of ethylene carbonate and ethyl methyl carbonate.

14. The battery of claim **1**, wherein the combination is such that the battery provides at least 79% of room temperature capacity at the temperature of −30° C.

15. The battery of claim **1**, wherein the fluorinated ester co-solvent has the volume-volume percentage concentration of 20-60%.

16. A lithium-ion electrolyte comprising a solvent and a lithium salt dissolved in the solvent, the solvent comprising a combination of:

ethylene carbonate having a volume-volume percentage concentration varying from 10% to 50%;

ethyl methyl carbonate having a volume-volume percentage concentration varying from 10% to 80%; and

a fluorinated ester co-solvent having a volume-volume percentage concentration of at least 20% and up to 80%, wherein the combination is such that the electrolyte provides a battery with greater capacity at a temperature of −40° or below, as compared to an all carbonate based electrolyte.

17. The lithium-ion electrolyte as set forth in claim **16**, wherein the lithium salt has a molarity concentration varying from 0.50 M to 1.50 M.

18. The lithium-ion electrolyte as set forth in claim **16**, the fluorinated ester cosolvent comprising one or more co-solvents selected from the group consisting of 2,2,2-trifluoroethyl butyrate, ethyl trifluoroacetate, trifluoroethyl acetate, methyl pentafluoropropionate, and 2,2,2-trifluoroethyl propionate.

19. The lithium-ion electrolyte as set forth in claim **16**, the lithium salt comprising one or more salts selected from the group consisting of lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium bis(oxalato) borate (LiBOB, or $LiB(C_2O_4)_2$), lithium hexafluoroarensate (LiAsF6), lithium perclorate (LiClO4), lithium trifluoromethanesulfonate ($LiCF_3SO_3$), and lithium bistrifluoromethanesulfonate sulfonyl imide ($LiN(SO_2CF_3)_2$).

20. The lithium-ion electrolyte as set forth in claim **16**, the solvent further comprising one or more non-fluorinated ester co-solvents selected from the group consisting of methyl butyrate, ethyl propionate, propyl butyrate, methyl propionate, methyl acetate, ethyl acetate, propyl acetate, ethyl butyrate, butyl butyrate, and propyl propionate.

21. The lithium-ion electrolyte as set forth in claim **20**, further comprising:

a cathode; and

an anode including carbon; and wherein:

the one or more non-fluorinated ester co-solvents have the volume-volume percentage concentration varying from 20% to 80% and

the greater battery capacity is at the temperatures of −40° C. and −60° C.

22. The lithium-ion electrolyte as set forth in claim **20**, the solvent further comprising one or more electrolyte additives selected from the group consisting of vinylene carbonate and dimethyl acetamide.

23. The lithium-ion electrolyte as set forth in claim **22**, the one or more electrolyte additives in the solvent having a concentration varying from 0.1% to 5.0% by weight.

24. The electrolyte of claim **16**, wherein the fluorinated ester co-solvent is ethyl trifluoroacetate.

25. The electrolyte of claim **16**, wherein the fluorinated ester co-solvent is trifluoroethyl butyrate.

26. The electrolyte of claim **16**, wherein the combination is such that the battery retains greater reversible capacity after storage at 55° C. as compared to a battery comprising an electrolyte that is a binary baseline formulation of ethylene carbonate and ethyl methyl carbonate.

27. The electrolyte of claim **16**, wherein the combination is such that the electrolyte provides the battery with at least 79% of room temperature capacity at the temperature of −30° C.

28. The electrolyte of claim **16**, wherein the fluorinated ester co-solvent has the volume-volume percentage concentration of 20-60% or 20-80% and the greater battery capacity is over a temperature range of −40° C. to −60° C.

29. A method of fabricating a lithium-ion electrolyte, comprising:

providing a solvent and a lithium salt dissolved in the solvent, wherein the solvent comprises a combination of:

ethylene carbonate having a volume-volume percentage concentration varying from 10% to 80%;

ethyl methyl carbonate having a volume-volume percentage concentration varying from 10% to 80%; and

a fluorinated ester co-solvent having a volume-volume percentage concentration of at least 20% and up to 80%, wherein the combination is such that the electrolyte provides a battery with greater capacity at a temperature of −40° C., as compared to an all carbonate based electrolyte.

30. The method of claim **29**, further comprising providing an anode and a cathode, wherein:

the fluorinated ester co-solvent has the volume-volume percentage concentration of 20%-60%,

the greater battery capacity is over a temperature range of −40° C. to −60° C., and

the anode comprises carbon.

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